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**PREPARAÇÃO, CARACTERIZAÇÃO E APLICAÇÃO DE ADSORVENTES À  
BASE DE LODO DE ESGOTO SANITÁRIO E POLISSILOXANOS PARA A  
REMOÇÃO DE POLUENTES ORGÂNICOS DE EFLUENTES AQUOSOS**

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Tese para obtenção do título de Doutor em Engenharia

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**Desenvolvimento de adsorventes à base de lodo de esgoto sanitário e polissiloxanos para a remoção de poluentes orgânicos de efluentes aquosos**

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**LISTA DE ARTIGOS PUBLICADOS A PARTIR DOS RESULTADOS DESCRITOS  
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- ❖ **G. Simões Dos Reis**, M. Wilhelm, T. C. A. Silva, K. Rezwan, C. H. Sampaio, E. C. Lima, S. M.A. G. U. Souza, The use of design of experiments for the evaluation of the production of surface rich activated carbon from sewage sludge via microwave and conventional pyrolysis, **Applied Thermal Engineering** 93 (2016) 590–597.
- ❖ **G. Simões Dos Reis**, M. Adebayo, C.H. Sampaio, E.C. Lima, S. P. Thue, I. A.S. de Brum, S.L.P. Dias, F. P. Pavan, Removal of phenolic compounds from aqueous solutions using sludge-based activated carbons prepared by conventional heating and microwave-assisted pyrolysis. **Water, Air and Soil Pollution** (2017) 228: 33.
- ❖ **G. Simões Dos Reis**, C.H. Sampaio, E.C. Lima, M. Wilhelm, Preparation of novel adsorbents based on combinations of polysiloxanes and sewage sludge to remove pharmaceuticals from aqueous solutions. **Colloids and Surfaces A: Physicochemical and Engineering Aspects** 497 (2016) 304–315.
- ❖ **G. Simões Dos Reis**, M.K. Bin Mahbub, M. Wilhelm, C.H. Sampaio, E.C. Lima, Silvio L.P. Dias, Activated carbon from sewage sludge for removal of sodium diclofenac and nimesulide from aqueous effluents. **Korean journal of chemical engineering** 33 (11) (2016) 3149–3161.

## LISTA DE ARTIGOS E TRABALHOS ACEITOS E/OU PUBLICADOS A PARTIR DOS ESTUDOS DE DOUTORADO

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- ✓ Silas P. Thue, **Glaidson S. dos Reis**, Eder C. Lima, Joseph M. Sieliechi, G.L. Dotto, Alfred G. N. Wamba, Silvio L.P Dias, Flavio A. Pavan. Activated carbons from Sapelli wood sawdust by microwave-heating process for o-cresol adsorption. **Research on Chemical Intermediates**. (2016) (published online) DOI: [10.1007/s11164-016-2683-8](https://doi.org/10.1007/s11164-016-2683-8)
- ✓ Cibele S. Umpierres, Lizie D.T. Prola, Matthew A. Adebayo, Eder C. Lima, **Glaidson S. dos Reis**, Diego D.F. Kunzler, G. Dotto, Leliz T. Arenas, Edilson V. Benvenuti. Mesoporous Nb<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub> material obtained by sol-gel method and applied as AQ1 adsorbent of crystal violet dye. **Environmental Technology**. (2016) (published online) <http://dx.doi.org/10.1080/09593330.2016.1202329>
- ✓ **G. Simões Dos Reis**, M. A. Adebayo, E. C. Lima, C. H. Sampaio, L. D. T. Prola, Activated Carbon from Sewage Sludge for Preconcentration of Copper, **Analytical Letters** 49 (2016) 541–555.
- ✓ **Simões dos Reis, G.**, E.C.Lima, C.H. Sampaio, Produção de carvão ativado a partir de lodo de esgoto doméstico e sua aplicação na adsorção do corante preto remazol 5 em solução aquosa. **Exacta.**, 8 (2) 2015.
- ✓ Saucier, C., Karthickeyan, P., Ranjithkumar, V., Lima, E.C., **Simões dos Reis, G.**, De Brum, I.A.S. Efficient removal of amoxicillin and paracetamol from aqueous solutions using magnetic activated carbon, **Environmental Science and Pollution Research**, (2017) (published online) DOI: [10.1007/s11356-016-8304-7](https://doi.org/10.1007/s11356-016-8304-7)

## Trabalhos publicados em congressos

**REIS, G. S.**; A. F. Castro, I. A.S. de Brum, C. H. Sampaio, E. C. Lima. Hydrophobic organosilica adsorbents for removal of sodium diclofenac from aqueous solutions, In: 71º Congresso Anual da ABM – Internacional, Proceedings of the ABM WEEK, 2016. p.1 – 10

**REIS, G. S.**; Sampaio, C. H. Lima, E. C. Application of experimental design to produce activated carbons from sludge sewage by microwave-heating process. In: Indo-Brazil Bilateral International Conference on Advanced Materials and Manufacturing - ICAMM, 2015, Tirunelveli. Proceedings of the ICAMM. p. 1-6.

**REIS, G. S.**; C.H. SAMPAIO, E.C. LIMA, Adsorption of crystal violet dye from aqueous solutions onto polysiloxanes. In: Indo-Brazil Bilateral International Conference on Advanced Materials and Manufacturing - ICAMM, 2015, Tirunelveli. Proceedings of the ICAMM, 2015.

**REIS, G. S.**; SAUCIER, C. ; ADEBAYO, M. ; LIMA, E. C. ; PROLA, L. . Comparison Of A Homemade Bacury Shell Activated Carbon With Mwcnt For The Removal Of Brilliant Blue Fcf Food Dye From Aqueous Solutions. In: Indo-Brazil Bilateral International Conference on Advanced Materials and Manufacturing - ICAMM, 2015, Tirunelveli. Proceedings of the ICAMM, 2015. p. 1-6.

**REIS, G. S.**; SAMPAIO, C. H. ; LIMA, E. C. . Activated Carbons Prepared From Sewage Sludge For Removal Of Remazol Black 5 Dye From Aqueous Solutions. In: Indo-Brazil Bilateral International Conference on Advanced Materials and Manufacturing - ICAMM, 2015, Tirunelveli. Proceedings of the ICAMM, 2015. p. 1-6.

**REIS, G. S.**; SAMPAIO, C. H. ; LIMA, E. C. ; C.R. Gally. Planejamento Estatístico Para Produzir Carvões Ativados De Lodo De Esgoto Doméstico Sua Aplicação Na Remoção De Diclofenaco Em Solução Aquosa. In: XXIII Jornadas de Jovens Pesquisadores da AUGM, 2015, La Plata. Anais de las XXIII Jornadas de Jovens Pesquisadores da AUGM, 2015.

**REIS, G. S.**; SAMPAIO, C. H. ; SANTOS, T. S. M. Produção De Carvão Ativado Proveniente De Lodo De Esgoto Domestico E Seu Uso Na Remoção De Corante Azul De Metileno. In: IV CONGRESSO BRASILEIRO DE CARVÃO MINERAL, 2013, Gramado. Anais do IV Congresso Brasileiro de Carvão Mineral, 2013. p. 977-985.

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## Resumo

Regulações ambientais cada vez mais rigorosas em relação ao gerenciamento dos resíduos orgânicos estão impelindo a indústria para uma maior sustentabilidade no sentido de melhorar a relação benefício/custo e também atender a demanda dos clientes. A valorização dos resíduos orgânicos é uma das áreas de investigação atuais que tem atraído grande atenção nos últimos anos como uma alternativa potencial à eliminação de uma vasta gama de resíduos em aterros sanitários. Os resíduos orgânicos como o lodo de esgoto têm sido encarados como um recurso com um potencial significativo para ser empregado como matéria-prima para a produção de vários tipos de produtos, materiais e combustíveis.

Este estudo tem como objetivo fornecer subsídios sobre o potencial de uso de lodo de esgoto para produzir carvões ativados e novos materiais adsorventes misturando com diferentes materiais polissiloxanos para adsorção de poluentes orgânicos a partir de soluções aquosas. Os materiais adsorventes foram caracterizados por várias técnicas analíticas e funcionais e utilizados na adsorção de diclofenaco (DCF), nimesulida (NM) e alguns compostos fenólicos a partir de soluções aquosas.

Esta tese visa contribuir em (i) comparar os métodos de pirólise (pirólise convencional e aquecimento assistido por micro-ondas) na preparação de carvões ativados a partir de lodo de esgoto. Para isso foi aplicado um planejamento experimental e metodologia de superfície de resposta no sentido de determinar quais as variáveis dos dois processos são as que influenciam na qualidade do carvão produzido; (ii) a combinação de lodo de esgoto com polissiloxanos para preparar adsorventes para adsorção de fármacos a partir de soluções aquosas por processos de adsorção.

Os achados gerais desta tese mostraram (i) que ambos os métodos de pirólise produzem carvões ativados com elevadas porosidades e áreas superficiais; (ii) demonstrou-se também que lodo de esgoto pode ser um excelente precursor para a preparação de carvões ativados e que pode com sucesso ser combinado com outros precursores (como polissiloxanos) a fim de se obter novos materiais com diferentes funcionalidades e características; (iii) foi demonstrado que os carvões ativados, híbridos e materiais compósitos desenvolvidos durante o presente estudo são ótimos adsorventes, especialmente para a remoção de diclofenaco DCF e NM a partir de solução aquosa e; (iv) tanto por microondas ou por pirólise convencional, é possível desenvolver CAs de lodo de esgoto com alta eficiência para a remoção de compostos fenólicos em comparação com outros tipos de CAs relatados na literatura.

Estes resultados indicam que o lodo de esgoto e polissiloxanos têm grande potencial como precursores para a preparação de materiais adsorventes para o tratamento de água poluída por compostos orgânicos.

**Palavras-chave:** Lodo de esgoto: carvão ativado: Polissiloxanos: adsorventes híbridos e compósitos: fenóis e fármacos: Adsorção.

## Abstract

Increasingly tighter regulations regarding organic waste are pushing the manufacturing industry toward higher sustainability to improve cost-effectiveness and meet customers' demand. Organic waste valorisation is one of the current research areas that have attracted a great deal of attention over the past few years as a potential alternative to the disposal of a wide range of residues in landfill sites. Bio-waste like sewage sludge emerged as a resource with a significant potential to be employed as a raw material for the production of chemicals, materials and fuels given its abundant volumes generated globally.

This study aims at providing insights into the potential of the use of the sewage sludge to produce activated carbons (ACs) and novel adsorbent materials mixing with different polysiloxanes materials for adsorption of organic pollutants from aqueous solutions. The characterization of adsorbents were achieved by several analytical and functional techniques and used for adsorption of diclofenac (DCF) and nimesulide (NM) from aqueous solutions.

The novelties of the present study are (i) to compare both pyrolysis methods (conventional pyrolysis and microwave assisted heating) for preparation of activated carbons from sewage sludge; for that It was applied an experimental design and response surface methodology were used for the preparation and comparison of activated carbon produced by both methods, conventional furnace and microwave; (ii) the combination of sewage sludge with polysiloxanes to prepare adsorbents to uptake pharmaceuticals and phenolic compounds from aqueous solutions by adsorption processes.

The general findings of this thesis showed (i) that both methods of pyrolysis produce very good activated carbons from sewage sludge with high specific surface areas and high developed porosities; (ii) It was also shown that the sewage sludge can be an excellent precursor to prepare activated carbons and novels materials by mixing it with other precursors such polysiloxanes; (iii) It was shown that the activated carbons, hybrids and composites materials developed during the present study are good adsorbents, especially for the removal of a model diclofenac (DCF) and nimesulide (NM) from aqueous solution and; (iv) that by microwave and conventional pyrolysis it is possible to develop sludge-ACs with very high efficiency for phenolic compounds compared with others kind of ACs reported in literature.

These results indicate that sewage sludge and polysiloxanes have great potential as precursors for preparation of adsorbent materials for water treatment polluted by organic pollutants compounds.

**Keywords:** Sewage sludge: Activated carbon: Polysiloxanes: Hybrids and composites adsorbents: Phenols and drugs compounds: Adsorption process.



**Capítulo Um**: Apresentação, Introdução, objetivos e a justificativa do trabalho.

# ***Capítulo Um***

**Capítulo Um:** Apresentação, Introdução, objetivos e a justificativa do trabalho.

## **APRESENTAÇÃO DO TRABALHO - INTEGRAÇÃO DE ARTIGOS**

Esta tese de doutorado, intitulada “**Preparação, caracterização e aplicação de adsorventes à base de lodo de esgoto sanitário e polissiloxanos para a remoção de poluentes orgânicos de efluentes aquosos**”, será apresentada em um formato alternativo no qual quatro dos seus oito capítulos correspondem a artigos científicos publicados e/ou submetidos em periódicos internacionais.

Esta tese é fruto, em grande parte, de uma cooperação internacional que foi desenvolvida entre Brasil e Alemanha pelos laboratórios de Processamento Mineral (LAPROM) vinculado ao Departamento de Engenharia Metalúrgica (DEMET) e de tecnologia analítica e ambiental (LATAMA) vinculado ao Instituto de Química (IQ) ambos da Universidade Federal do Rio Grande do Sul (UFRGS) juntamente com o Advanced Ceramics Group vinculado ao Department of Production Engineering, da University of Bremen na Alemanha, sob a orientação do Prof. Kurosh Rezwan e Dr. Michaela Wilhelm. O estágio no exterior teve a duração de um ano, compreendendo o período de Março de 2014 a Fevereiro de 2015, sendo financiado pelo Programa de Doutorado Sanduiche no Exterior (PDSE) da CAPES, através do Programa Ciência Sem Fronteiras.

O trabalho foi estruturado na forma de artigos científicos, conforme a Resolução N° 093/2007, de 12/06/2007 da Câmara de Pós-Graduação da Universidade Federal do Rio Grande do Sul (UFRGS), que estabelece orientações para fins de publicação e redação de Teses de Doutorado, Dissertações de Mestrado e trabalhos de conclusão de Cursos de Especialização.

Este trabalho apresenta-se dividido em oito capítulos, sendo este primeiro uma apresentação do trabalho trazendo a introdução ao tema, assim como a motivação e a importância deste trabalho, sendo delineados a justificativa de seu desenvolvimento, os objetivos e metas do trabalho.

No segundo capítulo é apresentada a revisão bibliográfica. Os principais tópicos a serem abordados referem-se: a problemática que envolve o lodo de esgoto doméstico e seus principais meios de disposição e potenciais usos; o uso do lodo de esgoto na preparação de adsorventes por meio de pirólise convencional e por micro-ondas; preparação de adsorventes (híbridos e compósitos) à base de polissiloxanos e lodo de esgoto; o uso de adsorventes na remoção de poluentes orgânicos em águas por meio de adsorção; conceitos sobre adsorção, etc.

**Capítulo Um:** Apresentação, Introdução, objetivos e a justificativa do trabalho.

No capítulo três é descrita a parte experimental pela qual este tese foi desenvolviuda.

Os demais capítulos (quatro, cinco, seis e sete) são compostos por artigos científicos publicados e/ou aceitos para publicação.

**Em vista disso, a tese está estruturada da seguinte forma:**

- **Capítulo Um:** apresentação do trabalho trazendo a introdução ao tema assim também a motivação e a importância deste trabalho, sendo delineados a justificativa de seu desenvolvimento, os objetivos e metas do trabalho.
- **Capítulo Dois:** revisão objetiva da literatura pertinente aos temas abordados neste trabalho, tais como: a problemática que envolve o lodo de esgoto doméstico e seus principais meios de disposição e potenciais usos; o uso do lodo de esgoto na preparação de adsorventes por meio de pirólise convencional e por micro-ondas; preparação de adsorventes (híbridos e compósitos) à base de Polissiloxanos e lodo de esgoto; o uso de adsorventes na remoção de poluentes orgânicos em águas por meio de adsorção; conceitos sobre adsorção, etc.
- **Capítulo Três:** apresenta a parte experimental da tese, incluindo os equipamentos e procedimentos experimentais.
- **Capítulo Quatro:** artigo intitulado “**The use of design of experiments for the evaluation of the production of surface rich activated carbon from sewage sludge via microwave and conventional pyrolysis**”, que objetivou identificar qual método de pirólise e em quais condições são produzidos carvões ativados com melhores propriedades texturais (a exemplo de área superficial específica). Para isso foi aplicado o uso de planejamento experimental e metodologia de superfície de resposta na preparação e comparação de carvão ativado produzido a partir de lodo de esgoto por dois tipos de pirólise: forno convencional e micro-ondas. O método de preparação foi realizado seguindo um planejamento fatorial fracionário completo ( $2^3$ ) para cada tipo de pirólise. Foram analisados os fatores: temperatura de pirólise ou potência de radiação, tempo de residência e proporção de agente de ativação química (cloreto de zinco) sobre a resposta área superficial ( $S_{BET}$ ).
- **Capítulo Cinco:** Artigo intitulado “**Removal of phenolic compounds from aqueous solutions using sludge-based activated carbons prepared by conventional heating and microwave-assisted pyrolysis**”, utilizou, a partir dos resultados obtidos pelo capítulo um, os melhores carvões ativados (em relação as suas áreas superficiais, ( $S_{BET}$ )) preparados tanto por pirólise convencional quanto por microondas. Os carvões foram

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caracterizados utilizando várias técnicas analíticas e funcionais e em seguida foram utilizados para a remoção de compostos fenólicos em soluções aquosas. Primeiro foi feito um estudo preliminar para adsorção de seis compostos fenólicos no intuito de determinar qual composto teria maior afinidade com os carvões ativados; diante do melhor resultado o composto fenólico que mais foi adsorvido (hidroquinona) foi também escolhido para fazer o estudo completo de adsorção englobando os estudos cinéticos de equilíbrio, de dessorção, mecanismo de adsorção e testes em efluentes sintéticos.

- **Capítulo Seis:** artigo intitulado “**Preparation of novel adsorbents based on combinations of polysiloxanes and sewage sludge to remove pharmaceuticals from aqueous solutions**”, que foca na preparação de novos adsorventes baseados em diferentes proporções de lodo de esgoto e vários polissiloxanos e seus usos na adsorção dos fármacos diclofenaco de sódio e nimesulida a partir de soluções aquosas.

- **Capítulo Sete:** Artigo intitulado “**Activated carbon from sewage sludge for removal of sodium diclofenac and nimesulide from aqueous effluents**”, que foca na preparação, caracterização e aplicação dos carvões ativados na remoção de diclofenaco de sódio e nimesulida a partir de soluções aquosas. Foi realizado um estudo completo de adsorção no tocante a influência do pH e da massa de adsorvente, aos estudos cinéticos de equilíbrio, assim como a influência da temperatura e também foi proposto o mecanismo de adsorção.

- **Capítulo Oito:** conclusões e propostas futuras

A proposta geral deste trabalho visa o preparo de materiais adsorventes a base de lodo de esgoto e polissiloxanos e utilizá-los como adsorventes para remoção de espécies orgânicas em efluentes aquosos. A ênfase deste trabalho é propor um uso mais nobre para o lodo de esgoto, utilizando-o como precursor para o preparo de novos materiais e também carvões ativados com boa aplicabilidade em remoção de espécies tóxicas em efluentes.

Para isto o objetivo geral desta tese foi sintetizar novos adsorventes à base de lodo de esgoto e vários polissiloxanos e utilizá-los como adsorventes para a remoção de espécies orgânicas em efluentes aquosos. Foram utilizados como precursores para preparação dos adsorventes o lodo de esgoto doméstico seco, metil-fenil-siloxanos (H44), metil-siloxanos (MK), ortossilicato de tetraetilo (TEOS). Cada precursor foi utilizado para a preparação dos adsorventes de maneira individual e também os misturando em diferentes proporções. Após a preparação dos adsorventes os mesmos foram utilizados na remoção de várias espécies orgânicas, em meio aquoso, por meio de adsorção em batelada. No processo de adsorção

vários parâmetros operacionais do sistema foram avaliados como, efeitos do tempo de contato, do pH inicial, da temperatura, da quantidade de massa de adsorvente etc.

## **1. INTRODUÇÃO**

Os problemas ambientais do mundo contemporâneo são, em sua grande maioria, gerados pela ação direta ou indireta de fatores antropológicos. O homem assumiu uma função essencial quanto ao impacto negativo no meio ambiente devido ao consumo, em grandes quantidades, de recursos naturais e as consequentes gerações de resíduos, que só se potencializa devido ao desenvolvimento acelerado das cidades e o grande adensamento populacional [1-3].

As atividades industriais, como sendo antrópicas, são responsáveis por gerar grandes volumes de resíduos, sejam resíduos sólidos ou de espécies nocivas em águas residuais. Com as crescentes necessidades de recursos materiais, assim como a necessidade de se cumprir os requisitos de proteção ambiental, tornou-se necessário estudar todas as possibilidades de reutilização e reciclagem dos vários tipos de resíduos industriais e urbanos no sentido de apresentar soluções mais sustentáveis para a escassez de matérias-primas [4,5]. A lógica é utilizar tais resíduos como matéria prima para a produção de energia e também produtos úteis para a indústria de modo geral [4,5].

Neste contexto, devido ao rápido desenvolvimento das atividades industriais nos últimos anos, têm sido reportados vários estudos sobre o desenvolvimento de novos materiais a partir de diferentes tipos de resíduos para diversas aplicações, tais como catálise [6], processos de separação [7,8], sistemas liberação de drogas [9] e aplicações em tecnologia ambiental como adsorventes para purificação de efluentes [10,11].

Dentre os vários tipos de adsorventes mencionados na literatura, o carvão ativado (CA) é o mais popular. Os carvões ativados são bem conhecidos pelas suas excelentes características de adsorção devido às suas estruturas de poros e área superficial específica elevada. No entanto, nem sempre os CAs podem ser aplicados eficientemente, pois podem ter um custo de preparação elevado, não possuem boa resistência mecânica e podem sofrer restrições em determinados processos industriais [12]. Portanto, ao longo dos anos, surgiram novas pesquisas no desenvolvimento de novos materiais, em relação ao carvão ativado, como no caso dos materiais híbridos organo-inorgânicos, no sentido de aplicá-los em situações em que o carvão ativado não possibilita boa eficácia [10-12].

## **Capítulo Um:** Apresentação, Introdução, objetivos e a justificativa do trabalho.

Com base neste contexto, adsorventes à base de organossilicas tais como polissiloxanos vêm ganhando grande notoriedade nos últimos anos [13,14]. Os polissiloxanos possuem suas estruturas baseadas em uma espinha dorsal inorgânica em cadeia de silício-oxigênio (-Si-O-Si-O-Si-O-) com grupos laterais orgânicos ligados aos átomos de silício [15,16]. Em relação ao carvão ativado, os materiais derivados de polissiloxanos possuem várias vantagens, que incluem uma melhor estabilidade mecânica e térmica e são fáceis de serem modificados e funcionalizados em muitas formas, devido à existência de grupos hidroxil livres (OH) sobre as suas superfícies [14-16], que podem ser utilizados para a anexação de grupos funcionais [14-16]. Essas vantagens possibilitam direcionar uma melhor aplicação para os materiais preparados com polissiloxanos para aquelas situações em que CA não é eficaz [14,16].

No entanto, materiais híbridos puros derivados de polissiloxanos são caros se forem utilizados como adsorventes em comparação com carvões ativados, principalmente se forem produzidos a partir de precursores de baixo custo, tais como lodo de esgoto [17].

O lodo de esgoto é um inevitável subproduto gerado nas estações de tratamento de esgoto sanitário e é produzido em grandes volumes em todo o mundo [18]. Estas enormes quantidades de resíduos, conseqüentemente, podem causar grandes problemas de manuseamento e eliminação, que estão associados ao alto custo [18]. Cerca de metade dos custos operacionais de uma estação de tratamento é aplicada ao manejo do lodo, de modo que, encontrar alternativas que minimizem este impacto, representa um grande desafio tecnológico e econômico [18]. Geralmente para destinação final do lodo são utilizados os aterros sanitários, no entanto, alguns estudos vislumbram sua aplicação como insumo agrícola, fertilizante, na construção civil e na produção de novos materiais [17,18].

Uma possibilidade de superar o problema colocado acima é combinar o lodo de esgoto com outros precursores, como os polissiloxanos, com o objetivo de combinar suas propriedades intrínsecas para produzir adsorventes com novas propriedades e/ou combinadas. Os materiais resultantes devem possuir boa rigidez como a dos polissiloxanos, associados com maior comportamento hidrofílico dos materiais de matriz orgânica, que podem ser utilizados para diversas finalidades, entre as quais como adsorventes para a remoção de diversos compostos orgânicos, como os fármacos e compostos fenólicos.

Os compostos orgânicos como fármacos e compostos fenólicos são considerados contaminantes ambientais devido a estas moléculas serem biologicamente ativas além de possuírem características lipofílicas e frequentemente apresentam baixa biodegradabilidade no

## **Capítulo Um:** Apresentação, Introdução, objetivos e a justificativa do trabalho.

ambiente. Estas propriedades intrínsecas apresentam um grande potencial para sua bioacumulação e toxicidade em organismos e elevada persistência no ambiente [19,20].

Devido a essas características, os fármacos e os compostos fenólicos são frequentemente encontrados em efluentes de estações de tratamento de esgotos e em estações de tratamento de águas para o abastecimento público e em águas naturais em concentrações na faixa de ng/L e µg/L [19,20].

De modo geral, a presença dos fármacos e dos fenóis nos mananciais de abastecimento é uma questão chave em relação à qualidade da água potável. Em virtude dos riscos que estes compostos podem vir a representar à saúde humana e por sua difícil remoção no tratamento convencional de água, muitos estudos estão sendo direcionados para o desenvolvimento e aprimoramento de novas tecnologias de remoção destas substâncias, de modo a resguardar a qualidade dessas águas para o consumo humano [19,20].

Diante das várias tecnologias envolvidas no processo de purificação de águas, o processo de adsorção tem sido extensivamente estudado devido ao seu potencial como alternativa ou complemento aos processos convencionais de tratamento de efluentes, uma vez que apresenta um baixo consumo de energia, tem possibilidade de regeneração do adsorvente, de recuperação da substância adsorvida, a não necessidade de uso de outros componentes para ajudar a separação, não forma subprodutos no processo e é economicamente mais viável [17].

Diante do exposto, nesta tese de doutorado avaliou-se (i) o uso de design of experiments (DOE) para otimização e preparação de carvões ativados provenientes de lodo de esgoto por pirólise convencional e por microondas; (ii) Preparação de adsorventes a partir de lodo de esgoto e polissiloxanos e seu uso na adsorção dos fármacos diclofenaco e nimesulida; (iii) caracterização e aplicação dos carvões ativados na remoção de diclofenaco e nimesulida em soluções aquosas e (iv) comparar, caracterizar e aplicar carvões ativados preparados por pirólise convencional e assistida por microondas na remoção de compostos fenólicos em efluentes aquosos.

## **2. OBJETIVO GERAL**

O objetivo global desse trabalho foi de preparar, caracterizar e aplicar adsorventes à base de lodo de esgoto e polissiloxanos. Os adsorventes foram utilizados para remoção de espécies orgânicas em efluentes aquosos. Foram utilizados como precursores para preparação dos adsorventes o lodo de esgoto doméstico seco, metil-fenil-siloxanos (H44), metil-siloxanos

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(MK), ortossilicato de tetraetilo (TEOS). Cada precursor foi utilizado para preparação dos adsorventes de maneira individual e combinada sob diferentes proporções. Os adsorventes que foram preparados através de lodo de esgoto puro foram chamados de carvões ativados, os que foram preparados e combinados com TEOS foram chamados de híbridos e os preparados através da combinação entre os polissiloxanos e lodo foram chamados de adsorventes compósitos.

Após preparação dos adsorventes, os mesmos foram utilizados na remoção de várias espécies orgânicas, em meio aquosos, por meio de adsorção em batelada. No processo de adsorção, vários parâmetros operacionais do sistema foram avaliados como efeito do tempo de contato, do pH inicial, da temperatura, da quantidade de massa de adsorvente etc.



# ***Capítulo Dois***

### **3. REVISÃO DE LITERATURA**

#### **3.1. LODO DE ESGOTO E SUA PROBLEMÁTICA**

Os processos de tratamentos de esgotos domésticos resultam na produção de um subproduto sólido ou semi-sólido denominado lodo. Basicamente o lodo é gerado nos reatores biológicos, em unidades de tratamento primário e secundário [21,22].

O lodo de esgoto é um material rico em matéria orgânica e nutrientes, tais como fósforo e nitrogênio [21]. Eventualmente podem conter metais pesados provenientes de despejos clandestinos de esgotos industriais. Em relação aos esgotos domésticos, a fração de lodo representa cerca de 1 a 2% do volume tratado de esgoto; parece pouco, no entanto, a crescente universalização do esgotamento sanitário no país provoca um crescente aumento na geração de lodo, tornando-se um sério problema a ser enfrentado pelos profissionais do saneamento [21,22]. O lodo, além de acumular passivos ambientais, gera custos operacionais que variam entre 20 a 60% de uma estação de tratamento de esgoto [21,22].

No Brasil, embora não disponha de dados consistentes referentes à produção de lodo, há projeções, baseadas em estimativas, feitas pela Sabesp, que apontam valores crescentes para a produção, uma vez que os serviços de coleta e tratamento de esgotos estão em ampliação por todo país [22]. Segundo a Sabesp, apenas a região metropolitana de São Paulo no ano de 2007 produziu 485 toneladas de lodo por dia (ou 177.075 mil toneladas por ano), em 2013 a produção foi de 890 toneladas por dia, totalizando uma geração anual próxima as 330 mil toneladas [22]. Um crescimento na geração de lodo de 83,5% em apenas seis anos, que pode ser explicado pelos investimentos no setor de saneamento, principalmente nas implementações de novas estações de tratamento de esgotos nos grandes centros populacionais. Segundo Andreoli [23], quando o Brasil igualar seus índices de cobertura no tratamento de esgotos aos dos países de desenvolvidos a produção saltará, facilmente, para alguns milhões de toneladas por ano [22,23]. Dados estes que ao mesmo tempo em que contemplam as necessidades ambientais de se tratar os esgotos, evitando o despejo direto e prejudicial em mananciais de água limpa, gera também preocupação em torno do destino que se dará ao lodo gerado [23].

Com a crescente geração de lodo de esgoto, exige-se que se pense em novas formas utilização e destino. Hoje em dia, a gestão do lodo de esgoto inclui principalmente sua destinação para: compostagem para uso como insumo agrícola e disposição em aterro

## **Capítulo Dois: Revisão de literatura.**

sanitário. No entanto, este último se mostra insustentável ao médio e longo prazo devido aos custos operacionais, redução da vida útil dos aterros e restrições ambientais mais rigorosas [21-24].

Sendo assim, a utilização do lodo de esgoto para produção de novos materiais, inclusive adsorventes, apresentam-se como uma alternativa promissora, por inúmeras vantagens, tais como eliminação total de agentes patogênicos, mineralização dos constituintes orgânicos, redução substancial do volume, e valorização econômica deste resíduo etc [5,25]. Vários estudos têm demonstrado a viabilidade deste tipo de conversão com muitas possibilidades de aplicação, esses estudos serão reportados no tópico a seguir.

### **3.2. LODO DE ESGOTO COMO PRECURSOR PARA PRODUÇÃO DE CARVÃO ATIVADO**

A aplicação do lodo de esgoto como matéria prima para produção de adsorventes é viável principalmente devido a sua composição predominantemente orgânica que, embora possa variar, este percentual gira em torno de 40 - 60% de matéria orgânica [21]. Isto viabiliza, após a pirólise, a geração de uma matriz carbonácea com teores elevados de carbono fixo [17].

Muitos pesquisadores têm reconhecido que o lodo de esgoto é um recurso com enorme potencial para usos mais nobres, utilizando-o como matéria prima para produção de novos materiais, o que, além de promover eliminação de seu uso direto, o que gera ganhos ambientais, econômicos e de melhoria de qualidade de vida dos que, por ventura, trabalhariam diretamente com este perigoso resíduo [17,21,23]. Beeckmans e Ng [25] propuseram, pela primeira vez, em 1971, que o lodo de esgoto poderia ser convertido em um adsorvente carbonáceo útil se pirolisados sob condições controladas ou com algum tipo de tratamento químico. Os resultados alcançados pelas primeiras pesquisas foram considerados tímidos em relação à qualidade dos adsorventes gerados, no entanto, serviram com ponto de partida para que a metodologia fosse sendo aprimorada ao longo dos anos [17,26-29]. Várias investigações foram realizadas no que diz respeito de estudos de viabilidade e de otimização do processo de conversão de lodo em materiais adsorventes, mais precisamente carvão ativado [17,26-32].

Ros et all. [30], Canals-Battle et all. [31] e Monsalvo et all. [32] desenvolveram adsorventes com ótimas propriedades, em relação a suas propriedades texturais,

principalmente devido as suas elevadas áreas superficiais. Para se ter uma ideia do potencial do lodo como precursor para produção de carvões ativados altamente porosos, em estudo proposto por Ros et all. [30] a área do carvão produzido foi de  $1686 \text{ m}^2 \text{ g}^{-1}$ , em outro estudo Monsalvo et all. [32] obteve uma área de  $1801 \text{ m}^2 \text{ g}^{-1}$ . Estes trabalhos denotam que a utilização do lodo de esgoto pode ser incrivelmente viável para produção de adsorventes porosos, inclusive com porosidade superior a alguns carvões comerciais.

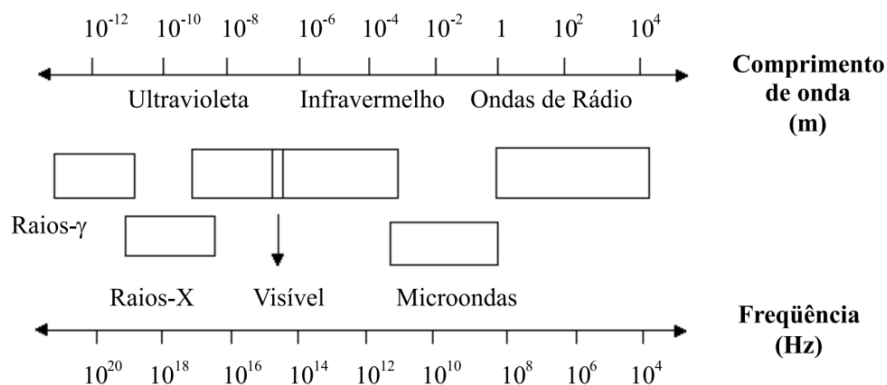
A qualidade dos carvões ativados obtidos pela pirólise do lodo de esgoto é influenciada pelas condições operacionais empregadas no processo. Por exemplo, quando através da pirólise convencional são empregadas baixas temperaturas e longos tempos de residência na pirólise, há o favorecimento na produção da fração sólida (por exemplo, carvão ativado) e com elevada porosidade [17,33-35]. O mesmo acontece quando utilizam elevada potência para o aquecimento por micro-ondas. Altas temperaturas e longos tempos de residência favorecem a formação de gases e na fração sólida ocorre o processo de sinterização [17,33-35]. Temperaturas moderadas e baixo tempo de residência favorecem a produção de líquidos [17,33-35].

Já o aquecimento, usando forno de micro-ondas, ocorre de maneira muito rápida e em curto período de tempo, podendo culminar em produtos de maior densidade relativa e menor tamanho médio de grão, comparativamente ao aquecimento convencional, o que culminaria na diminuição significativa na área de superfície dos adsorventes.

### 3.3. CONSIDERAÇÕES SOBRE OS PROCESSOS DE AQUECIMENTO

O aquecimento de um determinado material pode ser realizado em fornos convencionais ou em fornos de microondas, no primeiro o processo ocorre via condução ou convecção, já no segundo o aquecimento ocorre através de ondas eletromagnéticas [36,37]. O aquecimento em microondas gera menores perdas de energia para o ambiente, e consequentemente, tem maior economia de energia quando comparado aos fornos convencionais [36,37].

As microondas são radiação eletromagnética não ionizante, que possuem uma frequência que vai de 300 a 300.000 MHz e que corresponde a comprimentos de onda de 1 mm a 1 m. A região de micro-ondas situa-se entre a região de infravermelho e ondas de rádio no espectro eletromagnético [36,37] (**Figura 1**).



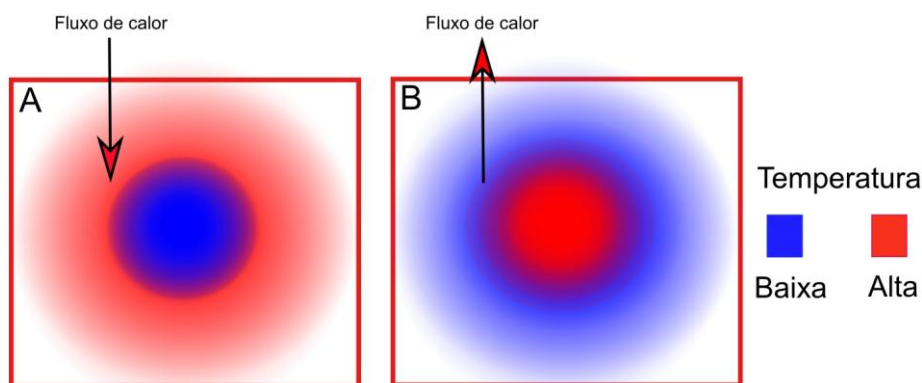
**Figura 1.** Localização da região de microondas no espectro eletromagnético

Como mencionado acima, o aquecimento por microondas é completamente diferente daquele que ocorre em um forno convencional. O aquecimento por microondas é também chamado de aquecimento dielétrico, e existem dois mecanismos principais para a transformação de energia eletromagnética em calor [36,37]. O primeiro deles é chamado rotação de dipolo, e relaciona-se com o alinhamento das moléculas (que tem dipolos permanentes ou induzidos) com o campo elétrico aplicado [36,37]. Quando o campo é removido às moléculas voltam a um estado desordenado, e a energia que foi absorvida para esta orientação nestes dipolos é dissipada na forma de calor. Como o campo elétrico na frequência de 2,45GHz oscila (muda de sinal)  $4,9 \times 10^9$  vezes por segundo, ocorre um pronto aquecimento destas moléculas [36,37].

O segundo mecanismo é chamado de condução iônica, e o calor é gerado através de perdas por fricção, que acontecem através da migração de íons dissolvidos quando sob a ação de um campo eletromagnético. Estas perdas dependem do tamanho, carga, condutividade dos íons dissolvidos e interação destes últimos com o solvente.

Em relação ao processo convencional, o aquecimento por micro-ondas está diretamente relacionado com o aquecimento interno do material. Neste sentido, a energia é transferida a partir da interação entre moléculas ou átomo, representando transformação de energia eletromagnética em energia térmica. Diferentemente, nos processos de aquecimento convencionais, baseados em condução, convecção e radiação, o calor é transferido da superfície do material em direção ao centro. A **Figura 2** esquematiza como os perfis de aquecimento se descolam entre as pirólises convencionais e por micro-ondas.

Uma vez que as micro-ondas são capazes de penetrar o material que então reterá esta energia, calor é gerado em toda a amostra. A uniformidade do aquecimento dependerá do tamanho da amostra e da profundidade de penetração das micro-ondas.



**Figura 2.** Comparação entre o perfil do gradiente de temperatura em amostras aquecidas por (A) processo convencional e (B) aquecimento por microondas.

As vantagens do processo de aquecimento pelo emprego de microondas em relação ao aquecimento convencional estão relacionadas ao fato de que as microondas proporcionam o aquecimento do material na ausência de contato, havendo transferência de energia com rapidez e uniformidade, aquecimento volumétrico, iniciando-se no interior do material, além do alto nível de segurança e potencial de automação [36,37]. Adicionalmente tal sistema oferece uma série de vantagens como agilidade de início e execução de processamento, elevada eficiência energética (quanto à quantidade de energia implicada pela quantidade efetivamente absorvida).

Contudo no tocante a produção de materiais adsorventes ainda não há uma definição categórica de qual dos dois métodos de aquecimento é o que gera melhores resultados quanto às qualidades físicas e químicas destes materiais, na literatura encontram-se inúmeros trabalhos relatando ora um método ora outro como a melhor técnica de aquecimento, o certo é que tais considerações devem ser analisadas caso a caso, pois o que de fato influencia na qualidade final de um adsorvente é um conjunto de fatores e não apenas o método de aquecimento em si, como por exemplo, as condições operacionais e a tipo de matéria prima utilizada.

A seguir são apresentados os principais parâmetros que influenciam na qualidade dos carvões ativados obtidos pela pirólise.

#### 3.4. INFLUÊNCIA DAS CONDIÇÕES OPERACIONAIS DA PIRÓLISE DE LODO DE ESGOTO NAS CARACTERÍSTICAS DOS CARVÕES ATIVADOS

## **Capítulo Dois:** Revisão de literatura.

Os principais parâmetros que irão determinar a qualidade e o rendimento do produto pirolisado são a taxa de aquecimento, potência de radiação, temperatura final e o tempo de residência, contudo a natureza da matéria-prima também possui uma enorme influência na qualidade e nas características do produto final, após a pirólise [17,33-35].

A taxa de aquecimento influencia diretamente na qualidade do produto gerado, quando a pirólise ocorre com uma taxa de aquecimento muito alta, as reações físico-químicas favorecem a formação de frações voláteis, principalmente gases, provocado pelo maior grau de destilação do material, com o consequente aumento na quantidade de líquido e gás não-condensável, em contrapartida ocorre uma redução no rendimento do produto sólido [17,38]. Por outro lado, quando o aquecimento ocorre de forma gradual, às reações favorecem a formação de sólidos, influenciada pela menor grau de volatilização do material orgânico [17,33-38]. A **Tabela 1** mostra resultados da preparação de carvões ativados a partir do lodo de esgoto e sob os dois tipos de pirólise e também diferentes condições de pirólise e consequentemente apresentaram diferentes características finais em relação às áreas superficiais.

A qualidade final dos produtos gerados, também, depende fortemente das propriedades físico-químicas da matéria-prima utilizada, por exemplo, na pirólise de madeira a lignina contribui para a formação de cerca de 50% do carbono fixo na fração sólida [17,35,38,39]. Portanto, materiais com alto teor de lignina são mais apropriados para a obtenção de alta concentração de carbono fixo na fração sólida, muito provavelmente pela estrutura química da lignina que possui uma maior estabilidade térmica devido ao seu arranjo químico, ou seja, cadeias carbônicas longas com isto se faz necessário uma maior energia (calor) para degradá-la termicamente [39].

Para a produção de carvões provenientes de lodo de esgoto é interessante que o mesmo contenha elevados teores de carbono em sua estrutura química. Uma vez que o carvão ativado tem sua estrutura química baseada em átomos de carbono ligados a oxigênio e outros elementos pode-se inferir que quanto maior a quantidade de carbono conter a matéria-prima maior será o teor de carbono no carvão ativado [40].

A **Tabela 1** mostra alguns estudos relacionando as condições de pirólise de lodo características físicas dos carvões ativados (área superficial). Nota-se que as duas maiores áreas obtida a partir da pirólise de lodo foram de  $1893 \text{ m}^2 \text{ g}^{-1}$  e  $1058 \text{ m}^2 \text{ g}^{-1}$ .

**Tabela 1.** Características físicas dos carvões ativados obtidos a partir do lodo de esgoto por diversos autores

Tipo de pirólise	Condições de pirólise				Ativação química	S <sub>BET</sub> (m <sup>2</sup> g <sup>-1</sup> )	Referência
	Temperatura (°C)	Potência (Watts)	Tempo (min)	Taxa (°C/min)			
Convencional	300	-	30	17	K <sub>2</sub> CO <sub>3</sub>	18	[41]
Convencional	500	-	30	17	K <sub>2</sub> CO <sub>3</sub>	90	[41]
Convencional	400	-	60	10	KOH	262	[42]
Convencional	750	-	60	10	KOH	1832	[42]
Convencional	450	-	30	125	ZnCl <sub>2</sub>	230	[43]
Convencional	700	-	30	5	KOH	1058	[44]
Convencional	700	-	30	5	NaOH	188	[44]
Convencional	950	-	30	10	Ar	103	[45]
Convencional	1000	-	60	20	-	96	[46]
Convencional	650	-	60	5	H <sub>2</sub> SO <sub>4</sub>		[47]
Microondas	-	8000	30	-	KOH	130	[48]
Microondas	-	8000	10	-	ZnCl <sub>2</sub>	83	[48]
Microondas	-	1200	2.5	-	ZnCl <sub>2</sub>	491	[49]
Microondas	-	800	10	-	ZnCl <sub>2</sub>	377	[50]
Microondas		800	10		H <sub>3</sub> PO <sub>4</sub>	291	[50]

Por outro lado, houve estudos em que as áreas superficiais geradas não foram tão elevadas [41,46,48]. As condições de pirólise e o agente químico impregnante podem ter causado forte influencia sob as áreas superficiais dos carvões ativados. Geralmente, os estudos indicam que a área de superfície do lodo de esgoto pirolisado é maximizada em altas temperaturas [30-35,44,45].

Bagreev e Badosz [51] e Calvo e colaboradores [52] relataram que esta foi uma consequência do aumento da aromatização da cadeia carbônica que ocorreu a altas temperaturas. Além disso, Inguanzo e colaboradores [47] propôs que a pirólise provoca o aumento da porosidade através da desobstrução dos poros obstruídos pela matéria volátil. Contudo, como se observa através **Tabela 1**, houve variações expressivas da temperatura final na pirólise do lodo de esgoto e isso refletiu em diferentes características dos carvões gerados. A grande faixa de temperaturas utilizadas pelos trabalhos podem sugerir que embora a matéria-prima (lodo de esgoto domestico) seja basicamente o mesmo, as diferentes fontes de



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coleta do lodo podem ter influenciados na temperatura ótima em que a “qualidade” do carvão é obtido, isto reforça ainda mais a ideia de implementação de uma metodologia que avalie uma ampla faixa do parâmetro temperatura de pirólise para a produção de carvões ativados, assim como os demais parâmetros, para assim determinar em que condições são gerados carvões com melhores propriedades (área superficial etc).

Em relação ao parâmetro taxa de aquecimento, a densidade aparente do carvão é sensivelmente influenciada pela velocidade de carbonização [38]. Observa-se que na carbonização rápida obtém-se um carvão menos denso do que na carbonização lenta, sugerindo que os carvões produzidos em altas taxas de aquecimento não apresentam boas características físicas [33,38]. A mesma tendência foi encontrada por Slocum, McGinnes e Beall [53], ao estudarem o efeito da taxa de carbonização sobre o rendimento em carvão. O que acontece é que taxas de aquecimento elevadas favorecem a maior volatilização do material e potencializa a produção de gases e líquidos fazendo com que a produção da fração sólida seja minimizada [38,53]. As taxas de aquecimento utilizadas variaram de 5 - 25°C/min, contudo, a taxa de aquecimento é improvável que seja o fator determinante na influência das características físicas dos carvões, uma vez que a natureza do material precursor, a temperatura final e o modo de ativação são relatados como os que mais influenciam na qualidade final do produto [30-39,43-45].

Geralmente, para pirólise de precursores carbonáceos, elevadas temperaturas acaba por necessitar de um menor tempo de residência no reator sob temperatura final [33,38]. Em temperaturas de 950 °C e 700°C, os tempos de permanência relatados por [41], [43], [45] e [48] foram de 30 min, no entanto, as áreas superficiais foram bastante distintas, variaram de 18 e 1058, respectivamente. A ideia de que aumentando a temperatura final de pirólise e diminuindo o tempo de permanência refletirá no aumento das áreas superficiais nem sempre é verdadeiro, haja vista que, no processo de pirólise, é o conjunto de parâmetros (temperatura final, tempo de reação, taxa de aquecimento e modo de ativação) que de fato influenciará na qualidade dos carvões produzidos.

Ainda em relação a submeter um precursor, predominantemente, carbonáceo, a exemplo do lodo de esgoto, a elevada temperatura de pirólise (superiores a 900 °C) pode ocorrer um efeito deletério no produto final, principalmente associado ao uso de tempos de permanência prolongados, pois resulta na solidificação e retração da matriz carbonácea [33,34,47]. Contração é uma consequência da aromatização excessiva do lodo, que resulta no estreitamento ou fechamento das entradas dos poros, reduzindo assim a área superficial

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acessível [33,34,47]. Essa contração foi verificada por Iguanzo et al. [47], que observou que a densidade do carvão ativado aumentou com o aumento da temperatura de carbonização. Rio et al. [46] pirolisou o lodo a 1000°C e obteve uma área superficial muito pequena (96 m<sup>2</sup>/g) em relação aos outros autores (ver Tabela 1), este resultado reforça a ideia de que temperaturas acima dos 900°C pode comprometer a qualidade do carvão levando em conta suas áreas superficiais. No entanto, como mostra a mesma Tabela 1, Iguanzo et al. [47] usou a temperatura de 650°C e obteve uma área muito pequena (82 m<sup>2</sup>/g) corroborando a ideia de que realmente não é um único parâmetro que vai determinar o sucesso na preparação de carvões ativados e sim a conjugação dos parâmetros.

As propriedades texturais do carvão ativado como SBET pode ser melhorada usando planejamento experimental por meio da metodologia de superfície de resposta (MSR). MSR é uma ferramenta muito valiosa para este fim, uma vez que apresenta modelos estatísticos que podem ser usados para compreender as interações entre os parâmetros que estão sendo analisados e otimizados [54-56]. MSR tem sido amplamente aplicada em vários processos para a otimização das condições experimentais, e se revelou útil para a preparação de carvão ativado. Conforme relatado recentemente, MSR tem sido aplicada na produção de AC usando diferentes precursores, tais como: lenhite Turco [54], sementes de *Albizia lebbek* [55] Bambu [56], casca de jatobá [57], policarbonatos [58] e casca de coco [59]. No entanto, até onde sabemos nenhum trabalho foi desenvolvido no sentido de aplicar planejamento estatístico de experimentos para preparar carvões ativados a partir de lodo de esgoto pela pirólise convencional e por microondas.

### 3.5. PLANEJAMENTO FATORIAL DE EXPERIMENTOS

A necessidade da otimização de processos e a minimização de custos e tempo, levam à busca de técnicas sistemáticas de planejamento de experimentos [60-62]. Experimentos delineados em esquemas fatoriais são aqueles que envolvem combinações entre os níveis de dois ou mais fatores escolhidos para estudo do processo [60,61].

O uso de projeto de experimentos permite que se estruture a seqüência de ensaios de forma a traduzir os objetivos preestabelecidos pelo pesquisador [60-62]. Segundo Montgomery [60] e Bezerra et al. [62], planejar um experimento fatorial, ao invés de um fator-por-vez, é a maneira mais eficaz de determinar a influência de dois ou mais fatores sobre a variável resposta, porque:

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(i) requer menos recursos (experimentos, tempo, material) para a quantidade de informação obtida;

(ii) as estimativas dos efeitos fatoriais são mais precisas. Usando mais observações para estimar um efeito resulta em maior precisão;

(iii) o efeito das interações entre os fatores podem ser estimadas sistematicamente;

(iv) obtém-se informações para uma região experimental maior.

Pelos experimentos fatoriais obtém-se informações para uma região experimental maior porque cada efeito fatorial é calculado sobre todas as combinações possíveis dos níveis dos outros fatores, o que não necessariamente ocorre com a estratégia um-fator-por-vez [57-62]. Uma grande vantagem de experimentos fatoriais é que eles permitem estudar uma série de fatores simultaneamente e, em especial, o efeito de interação [57-62].

O planejamento de experimento é comumente utilizado em associação à análise de superfície de resposta (através da metodologia de superfície de resposta (MSR)), com intuito de determinar as condições ótimas operacionais, fornecendo informações seguras do processo, minimizando ou maximizando-o [57-62]. A MSR é uma técnica estatística utilizada para a modelagem e análise de problemas nos quais a variável resposta é influenciada por vários fatores, cujo objetivo é a otimização dessa resposta [62]. Modelos de superfície de resposta são frequentemente usados na substituição de modelos físicos complexos, a fim de gerar correlação entre dados experimentais e de reduzir os custos em problemas de otimização [60-62].

Recentemente, planejamento estatístico de experimentos e MSR tem sido amplamente aplicada em vários processos para a otimização das condições experimentais, e tem se tornado uma ferramenta útil para a preparação de carvão ativado.

Karacan , Ozden e Karacan [54] aplicou planejamento de experimentos e metodologia de superfície de resposta para produzir carvões ativados a partir de lignite turca pela ativação com  $K_2CO_3$ . Foram analisados a influência de dois fatores (proporção de  $K_2CO_3$  e temperatura) sobre quatro respostas (rendimento de carvão, SBET, volume de poros e fração de microporos). As condições ótimas para a preparação de carvão ativado a partir de lignite turca foram, a proporção de lignite/  $K_2CO_3$  de 02/05 e temperatura de carbonização de 800° C.

González, Hernández-Quiroz e García-González [54] também usou a metodologia de superfície de resposta para produzir carvões ativados a partir de bamboo. Os autores avaliaram a influência de quatro fatores (temperatura de ativação, tempo de ativação,

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temperatura de carbonização e agente de ativação) sobre cinco respostas ( ponto de carga zero, densidade do carvão, umidade, capacidade adsorviva, grupos ácidos de superfície e rendimento). De acordo com a análise estatística os agentes de ativação ( $H_3PO_4$  e  $NaOH$ ) foram os que mais influenciaram nas propriedades físicas dos carvões.

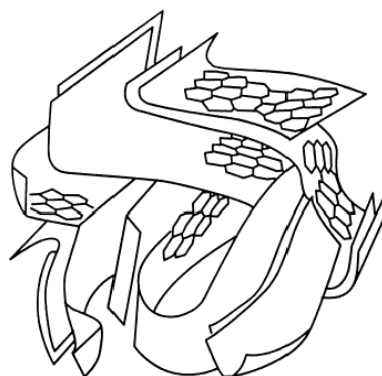
Similar procedimento foi avaliado por Gratuito et al. [59] que utilizou a mesma metodologia para preparar carvão ativado usando a casca de coco como precursor e ácido fosfórico ( $H_3PO_4$ ) como agente de ativação. Quinze combinações de três variáveis tais como; proporção de impregnação (1, 1,5, e 2); O tempo de ativação (10, 20, e 30 min); e temperatura de ativação (400, 450, 500°C) foram otimizadas com base nas respostas avaliadas (rendimento, densidade aparente, diâmetro médio de poro, diâmetro de poro pequeno, e número de poros por unidade de área). Baseado na MSR, as condições ótimas para preparação de carvão ativado provenientes da casca de coco são 1,725, 19,5 min e 416° C para proporção de impregnação, tempo de ativação e temperatura de ativação, respectivamente.

Nesta tese, um dos objetivos deste trabalho foi preparar carvões ativado provenientes de lodo de esgoto doméstico otimizando as condições de pirólise (por pirólise convencional e irradiação por micro-ondas). Para isto foi utilizada a metodologia do planejamento experimental fatorial e análise de superfície de resposta para verificar as influências das variáveis: temperatura, potência de micro-ondas, tempo de residência e proporção de agente de ativação sob a qualidade do carvão ativado, em relação a suas áreas superficiais.

### 3.6. CARVÃO ATIVADO

Carvão ativado é um dos adsorventes mais utilizados na remoção de impurezas, seja gases e/ou líquidos devido, principalmente, a sua alta capacidade de adsorção. O carvão ativado é um material carbonáceo que apresenta uma pequena quantidade de heteroátomos, principalmente oxigênio, ligado aos átomos de carbono. Além disso, possui uma estrutura porosa bem desenvolvida e sua alta capacidade de adsorção está associada principalmente com sua área superficial, que pode variar entre 500-1500  $m^2/g$ , distribuição de tamanho e volume de poros [63,64].

Os carvões são constituídas de lâminas carbônicas de cadeia curta e distorcidas, empilhadas de forma irregular e unidas entre si para formar um rede tridimensional [63,64]. Os espaços ociosos entre essas lâminas formam os poros do carvão, como mostrado esquematicamente na **Figura 3**.



**Figura 3.** Esquema da microestrutura do carvão ativado.  
Fonte: [61].

O carvão ativado pode ser produzido a partir de diversos materiais carbonáceos. Na literatura, encontram-se vários trabalhos envolvendo diversos tipos de matéria prima para a obtenção de carvão ativado como, sementes e resíduos de vegetais [34,38], bambu [56], casco de Jatobá [57], Policarbonato [58], casca de cocô [59], espiga de milho [65], caroço de pinhão [66] entre muitos outros precursores. Entretanto, outro precursor em potencial é o lodo de esgoto [25-32,40-51]. Na literatura internacional há muitos trabalhos que envolvem este tipo de material para produção de carvões ativados [25-32,40-51]. No entanto, o potencial do lodo de esgoto como matéria-prima para a produção de adsorvente foi reconhecido por Kemmer *et al.*, (1971), citado por Beeckmans e Ng [25], no qual patentearam um processo para a produção de adsorventes por ativação química de lodo seco. No mesmo ano, Beeckmans e Ng [25] produziu o primeiro estudo sobre a produção de adsorventes de lodo de esgoto pelo processo de carbonização. Após estes estudos, uma série de pesquisas vem sendo conduzidas no sentido de aprimorar a técnica de pirólise na produção de adsorvente [25-32, 40-51].

Agrafite *et al.* [41] ao pirolisar o lodo de esgoto gerou carvões com áreas superficiais na faixa de  $18-90 \text{ m}^2 \text{ g}^{-1}$ . Smith *et al.* [17] também produziu carvão ativado a partir de lodo de esgoto e originou áreas entre  $197-297 \text{ m}^2 \text{ g}^{-1}$ . Monsalvo *et al.* [32] encontraram áreas que variaram de  $15-1832 \text{ m}^2 \cdot \text{g}^{-1}$ . Estas variações, nos valores das áreas superficiais, podem ser explicadas pelas condições nas quais os lodos foram pirolisados como também pelos diferentes modos de ativação [41-43].

No Brasil ainda é pouco o número de trabalhos referenciando pesquisas empregando o lodo de esgoto como precursor na produção de carvão ativado, contudo, embora os poucos

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resultados tenham se mostrado tímidos podem ser considerados promissores [67]. O ensaio de adsorção de iodo, que serve para caracterizar os adsorventes quanto a sua microporosidade, indicou uma microporosidade elevada, adsorvendo 618 mg de iodo por grama de carvão ativado, indicativo que o adsorvente possui grande capacidade de retenção de moléculas pequenas [67].

Ainda de acordo com Mocelin [67] a utilização do lodo de esgoto sanitário para a produção de carvão ativado apresenta inúmeras potencialidades, que além de ser viável tecnicamente, pode ser impulsionado pelas restrições ambientais impostas pelas legislações virgentes. Os carvões obtidos proveniente do lodo de esgoto apresentaram grande heterogeneidade e presença de poros irregulares, devido ao lodo também ser um material altamente heterogêneo [43-45,66].

O poder adsorvente do carvão é proveniente, principalmente, da elevada área superficial e da presença de uma variedade de grupos funcionais em sua superfície. Uma vez ativado, o carvão apresenta uma alta porosidade interna que, dependendo do tamanho do poro, são classificados em macro, meso ou microporos conforme mostra o **quadro 1**.

**Quadro 1** - Classificação, tamanho e função dos poros do carvão ativado segundo a IUPAC

<b>Tipo de poro</b>	<b>Diâmetro médio</b>	<b>Função Principal</b>
MICROPOROS	$\theta_m < 2 \text{ nm}$	Contribuem para a maioria da área superficial que proporciona alta capacidade de adsorção para moléculas de dimensões pequenas, tais como gases e solventes comuns.
MESOPOROS	$2\text{nm} < \theta_m < 50\text{nm}$	São importantes para a adsorção de moléculas grandes tais como corantes e proporcionam a maioria da área superficial para carvões impregnados com produtos químicos.
MACROPOROS	$\theta_m > 50 \text{ nm}$	São normalmente considerados sem importância para a adsorção e sua função é servir como meio de transporte para as moléculas gasosas e solutos sólidos que percolam pelos poros dos carvões.

Fonte: [63]

O **Quadro 1** mostra que os tipos de poros possuem diferentes finalidades dentro do processo de adsorção e que a distribuição destes, vai dar maior qualidade aos carvões ativados em relação a sua área superficial e sua capacidade de adsorver determinadas moléculas e/ou poluentes. Quanto mais microporosa a superfície do carvão, maior será sua área superficial. Contudo, além disso, os carvões também devem conter macroporos, que são muito importantes na acessibilidade das moléculas (líquidos ou gases) para o interior das partículas de carvões, através da difusão intra-particular. A presença de micro-mesoporos influencia substancialmente suas propriedades adsorptivas de uma determinada substância, pois a quantidade de material adsorvido nos macroporos é desprezível em comparação àquela nos microporos [63-65].

Uma das questões chave para obter um material poroso, além das condições de pirólise, como fora discutido anteriormente, é o modo de ativação pelo qual o precursor é submetido. Sabe-se que tanto o tipo substância como o modo de como é feito o processo de ativação possui forte influência sobre as características dos materiais adsorventes. Em seguida serão apresentados os processos de ativação para carvões ativados.

### 3.7. PROCESSO DE ATIVAÇÃO DE CARVÃO ATIVADO

A etapa de ativação pode ser definida como um processo físico e/ou químico que desordena o material precursor, liberando compostos voláteis ricos em hidrogênio e oxigênio e deixando um sólido rico em carbono, com estrutura porosa muito desenvolvida [27,52,69].

No processo de ativação, o carvão é submetido à reação com gases e, às vezes, é feita a adição de produtos químicos antes e/ou depois à carbonização, para aumentar a porosidade [44,48,69]. Deseja-se no processo de ativação, controlar as características básicas do material (distribuição de poros, área superficial específica, atividade química da superfície, resistência mecânica).

Ros et all. [30] submeteram o lodo de esgoto a um pré-tratamento alcalino com NaOH e KOH e encontraram áreas superficiais bastante elevadas 689-1224m<sup>2</sup>/g e 853-1686 m<sup>2</sup>/g, respectivamente. Já Calvo et all. [52] produziram carvões ativados proveniente do lodo de esgoto seco para remover corante azul de metileno, em seguida o ativou quimicamente com H<sub>2</sub>SO<sub>4</sub> e fisicamente por calor (seco à 105 °C), constatou baixa capacidade de adsorção do

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corante devido, principalmente, ao elevado volume de microporos, a adsorção de azul de metileno é potencializada em adsorventes mesoporosos.

De acordo com Yin et al. [70] o tratamento ácido pode prejudicar a captura dos corantes. Este efeito foi reportado por Wang e colaboradores [71], o qual concluiu que os carvões ativados tratado com os ácidos clorídrico e nítrico resultaram na redução da captura de corantes catiônicos. Isto ocorreu porque o tratamento por ácido nítrico removeu os grupos hidróxidos, por neutralização, e produziu grupos funcionais de oxigênio ácidos na superfície do carvão, reduzindo as interações entre as moléculas dos corantes e o carvão.

A **Quadro 2** mostra um resumo das principais vantagens e desvantagens em relação ao modo de ativação dos carvões ativados.

Quadro 2 - Vantagens e desvantagens da ativação química e física de carvões ativados.

Modificação	Tratamento	Vantagens	Desvantagens
Características químicas	Ácido	Aumenta a presença de grupos funcionais ácidos na superfície do CA. Melhora a capacidade de quelação com espécies metálicas	Pode diminuir a adsorção de cátions metálicos e pode ter efeito adverso na remoção de orgânicos catiônicos.
	Básico	Melhora a adsorção de poluentes orgânicos e de cátions metálicos	Pode diminuir a adsorção de corantes aniônicos.
Características físicas	Calor	Aumenta a área superficial e volume de poros	Diminui a presença de oxigênio nos grupos funcionais da superfície

Fonte: [70,71]

De acordo com Soares [72,73] de modo geral, a ativação física (por meio de calor) produz uma estrutura de poro tipo fenda bastante fina, tornando os carvões assim obtidos apropriados para o uso em processo de adsorção de gases. Já a ativação química gera carvões com poros maiores, sendo mais apropriados para aplicações de adsorção em fase líquida [72,73].



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A ativação química é realizada pela incorporação de um ou mais elementos ou grupos funcionais na estrutura de carbono, pela impregnação de um agente desidratante (ácido fosfórico, hidróxido de potássio, cloreto de zinco, cloreto de cálcio e outros) ou oxidante (peróxido de hidrogênio, ácido nítrico e outros), geralmente sobre o precursor ainda não carbonizado para posterior carbonização.

A ativação química promove reações químicas na matriz de carbono que, por sua vez, promovem alterações físicas no material precursor por favorecer a criação e, algumas vezes, o alargamento dos poros, aumentando a área superficial interna e o volume de poros, resultando em uma mudança na formação dos mesoporos e macroporos [72,73]. Também modifica a química superficial do adsorvente, alterando sua funcionalidade com relação a sua afinidade por adsorvatos específicos. Neste sentido, a ativação com cloreto de zinco é a que se tem mostrado mais eficaz, sendo a substância mais usada industrialmente [26-29,43,48-50]. Esse tipo de ativação apresenta algumas vantagens quando comparada à ativação física, entre elas estão: menor temperatura na pirólise, o processamento ocorre geralmente em apenas uma etapa, alto rendimento, área superficial maior, a micro e mesoporosidade podem ser mais bem desenvolvida e controlada, se desejável [26-29, 43,48-50].

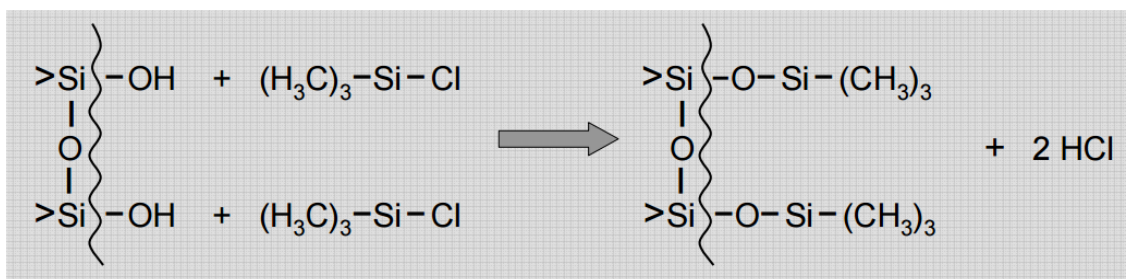
Como já foi, amplamente, mencionado neste trabalho, os carvões ativados são bem conhecidos pelas suas excelentes características de adsorção devido a sua elevada porosidade. No entanto, o processo de preparo dos carvões podem ser custosos e também a aplicabilidade dos carvões podem ser restringidas em determinados processos industriais [12]. Portanto, nos últimos anos, surgiram novas pesquisas no desenvolvimento de novos materiais, em relação ao carvão ativado, no sentido de aplicá-los em situações em que o carvão ativado não possibilita boa eficácia, como no caso dos materiais híbridos a base de silício e carbono [10-12].

A grande questão deste procedimento está relacionado à obtenção de novos materiais porosos que podem desempenhar as mais variadas funções. Baseado nisto, uma classe de materiais que vem sendo investigado nos últimos anos são os polissilxanos.

### **3.8. POLISSILOXANOS**

Os polissiloxanos são uma classe importante de polímeros que têm sido comercialmente disponíveis desde a década de 1940. Polissiloxanos são polímeros obtidos por

reações de hidrólise/condensação de misturas de cloro ou alcoxissilanos, conforme exemplificado na reação abaixo (ver **Figura 4**) [15,16].

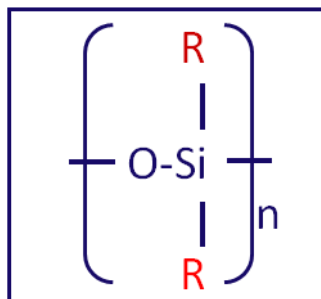


**Figura 4.** reações de hidrólise/condensação de misturas de cloro ou alcoxissilanos para obtenção de polissiloxanos.

Neste processo, os grupos cloreto vão ser substituídos por grupos OH [15,16,74]. A reação entre água do poro e R<sub>2</sub>SiCl<sub>2</sub> é muito rápida, de modo a retardar este processo, o etanol ou outro solvente alcoólico é usado, o qual reage também com R<sub>2</sub>SiCl<sub>2</sub> em uma etapa de substituição [15,16,74]. O processo entre a R<sub>2</sub>SiCl<sub>2</sub> e álcool diminui a velocidade da reação de R<sub>2</sub>SiCl<sub>2</sub> com água dos poros, o que é favorável para alcançar aerogels sem fissuras [16,74]. Os grupos ativos de OH serão convertidos em inativos O-Si-R, por exemplo, grupos (O-Si-(CH<sub>3</sub>)<sub>3</sub>) (**Figura 4**) [15,16,74]. Quando R não é volumoso, os grupos silanol são simultaneamente condensado e, assim, um polissiloxano com uma estrutura principal de Si-O é obtido [15,16,74].:

Contudo, uma parte dos silanóis permanece como grupos terminais, e polissiloxanos com algumas estruturas em anel aromático também pode ser obtida nas misturas resultantes. A unidade de repetição de um polissiloxano contém alternados átomos de oxigênio [Si-O] e com grupos orgânicos [-R] ligados a cada átomo de silício, conforme, um exemplo, mostrado nas **Figuras 4 e 5**.

Os grupos “R” são substituintes orgânicos que podem incluir metil (CH<sub>3</sub>), vinil (-CH = CH<sub>2</sub>), fenil (C<sub>6</sub>H<sub>5</sub>), hidrogênio (H), e grupos (CF<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>), mas talvez a espécie mais importante seja o grupo metil.



**Figura 5.** Estrutura geral do polissiloxano.

Os polissiloxanos são química e fisicamente inertes (exceto na presença de ácidos fortes e bases), são resistentes à oxidação e às altas temperaturas, têm baixas tensões de superfície, relativamente pequenas alterações na viscosidade com a temperatura, repelência de água, elevada compressibilidade e bem solúvel em muitos solventes orgânicos. Devido a todas estas características (ou vantagens), polissiloxanos tem recebido enorme atenção nos últimos anos, como precursores na preparação de materiais para varias aplicações industriais e domésticas, incluindo como agentes antiespuma, em produtos de cuidados automotivos como revestimentos, na construção civil como materiais selantes, e em cosméticos e produtos de higiene pessoal (xampus, loções, cosméticos, produtos para o cabelo, desodorantes, anti-transpirantes, produtos de limpeza da pele etc).

Não é surpreendente, portanto, notar que a superfície química e as propriedades físicas dos polissiloxanos desempenham um papel fundamental em suas aplicações, estas propriedade que fazem com que os polissiloxanos sejam materiais extremamente atrativos para o uso como catalisadores, suportes de catalisadores e adsorventes para uma ampla gama de aplicações tecnológicas e ambientais.

A literatura reporta alguns métodos para a síntese de polissiloxanos, porém o método sol-gel tem sido um dos mais estudados por gerar produtos com elevada pureza e homogeneidade, além de sua versatilidade e boa reprodutibilidade [75].

### 3.9. O PROCESSO SOL-GEL

Uma das principais rotas de obtenção de materiais híbridos orgânico-inorgânicos, como no caso dos polissiloxanos, é o processo sol-gel. Os géis poliméricos são, geralmente, preparados a partir de soluções, onde promovem-se as reações de hidrólise e condensação [16,74]. O sol é constituído de uma suspensão de partículas coloidais (dimensão entre 1 e

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1000 nm) em um líquido e o gel é formado pela estrutura rígida de partículas coloidais (gel coloidal) ou por cadeias poliméricas (gel polimérico) que imobilizam a fase líquida nos seus interstícios [50,74,76].

O interesse pelo processamento sol-gel começou em meados de 1900 com estudos de Ebelman [76] e Graham [50] em géis de sílica. Estes primeiros investigadores observaram que a hidrólise de tetraortossilicato (TEOS), sob condições ácidas, produziu SiO<sub>2</sub> na forma de um “material vítreo” [76]. Em 1950, Roy e colaboradores [77,78] reconheceram o potencial para atingir níveis muito elevados de homogeneidade química em géis coloidais utilizando o método sol-gel e para sintetizar um grande número de novas cerâmicas com composições de óxido, envolvendo Al, Si, Ti, Zr, que não poderiam ser feitas utilizando métodos tradicionais. Desde então, o interesse pelo método sol-gel tem crescido no meio da comunidade científica. A maior motivação para tal interesse é o fato desta técnica proporcionar a obtenção de pós com elevada pureza e homogeneidade química e também as baixas temperaturas de processamento.

O processo Sol-Gel pode ser definido como um método de obtenção de materiais vítreos ou cerâmicos através da preparação de um Sol, seguida pela sua geleificação e remoção da fase líquida. O processo envolve basicamente o uso de precursores (alcóxidos, soluções inorgânicas em meio aquoso, etc.), água, catalisador (ácido ou básico) e, no caso dos alcóxidos, a necessidade de solventes orgânicos, geralmente álcoois, na qual todos os reagentes devem ser solúveis no meio reacional. Os precursores alcóxidos são mais utilizados em relação às soluções inorgânicas devido a maior versatilidade. A água e o catalisador atuam na hidrólise. O álcool em excesso é necessário como solvente, pois alcóxidos não são solúveis em água.

As reações químicas envolvidas num processo sol-gel convencional, baseado em derivados alcóxidos, são:

1 – Hidrólise do precursor [75]

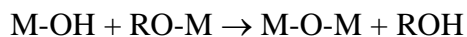
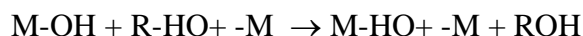
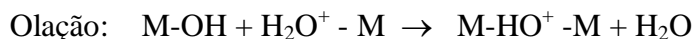


onde M=Si, Sn, Ti, Al, Mo, etc

Onde ROH representa o álcool (Metanol, Etanol, Propanol, e outros).

2 – A etapa posterior envolve reações de condensação que podem se processar por oxidação e oxolação [75]:

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Onde ROH representa o álcool (Metanol, Etanol, Propanol, e outros).

O processo sol-gel é relativamente complexo, envolvendo diversas variáveis, como tempo e temperatura da reação, natureza do catalisador, concentração de reagentes, etc [75-77]. Estas variáveis determinam as características finais dos materiais, incluindo a porcentagem de hidrólise e condensação de grupos reativos, densidade de reticulação, homogeneidade do produto, etc.

A natureza do catalisador, ácido ou básico, influencia fortemente na cinética de reação, assim como na estrutura final do gel [75,77-79]. Se a hidrólise for catalisada por base, a reação deve se processar através de uma substituição nucleofílica, e a velocidade de hidrólise será maior que a velocidade de condensação, levando à formação de cadeias mais ramificadas no início do processo. Se a hidrólise for catalisada por ácido, vai ocorrer uma reação eletrofílica, e a velocidade da condensação será maior que a da hidrólise, levando à formação de cadeias mais longas e menos ramificadas.

As mais recentes tecnologias requerem materiais com combinação de propriedades que, normalmente, não são encontradas nos materiais convencionais. Neste cenário, os materiais híbridos surgem como uma alternativa para a obtenção de novos materiais com características multifuncionais e potencialidade para aplicações nas mais diversas áreas.

### 3.10. MATERIAIS HÍBRIDOS

O termo “material híbrido” é muito amplo e abrange um grande número de sólidos, tão diferentes como polímeros de coordenação de elevada cristalinidade ou compostos amorfos obtidos por meio de processos de sol-gel. Em seu sentido mais geral, um material híbrido pode ser definido como um que inclui na sua composição, pelo menos, dois tipos de unidades ou frações de naturezas diferentes, pela combinação dos componentes orgânicos e inorgânicos que, normalmente, apresentam propriedades complementares, dando origem a um único material com propriedades diferenciadas daquelas que lhe deram origem [75,80]. Esses

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materiais são homogêneos, devido à mistura dos componentes em nível molecular, usualmente em escala manométrica [75,80].

Os materiais híbridos são de grande interesse em aplicações comerciais devido às suas propriedades mecânicas, ópticas e térmicas, que combinam a estabilidade térmica e química dos materiais a base de sílica, por exemplo, com a flexibilidade dos compostos e polímeros orgânicos. Além de representarem uma alternativa criativa para a pesquisa de novos materiais, estes compósitos também permitem o desenvolvimento de aplicações industriais inovadoras, tais como: células combustíveis, membranas, fotocatalisadores, catalisadores, sensores, biosensores, dispositivos microeletrônicos inteligentes, cosméticos, compósitos que combinam cerâmicas e polímeros, adsorventes entre outros.

Os materiais híbridos são classificados de acordo com suas interações entre as duas fases, orgânicas e inorgânicas. Estas interações ocorrem, como já foi dito, a nível molecular a nanométrico e é de extrema importância, pois por meio desta controla-se a transparência, a estabilidade e a homogeneidade química do material [75,80]. Entretanto, as propriedades de um material híbrido não são apenas um somatório das contribuições individuais de seus constituintes. Este sinergismo também depende da natureza química dos segmentos orgânicos e inorgânicos, do tamanho e da morfologia dos correspondentes domínios.

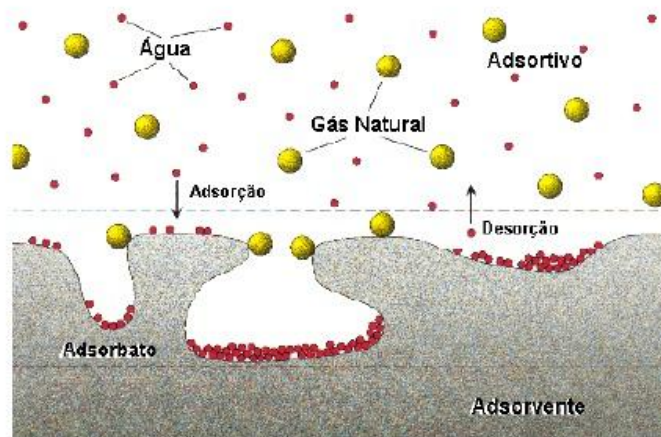
Os híbridos são classificados em duas classes principais. A classe I para aqueles em que as ligações são realizadas através de ligações “fracas” tais como ligações de hidrogênio, interações de Van der Waals, interações  $\pi$ - $\pi$  e interações eletrostáticas [75,80]. A classe II é baseada em interações fortes entre os componentes estruturais através de ligações covalentes ou iônico-covalentes [75,80]. O maior desafio na síntese de combinações híbridas é manter ou acentuar as propriedades mais interessantes e diminuir ou eliminar as propriedades indesejadas de cada componente. Com isso pode surgir materiais de grande interesse nas mais diversas aplicações comerciais devido às suas propriedades mecânicas, ópticas e térmicas, que combinam a estabilidade térmica e química dos materiais cerâmicos, com a processabilidade e a flexibilidade dos compostos e polímeros orgânicos.

Uma das possíveis aplicações pode estar no campo ambiental, voltado ao tratamento de água por meio de processos de separação sólido-líquido ou sólido-gás por meio de processo de adsorção.

### 3.11. FENÔMENO DE ADSORÇÃO

O fenômeno de adsorção é uma operação unitária que envolve o contato entre um sólido e um fluido, originando uma transferência de massa da fase fluida para a superfície do sólido. A transferência de massa é do tipo sólido – fluido, onde moléculas de uma fase fluida, chamado de adsorbato (gás, vapor ou líquido) se concentram espontaneamente sobre uma superfície, geralmente sólida, chamado de adsorvente, na qual se explora a habilidade destes sólidos em concentrar na sua superfície determinadas substâncias existentes em soluções líquidas ou gasosas, o que permite separá-las dos demais componentes dessas soluções, conforme esquematizado na **Figura 6**. Dentro do fenômeno da adsorção, distinguem-se duas diferentes classes de interação entre as moléculas do fluido e do sólido, baseando-se na natureza das forças que as unem: a adsorção física e a adsorção química [81].

A adsorção é geralmente aplicada na remoção de compostos tóxicos (orgânicos e inorgânicos), como metais pesados, corantes, fármacos e fenóis cuja remoção se torna difícil por processos de tratamentos biológicos convencionais, como também a desumificação de gases, recuperação de vapores de solventes dispendiosos e remoção de contaminantes da gasolina.



**Figura 6.** Processo esquemático da adsorção.

Conforme a natureza das forças envolvidas, pode-se distinguir dois tipos de adsorção, adsorção física e adsorção química. O Quadro 3 mostra algumas diferenças em relação aos dois tipos de adsorção.

Quadro 3- Comparação sucinta entre adsorção física e química .

ADSORÇÃO FÍSICA	ADSORÇÃO QUÍMICA
Baixo calor de adsorção (< 10 kcal/mol ou < 40 kJ/mol).	Alto calor de adsorção (> 20 kcal/mol ou > 80 kJ/mol).
Não especificidade.	Altamente específica.
Pode ocorrer tanto em monocamada como também em multicamadas.	Pode ocorrer tanto em monocamada como também em multicamadas.
Não há dissociação das espécies adsorvidas.	Pode envolver dissociação
Só é significativa a baixas temperaturas.	É possível numa grande faixa de temperaturas.
Rápida, não ativada é reversível.	Ativada, pode ser lenta e irreversível
Causada por forças de Van der Waals. Não há transferência de elétrons.	Causada por ligação covalente. Há transferência de elétrons com formação de ligação química entre adsorbato e adsorvente

Fonte: [81]

Na adsorção física, também denominada de fisissorção, os efeitos atrativos que ocorrem entre o adsorvente e o adsorbato são relativamente fracos, não havendo formação de novos compostos entre o adsorbato e a superfície do sólido em questão, portanto este processo é de natureza reversível, o que facilita que a substância adsorvida seja facilmente recuperada. As interações que prevalecem neste tipo de adsorção são principalmente interações de van der Waals.

### 3.12. CINÉTICA DE ADSORÇÃO

A cinética de adsorção descreve a velocidade com que as moléculas do adsorbato são adsorvidas pelo adsorvente. Esta velocidade depende das características físico-químicas do adsorbato (natureza do adsorbato, massa molecular, solubilidade, etc.), do adsorvente (natureza, estrutura dos poros) e da solução (pH, temperatura e concentração). É preciso conhecer a taxa de adsorção para projetar e avaliar o adsorvente e todo o processo de



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adsorção. Também a taxa de dessorção é importante no planejamento e regeneração do adsorvente [82,84]. Além disso, por meio do estudo cinético podem ser obtidas indicações importantes a respeito do mecanismo de adsorção limitante no processo [82-85]. Assim é de interesse reconhecer a cinética de adsorção e dessorção e determinar seus coeficientes fenomenológicos, caracterizando o transporte do adsorbato dentro dos adsorventes [82-85].

De maneira simplificada pode-se simplificar o mecanismo de adsorção em quatro etapas:

- Transferência do soluto presente na solução até o filme na interface sólido- líquido que engloba o adsorvente (esta etapa é a etapa rápida caso a agitação do sistema seja eficiente);
- Difusão do soluto pelo filme até a superfície do adsorvente, também chamada transferência de massa no filme ou difusão através da camada interfacial;
- Difusão do soluto pelos poros do adsorvente (difusão intrapartícula);
- Ligação do soluto aos sítios ativos do adsorvente. Com exceção da primeira e da última, que são extremamente rápidas, essas etapas podem ser vistas como um conjunto de resistências em série à transferência de massa [82,83,85].

Vários modelos cinéticos têm sido sugeridos para adsorção, contudo, neste trabalho, serão mencionados os mais aplicados para a remoção de poluentes em soluções aquosas que são: modelo de pseudo-primeira ordem, modelo de pseudo-segunda ordem, modelo de ordem fracionaria ou avrami e o modelo de ordem geral.

### 3.12.1. Modelos de cinética de adsorção

Numa reação química ou processo, os expoentes da lei de velocidade da reação não apresentam relação com os coeficientes estequiométricos da equação química [59,61]. Quando isso ocorre é uma mera coincidência. Isso significa que não existe uma forma de prever a ordem da reação, sem a obtenção de dados experimentais de sua cinética. A fim de estabelecer uma equação de lei geral para a taxa de adsorção, o processo de adsorção na superfície do adsorvente é assumido como a etapa determinante (lenta) da taxa de adsorção. Neste caso, foca-se na concentração de adsorbato na solução e na mudança do número efetivo de sítios ativos na superfície do adsorvente durante o processo de adsorção.

Se a lei de velocidade de adsorção é aplicada à **equação 1**, a expressão da taxa de adsorção pode ser obtida:

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$$\frac{dq}{dt} = k_N (q_e - q_t)^n \quad \text{Eq. 1}$$

na qual  $k_N$  é a constante da taxa de adsorção; e  $n$  é a ordem da adsorção com relação a concentração efetiva dos sítios de adsorção disponíveis na superfície do adsorvente;  $q_e$  é a quantidade adsorvida no equilíbrio; e  $q_t$  é a quantidade adsorvida a qualquer tempo. Eq. 1 é o resultado da aplicação da lei universal da lei de velocidade de reação ao processo de adsorção e pode ser usada sem qualquer outro pressuposto adicional [61]. Teoricamente, o expoente  $n$  na Eq. 1 pode ser um valor inteiro ou um número fracionário [61].

O número de sítios ativos ( $\theta_t$ ) disponíveis na superfície do adsorvente pode ser definido pela seguinte equação:

$$\theta_t = 1 - \frac{q_t}{q_e} \quad \text{Eq. 2}$$

A Eq.3 descreve a taxa de adsorção em função da variável ( $\theta_t$ ).

$$\frac{d\theta_t}{dt} = -k \cdot \theta_t^n \quad \text{Eq. 3}$$

onde por definição  $k$  é:

$$k = k_N (q_e)^{n-1} \quad \text{Eq. 4}$$

Para um adsorvente virgem  $\theta_t$  é igual a 1, e esse valor diminui durante a adsorção. Quando o processo de adsorção alcança o equilíbrio,  $\theta_t$  tende a um valor constante. Se a saturação dos sítios ativos do adsorvente ocorrer,  $\theta_t$  tende a zero [61].

Integrando-se a Eq. 3,

$$\int_1^{\theta} \frac{d\theta_t}{\theta_t^n} = -k \int_0^t dt \quad \text{Eq. 5}$$

Leva-se a:

$$\frac{1}{1-n} \cdot [\theta_t^{1-n} - 1] = -k \cdot t \quad \text{Eq. 6}$$

Que resulta em:

$$\theta_t = [1 - k \cdot (1-n) \cdot t]^{1/(1-n)} \quad \text{Eq. 7}$$

Aplicando-se as Eqs. 2 e 4 na Eq 7, obtém-se:

$$q_t = q_e - \frac{q_e}{\left[ k_N (q_e)^{n-1} \cdot t \cdot (n-1) + 1 \right]^{1/(n-1)}} \quad \text{Eq. 8}$$

A Eq. 8 é a equação de ordem geral cinética que é válida para  $n \neq 1$ .

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O modelo cinético de pseudo-primeira é um caso especial da Eq. 1, quando  $n=1$  [61].

$$\frac{d\theta_t}{dt} = -k_1 \theta_t \quad \text{Eq. 9}$$

Integrando-se Eq. 9, resulta em:

$$\theta_t = \exp(-k_1 t) \quad \text{Eq. 10}$$

Substituindo-se Eq. 2 na Eq. 10 e considerando-se  $k=k_1$ , o modelo cinético de pseudo-primeira ordem é obtido:

$$q_t = q_e [1 - \exp(-k_1 t)] \quad \text{Eq. 11}$$

Portanto, conclui-se que a equação de pseudo-primeira ordem é um caso especial da equação da lei cinética de adsorção [61].

O modelo cinético de pseudo-segunda ordem é um caso especial da Eq. 8 (Equação de ordem cinética geral), quando  $n=2$  [61]. Portanto:

$$q_t = q_e - \frac{q_e^2}{[1 + k_2(q_e)t]} \quad \text{Eq. 12}$$

Rearranjando-se essa equação, leva-se a:

$$q_t = \frac{q_e^2 k_2 t}{[1 + k_2(q_e)t]} \quad \text{Eq. 13}$$

A equação da difusão intra-partícula foi previamente definida como [61]:

$$q_t = k_{id} \sqrt{t} + C \quad \text{Eq. 14}$$

Na qual  $k_{id}$  é a constante da taxa de difusão intra-partícula ( $\text{mg g}^{-1} \text{h}^{-0.5}$ );  $C$  é a constante relacionada com a espessura da camada de difusão ( $\text{mg g}^{-1}$ ).

Nesse projeto de pesquisa, as equações de pseudo-primeira ordem (Eq. 11), pseudo-segunda ordem (Eq. 13), equação de ordem geral (Eq. 8) e difusão intra-partícula (Eq. 14) foi utilizado o modelo de ordem fracionária ou modelo de Avrami que é mostrada pela Eq. 15.

$$q_t = q_e \cdot \left\{ 1 - \exp[-(k_{AV} \cdot t)] \right\}^{\alpha} \quad \text{Eq. 15}$$

Onde:

- $\alpha$  é a fração de adsorção ( $q_t/q_e$ ) no tempo  $t$ ;
- $k_{AV}$  é a constante cinética de Avrami ( $\text{h}^{-1}$ );

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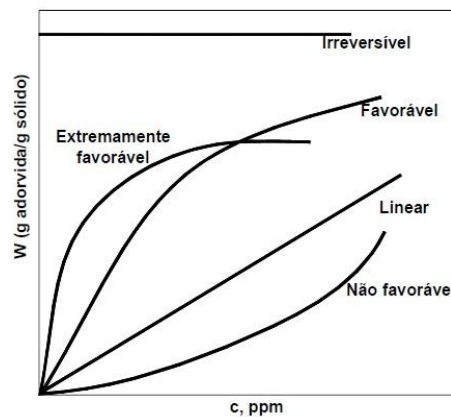
- $n_{AV}$  é a ordem fracionária do processo que está associada as mudanças de ordem de adsorção de acordo com o tempo de contato entre o adsorvente e o adsorvato.

### 3.13. Isotermas de adsorção

Para o desenvolvimento de um sistema de adsorção é importante e necessário entender sobre os dados de equilíbrio e este entendimento só é possível pela aplicação de modelos matemáticos específicos, a estes modelos podemos chamar de isotermas de adsorção [81,82].

As isotermas são úteis para descrever a capacidade de adsorção, selecionar o adsorvente mais eficiente, bem como estabelecer as quantidades requeridas numa determinada aplicação. Além disso, as isotermas desempenham um papel importante na construção de modelos para análise e descrição dos sistemas de adsorção, permitindo uma melhor avaliação analítica e teórica dos resultados termodinâmicos, cinéticos e de equilíbrio do fenômeno de adsorção [81,82].

As isotermas podem apresentar-se de várias formas, fornecendo informações importantes sobre o mecanismo de adsorção. Elas mostram a relação de equilíbrio entre a concentração na fase fluida e a concentração nas partículas adsorventes em uma determinada temperatura. Algumas formas mais comuns estão apresentadas na **Figura 7**. A isoterma linear passa pela origem e a quantidade adsorvida é proporcional à concentração do fluido. Isotermas convexas são favoráveis, pois grandes quantidades adsorvidas podem ser obtidas com baixas concentrações de soluto.



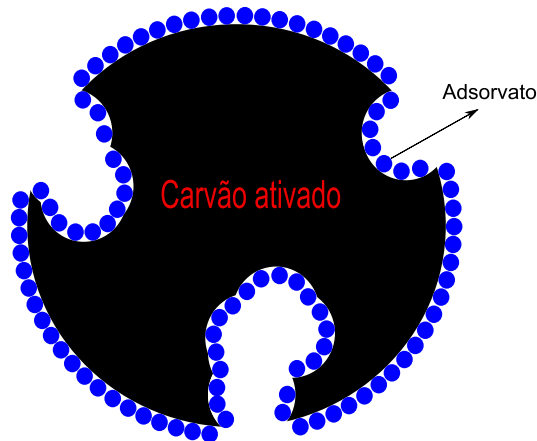
**Figura 7.** Isotermas de adsorção.

Há na literatura diversos modelos que descrevem os dados experimentais das isotermas de adsorção. Considerando a proposta do presente trabalho não serão abordados

todos os tipos de isotermas, apenas as isotermas mais utilizadas que são os modelos de Langmuir [86], Freundlich [87], Liu [88], Sips [89] e Redlich-Paterson [90], os quais são apresentados a seguir.

### 3.13.1. Modelo de Langmuir

O modelo de Langmuir considera que o fenômeno de adsorção ocorre sobre a superfície homogênea do adsorvente com sítios idênticos, igualmente disponíveis e energeticamente equivalentes. Na superfície na qual ocorrerá a adsorção, haverá a formação de uma camada superficial monomolecular, em que as moléculas adsorvidas não sofrem interação com o meio e nem com moléculas de sítios vizinhos [80,84], conforme mostrado na **Figura 8**.



**Figura 8.** Esquema da adsorção segundo o modelo de Langmuir.

A equação de Langmuir foi baseada em adsorção localizada, química em superfície homogênea com ausência de forças de atração entre as moléculas adsorvidas e em monocamadas, considerando-se a adsorção de um único soluto e que um sítio na superfície do adsorvedor pode ser ocupado apenas por uma molécula de adsorbato (ilustrado na **Figura 8**) [82,86]. Ou seja, o modelo de Langmuir foi desenvolvido considerando que o adsorvente possui um número limitado de posições disponíveis na superfície, e que as moléculas podem ser adsorvidas até que todos os sítios superficiais disponíveis sejam ocupados.

A isoterma de Langmuir, aplicada à adsorção de líquidos, tem a forma geral apresentada na equação 16:

$$q_e = \frac{K_L C_e q_{\max}}{1 + (K_L C_e)} \quad \text{Eq. 16}$$

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em que  $C_e$  ( $\text{mg L}^{-1}$ ) é a concentração da solução no equilíbrio e  $q_{max}$  ( $\text{mg g}^{-1}$ ) a quantidade máxima adsorvida no equilíbrio por unidade de massa de adsorvente. Os parâmetros  $K_L$  ( $\text{L mg}^{-1}$ ) e  $q_{max}$  ( $\text{mg g}^{-1}$ ) dependem do material adsorvente e podem ser usados para comparar o desempenho da adsorção. O parâmetro  $q_{max}$  (limite de saturação) está relacionado com a capacidade máxima de adsorção e  $K_L$  (constante de Langmuir) com as forças de interação entre adsorvato e adsorvente.

Os parâmetros de adsorção,  $q_{max}$  e  $K_L$ , podem ser determinados transformando a equação de Langmuir para a forma linear. A equação linearizada de Langmuir é expressa na Equação 17.

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \quad \text{Eq.17}$$

As características da isoterma de Langmuir podem ser expressas em termos do parâmetro de equilíbrio ou fator de separação  $R_L$ , que é uma constante adimensional definida, conforme equação 18.

O parâmetro de equilíbrio  $R_L$ , permite prever a forma da isoterma de adsorção, indicando se a adsorção é favorável ou desfavorável e pode ser calculado pela Eq. 18.

$$R_L = \frac{1}{(1 + K_L C_m)} \quad \text{Eq. 18}$$

Em que  $C_m$  é a maior concentração inicial do soluto em solução e  $K_L$  é a constante relacionada à energia de adsorção (constante de Langmuir).

Quadro 4- Limites de valores de  $R_L$  para o comportamento de processos de adsorção.

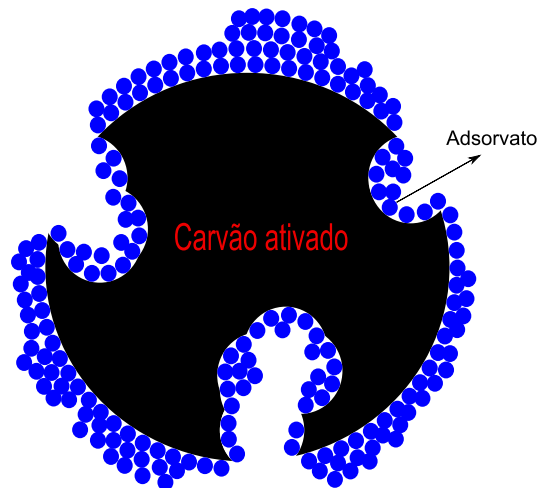
Valores ( $R_L$ )	Tipos de isotermas
<b><math>R &gt; 1</math></b>	Linear
<b><math>0 &gt; R &lt; 1</math></b>	Irreversível
<b><math>R &gt; 1</math></b>	Linear
<b><math>0 &gt; R &lt; 1</math></b>	Irreversível

Fonte: [80,81].

### 3.13.2. Modelo de Freundlich

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A equação de Freundlich foi originalmente introduzida admitindo-se uma distribuição logarítmica de sítios ativos, que constitui um tratamento válido quando não existe interação apreciável entre as moléculas de adsorvato [87]. Para Rozada et all. [91] o modelo de Freundlich admite adsorção em multicamadas e é útil para descrever a adsorção em superfícies altamente heterogêneas. A **Figura 9**, ilustra um esquema de adsorção de acordo com o modelo de Freundlich.



**Figura 9.** Esquema da adsorção de Freundlich.

O modelo de adsorção proposto por Freundlich (Eq. 19) foi um dos primeiros a relacionar a quantidade de adsorvato adsorvido e a concentração do adsorvato na solução, em um modelo empírico.

$$q_e = K_F C_e^{\frac{1}{n}} \quad \text{Eq. 19}$$

em que  $K_F$  e  $n$  são constantes de Freundlich que indicam a capacidade de adsorção e eficiência do processo de adsorção, respectivamente.

A isoterma de Freundlich é obtida com a construção do gráfico ( $q_e \times C_e$ ), o logaritmo pode ser utilizado como artifício de linearização (Eq. 20), onde o coeficiente angular da equação da reta obtida corresponderá a  $1/n$  e o coeficiente linear corresponderá a  $\log K_F$ .

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad \text{Eq. 20}$$

Na isoterma de Freundlich o coeficiente angular da equação da reta obtida corresponde a  $1/n$  e o coeficiente linear corresponde a  $\log K_F$ . O valor de  $K_F$  obtido é uma indicação da capacidade do material adsorvente em estudo, o valor de  $n$  deve ser sempre  $> 1$  e quando se encontrar no intervalo entre 2 e 10 indica que o processo de adsorção é favorável [82,87].

### 3.13.3. Modelo de Liu

Modelo de Liu Outra proposição para descrever o comportamento de isotermas foi sugerido por Liu et al [88]. Esse modelo corresponde à combinação dos modelos de isotermas de Langmuir, Freundlich e Hill e é expresso segundo a Eq. 21:

$$q_e = \frac{Q_{\max} \cdot (K_g \cdot C_e)^{n_L}}{1 + (K_g \cdot C_e)^{n_L}} \quad \text{Eq. 21}$$

Onde  $k_g$  é a constante de equilíbrio de adsorção de Liu ( $L \text{ mg}^{-1}$ ),  $n_L$  é o expoente de Liu (adimensional) e  $Q_{\max}$  é a capacidade máxima de adsorção ( $\text{mg g}^{-1}$ ). Ao contrário do modelo de Sips, o modelo de Liu não prevê restrição quanto ao valor do expoente, o que não o torna limitado [88].

### 3.13.4. Modelo de Sips

Outro modelo de isotermas de adsorção é o empírico de Sips [89], que é uma combinação matemática dos modelos de isotermas de Langmuir e Freundlich. O modelo de Sips segue a Eq. 22:

$$q_e = \frac{Q_{\max} \cdot K_s \cdot C_e^{1/n_s}}{1 + K_s \cdot C_e^{1/n_s}} \quad \text{Eq. 22}$$

Na qual  $K_s$  é a constante de equilíbrio de adsorção de Sips ( $\text{mg L}^{-1}$ )<sup>-1/n</sup>,  $Q_{\max}$  é a capacidade máxima de adsorção ( $\text{mg g}^{-1}$ ), e  $n_s$  é o expoente de Sips (adimensional). Em baixas concentrações de adsorvato, esse modelo assume a forma de Freundlich, enquanto que, em altas concentrações, assume a forma de adsorção de Langmuir em monocamadas.

### 3.13.5. Modelo de Redlich-Peterson

A isoterma de Redlich-Peterson é usada para representar o equilíbrio de adsorção em uma ampla faixa de concentrações e, devido a essa versatilidade, pode ser aplicada em sistemas homogêneos e heterogêneos [82,90]. A isoterma de Redlich-Peterson combina elementos das equações de Langmuir e Freundlich; O mecanismo de adsorção é híbrido e não segue um comportamento ideal em monocamada [82,90]. O modelo de Redlich-Peterson é apresentado pela Eq. 23:



$$q_e = \frac{K_{RP} \cdot C_e}{1 + a_{RP} \cdot C_e^g} \quad \text{Eq. 23}$$

onde,  $k_{RP}$  e  $a_{RP}$  são as constantes de Redlich-Peterson ( $L \text{ mg}^{-1}$ ) e ( $L \text{ mg}^{-1}$ ) e “g” é o expoente que varia de 0 a 1.

### 3.14. POLUENTES ORGÂNICOS

Ao longo dos anos, a poluição de águas por compostos orgânicos vêm sendo estudados mundialmente, devido aos níveis crescentes de utilização e ao risco potencial à saúde e ao ambiente. Micropoluentes orgânicos compreendem uma gama de substâncias presentes em medicamentos, desinfetantes, meios de contraste, detergentes, surfactantes, pesticidas, corantes, tintas, conservantes, aditivos alimentares e produtos para cuidados pessoais, que podem ser encontrados em matrizes ambientais como esgoto, corpos receptores, sedimentos, lodo biológico e mesmo em águas de abastecimento. Tais substâncias podem causar diferentes impactos no meio ambiente e representam um risco de saúde pública, por exemplo, causando desregulação endócrina.

Assim, uma questão emergente na ciência e engenharia do meio ambiente é desenvolver processos que promovam a remoção efetiva de fármacos e compostos fenólicos, junto com outros poluentes, antes do seu descarte ao meio ambiente.

Até recentemente muito pouco ou nenhum esforço foi dedicado ao estudo da interação desta enorme variedade de novos compostos, e seus subprodutos, no meio ambiente, bem como pouca atenção foi dispensada ao gerenciamento adequado dos produtos químicos que contém tais substâncias.

Nesta tese foram abordados estudos de remoção de fármacos e compostos fenólicos.

#### 3.14.1. Fármacos

Os fármacos têm uma inquestionável relevância em nossa sociedade, desde sua importância fundamental no combate das enfermidades até funções mais recentes, como o de proporcionar cada vez mais o prolongamento da longevidade humana.

Os fármacos são um grupo de compostos químicos complexos, com massa molecular entre 200 e 1.000 Daltons, que têm propriedades medicinais. Essas substâncias incluem

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compostos inorgânicos e orgânicos, embora a maioria dos modernos fármacos seja formada por compostos orgânicos.

Os fármacos são desenvolvidos para ser persistentes, mantendo suas propriedades químicas o bastante para servir a um propósito terapêutico; contudo, presentes no meio ambiente, devido a sua persistência, podem bioacumular em corpos d'águas e seres vivos, causando efeitos adversos. Segundo Mulroy [91], 50% a 90% de uma dosagem do fármaco é excretado inalterado e persiste no meio ambiente. O uso desenfreado de antibióticos acarreta dois problemas ambientais: um, é a contaminação dos recursos hídricos e o outro, é que alguns microorganismos criam resistência a esses fármacos. Portanto, é de suma importância que tais compostos sejam removidos dos efluentes antes dos seus descartes no meio ambiente. O mesmo para as demais substâncias tóxicas como os compostos fenólicos.

### 3.14.2. Compostos fenólicos

O fenol foi descoberto em 1834 pelo químico F. F. Runge, no fracionamento do alcatrão da hulha. Atualmente é obtido por fracionamento ou por síntese a partir do cloro benzeno. O fenol utiliza-se para a desinfecção de edifícios e utensílios e no fabrico de plásticos, corantes, medicamentos, explosivos, entre outros produtos. Apesar de os compostos fenólicos serem descritos simplesmente como fenóis, esta categoria de resíduos pode englobar uma variedade de compostos químicos similares, tais como polifenóis, clorofenóis e ácidos fenólicos. Muitas das indústrias são fontes características de poluentes fenólicos, incluindo a indústria petroquímica e refinarias (lavagem e condicionamento de produtos fracionados alcalinos ou ácidos), coquearias, fundições (lavagem de efluentes gasosos), indústrias químicas e farmacêuticas (corantes, pesticidas, medicamentos), fábricas de pólvora (nitrofenóis), manufatura de resinas, tintas, explosivos e engenhos químicos, entre outras. Atualmente são aplicados diversos processos, físico-químicos e biológicos, eficazes no tratamento dos compostos fenólicos. No entanto, na aplicação industrial de determinado processo de tratamento, podem surgir algumas dificuldades devido à existência de outros compostos nas águas residuais que requeiram técnicas específicas de remoção.

A toxicidade dos compostos fenólicos revela-se por modificações das características organolépticas da água (gosto desagradável provocado pela formação de clorofenóis) e por efeitos sobre a fauna e flora aquática (variam conforme a natureza dos compostos, a concentrações elevadas provocam a desnaturação de proteínas e destroem as paredes

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celulares, modificam o equilíbrio do meio aquático e inibem o funcionamento das estações de depuração).

### 3.14.3. Ocorrência de fármacos e fenóis no meio ambiente

Os meios hídricos são um meio receptor de esgotos domésticos, industriais e agropecuários e, conseqüentemente, são o principal veículo de dispersão ambiental dos poluentes químicos. Poluentes esses nos quais se insere os fármacos e os compostos fenólicos, os quais são permanentemente libertados para o meio ambiente e que tendo sido foco de vários estudos sobre seu impacto ambiental.

A presença destes resíduos orgânicos no meio ambiente podem apresentar efeitos adversos em organismos aquáticos e terrestres. Este efeito pode ocorrer em qualquer nível da hierarquia biológica, tais como célula, órgão, organismo, população e ecossistema, e pode ser observado em concentrações na ordem de ng/L, para certos tipos de compostos.

Vários estudos veem demonstrando que esses fármacos e seus metabólitos estão presentes em ambientes aquáticos em várias partes do mundo, como Alemanha [92], Brasil [93], Canadá [93], Suécia [94], Holanda [95], Itália [96], Estados Unidos [97] entre outros.

A preocupação com o impacto ambiental, por exemplo, dos fármacos é de extrema relevância, pois muito embora os fármacos desempenhem um importante papel no tratamento e/ou prevenção de inúmeras patologias, podem induzir efeitos indesejados sobre organismos não alvo [97]. Com efeito, é do conhecimento da comunidade científica que os fármacos são compostos orgânicos bioativos [92,96,97] com elevada atividade farmacológica que podem sofrer bioacumulação numa grande variedades de bio-organismos.

Ternes et al. [93] identificaram a ocorrência de 36 fármacos diferentes em diversos rios na Alemanha, dentre os quais estão antilipidêmicos, analgésicos-antipiréticos, anti-inflamatórios e anti-hipertensivos. Na Itália, Calamari et al. [98] detectaram a presença de 18 fármacos em 8 estações de tratamento de esgoto ao longo dos rios. Zuccato et al [96] observaram, em 9 estações de tratamento de esgoto fármacos como o floxacino, furosemida, atenolol, hidroclorotiazida, carbamazepina, ibuprofeno, benzafibrato, eritromicina, lincomicina, e claritromicina.

O Brasil é um dos maiores consumidores de fármacos do mundo, juntamente com Estados Unidos, França e Alemanha [95]. Ternes et al. [93] e Stumpf et al. [99] encontraram

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estrogênios naturais, contraceptivos sintéticos diclofenaco e naproxeno na estação de tratamento de efluentes (ETE) da Penha, Rio de Janeiro.

Muitos dos compostos frequentemente detectados nas águas naturais e efluentes tratados pertencem às classes dos anti- inflamatórios e antibióticos, nos quais se inserem o diclofenaco e nimesulida. Portanto é de extrema importância propor métodos de remoção destes compostos antes de serem dispostos no meio ambiente.

### 3.14.4. Tratamentos para remoção de fármacos e compostos fenólicos de efluentes

Os compostos orgânicos como os fármacos e os compostos fenólicos, como já referidos anteriormente, não são facilmente destruídos por meio biológicos e as ETE's são uma das principais fontes de fármacos, seus metabolitos e produtos de transformação no meio aquático, uma vez que muitos destes compostos não são totalmente removidos pelos processos convencionais de tratamento neles utilizados [94,96-98].

As ETE's convencionais são projetadas e otimizadas para remover os poluentes, predominantemente, orgânicos e em concentrações elevadas, como a matéria orgânica dissolvida facilmente biodegradável, sólidos em suspensão, patogênicos e nutrientes (nitrogênio e fósforo etc), não objetivando especificamente a remoção de fármacos e compostos fenólicos presentes no esgoto sanitário, com isso apresenta, frequentemente, baixas eficiências nas remoções para os poluentes, específicos, presentes em concentrações muito baixas onde se incluem os fármacos [100-103]. Contudo, deve-se salientar que, mesmo assim, podem ocorrer remoções destes compostos em ETE's o que é inerente ao processo de tratamento.

As eficiências de remoção dos fármacos e dos compostos fenólicos em ETE's convencionais podem variar significativamente uma para outra, estando dependente de vários fatores, tais como, a composição das águas residuais, as condições climáticas (por exemplo, a temperatura e a intensidade da luz solar), o tipo de tratamento utilizado e as condições de operação do processo de tratamento (pH, condições redox, tempo de retenção hidráulico, idade de lodo) etc.

Por exemplo, a remoção biológica de ibuprofeno é geralmente superior a 75% e a média indicada de remoção de estrona é 83% e a remoção de 17 $\alpha$ -etinilestradiol é maior do que 44% [104]. A remoção de diclofenac é menos eficiente (<25%) e extremamente variável.

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Nos últimos anos, algumas tecnologias de remoção de fármacos e fenóis já vêm sendo estudadas e estão disponíveis para a uma mais efetiva remoção desses compostos. Dentre os mais estudados para a remoção dos fármacos estão, a oxidação química (ozonização, oxidação catalítica), filtração por membranas, reatores de membranas, adsorção em carvão ativado. No entanto, consomem um nível elevado de energia, exigem instalações caras e não os removem completamente dos efluentes [104]

Neste trabalho, será abordado o processo de adsorção como tratamento para remoção de fármacos e compostos fenólicos de efluentes contaminados.

### **3.15. ADSORÇÃO DE FÁRMACOS SOBRE CARVÕES ATIVADOS PROVENIENTES DE LODO DE ESGOTO**

A aplicação do processo de adsorção tem sido amplamente reportada na literatura na remoção de diversos poluentes assim também como no tratamento terciário combinado com outro tratamento avançado de efluentes de estações de tratamento de esgoto.

Vários são os trabalhos relacionados com a adsorção de compostos orgânicos sobre materiais adsorventes [100-107]. Entretanto, até a presente data, não existem muitos trabalhos na literatura referentes ao estudo da adsorção de fármacos a partir de carvões ativado provenientes de lodo de esgoto, e que na maioria dos casos, são empregados carvões ativado comerciais. Para nosso conhecimento, apenas um trabalho foi reportado usando carvão ativado de lodo de esgoto doméstico na remoção de diclofenaco [90] e nenhum trabalho tem sido reportado na adsorção de nimesulida.

Vários são os trabalhos reportando o uso de carvões ativado e outros tipos de adsorventes na remoção de fármacos em efluentes aquosos, no entanto adsorventes a base de lodo de esgoto não tem sido reportado na literatura.

Baccar et al. [102] produziram um carvão ativado usando forno convencional e resíduos de oliveira como precursor, sob ativação com  $H_3PO_4$ , e o aplicou na remoção de diclofenaco de sódio. Obteve uma capacidade máxima de adsorção ( $Q_{max}$ ) de  $56,2 \text{ mg g}^{-1}$ . Saucier et all. [103] preparou carvões ativado de casca de cocô usando um forno de micro-ondas, em seguida os aplicam na remoção de diclofenaco e nimesulida, obtiveram umas capacidades máximas de  $63,47$  e  $74,81 \text{ mg g}^{-1}$  para o diclofenaco e o nimesulida, respectivamente.

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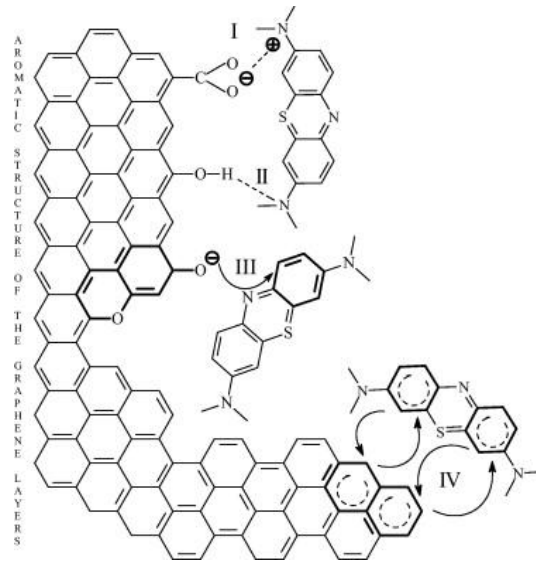
Um carvão ativado foi produzido, por Coimbra et al. [104], a partir de lodo de celulose primária. O carvão foi aplicado na adsorção de diclofenaco e obteve o  $Q_{\max}$  de 53,16 mg g<sup>-1</sup>.

Tiwari, Lalhriatpui e Lee [105] sintetizaram um adsorvente híbrido a base de serecite (uma espécie de mica natural) e grupos orgânicos (hexadeciltrimetilamônio). Os híbridos foram aplicados também na adsorção de diclofenaco em soluções aquosas e obtiverem uma  $Q_{\max}$  bastante tímida, de apenas 1,056 mg g<sup>-1</sup>.

Hasan, Khan e Jung [106] reportaram a preparação de redes Metalorgânicas (MOFs), formadas por clusters metálicos de zinco (ZrCl<sub>4</sub>) conectados por ligante ditópico, ácido tereftálico (1,4- H2BDC) para uso na remoção de diclofenaco; foi obtida uma ótima eficiência de remoção com capacidade máxima adsortiva de 263 mg g<sup>-1</sup>.

A razão para diferentes valores de  $Q_{\max}$  pode residir no fato destes trabalhos terem utilizados diferentes condições experimentais tais como concentrações iniciais diferentes, os diferentes tipos de adsorventes, assim como diferentes tempos de contato e pH.

Um fator que pode exercer grande influência na  $Q_{\max}$  de espécies orgânicas, em especial fármacos e compostos fenólicos (como diclofenaco, nimesulida e chidroquinona), pode estar associado à presença de determinados grupos funcionais nas superfícies, pois a superfície desempenha um papel importante no mecanismo de adsorção de espécies orgânicas [106]. Este mecanismo foi subdividido em quatro, evidenciados na **Figura 10**. Citam-se as interações eletrostáticas como mecanismo I, que ocorre quando o adsorbato e o adsorvente possuem cargas diferentes o que viabiliza a atração entre as partes. A formação de ligação de hidrogênio como mecanismo II ocorre quando há uma interação entre átomos de hidrogênio com átomos de elementos altamente eletronegativos como, oxigênio, flúor e nitrogênio, de forma que o hidrogênio sirva como "elo" entre os átomos com os quais interage. O mecanismo III é o doador e aceitador de elétrons, ocorre quando o elétron é transferido espontaneamente de um centro "doador" que pode ser, por exemplo, + (NH<sub>2</sub>), + (OH), + (CH<sub>3</sub>) para um centro "receptor", por exemplo, -(NO<sub>2</sub>), -(CN), -(CHO) [100,104,106]. E por fim a interação de dispersão como mecanismo IV, esta interação acontece quando compostos apolares interagem. O contato de uma molécula com a outra faz com que apareça uma força atrativa muito fraca que pode ser vista como uma interação dipolo induzido-dipolo induzido. Isto é, são as polaridades das duas moléculas em contato é que irão determinar a força de tal interação.



**Figura 10.** Esquema demonstrativo dos mecanismos de adsorção.  
Fonte: [107]

Estes mecanismos, como mencionam Vargas et al. (2011), são regidos pela interação entre os carvões ativados e poluentes orgânicos, em geral corantes ou substâncias a base de hidrocarbonetos.

# ***Capítulo Três***

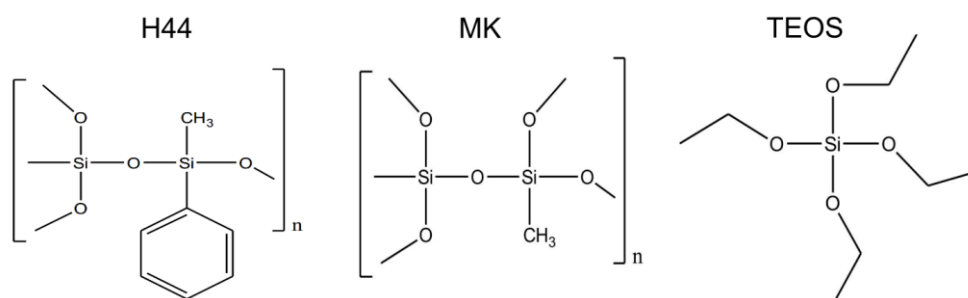


## 4. METODOLOGIA

### 4.1. PRECURSORES

O lodo de esgoto sanitário foi coletado na ETE Navegantes, no município de Porto Alegre, Rio Grande do Sul, localizada na avenida A.J Renner, 495, bairro Humaitá. Trata-se de um resíduo proveniente de um sistema de lodo ativado convencional, portanto um lodo aeróbio.

Para a síntese dos materiais híbridos e compósitos, foram utilizados os Metil-fenil polissiloxano (H44) e Metil polissiloxano (MK), 99% de pureza, de procedência da Silres®, Wacker Chemie, Alemanha, e o monômero orgânico ortossilicato de tetraetilo (TEOS), com 99%, de pureza. As estruturas moleculares destes compostos estão apresentadas na **Figura 11**.



**Figura 11.** Estruturas dos polissiloxanos utilizados neste trabalho.

Para o preparo dos materiais híbridos e compósitos foi utilizado o solvente Etanol com grau de pureza P.A., de procedência da Merck.

### 4.2. PLANEJAMENTO EXPERIMENTAL

Neste trabalho, um planejamento fatorial  $2^3$  com três pontos centrais, foi utilizado, visando a determinação das melhores condições para a obtenção dos carvões ativados com elevadas áreas superficiais  $S_{BET}$ . Neste método as variáveis são exploradas em 2 níveis é comum codificá-los usando os sinais (1) e (-1). As variáveis estudadas foram Temperatura ( $X_1$ ) para a pirólise convencional (Ver Tabela 2) e Potência ( $X_1$ ) para a pirólise por micro-ondas (ver **Tabela 2**), Tempo de residência ( $X_2$ ) e relação zinco/lodo ( $X_3$ ), tendo a área superficial específica  $S_{BET}$  como resposta do planejamento experimental. A **Tabela 2**

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mostram as variações e os níveis das variáveis estudadas e os valores da resposta  $S_{BET}$  para a pirólise convencional e por micro-ondas, respectivamente.

Os experimentos foram realizados randomicamente e as variáveis consideradas foram (a) temperatura estabelecida ( $t=500, 650$  e  $800$  °C); (b) potência estabelecida ( $t= 700, 840$  e  $980$  watts); (c) tempo de permanência sob temperatura estabelecida ( $t=15, 37$  e  $60$  minutos); (d) tempo de permanência sob potência estabelecida ( $t= 8, 10$  e  $12$  minutos); (e) proporção de agente de ativação, cloreto de zinco (01/0.5; 01/01; 01/1.5).

Tabela 2 – Planejamento experimental para preparação de carvões ativados por pirólise convencional e microondas.

Fatores	nome	Convencional			Microondas		
		Níveis			Níveis		
		-1	0	+1	-1	0	+1
		-1	0	+1	-1	0	+1
X1	Temperatura	500	650	800	-	-	-
X1	Potência	-	-	-	700	840	980
X2	Tempo de permanência	15	37	60	8	10	12
X3	Proporção $ZnCl_2$ /lodo	0.5	1.0	1.5	0.5	1.0	1.5

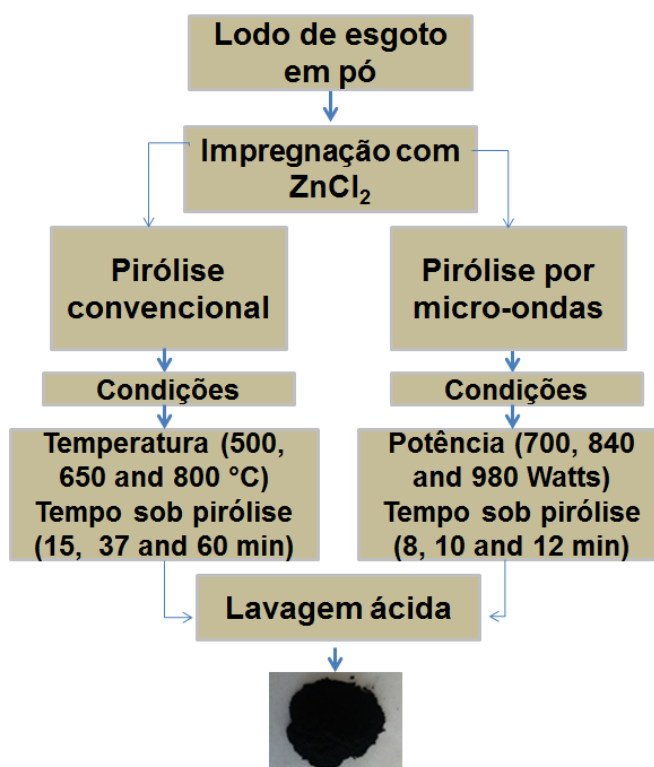
  

Amostras	Variáveis codificadas			Convencional			Microondas		
	$T_f$	$t_r$	m	$T_f$	$t_r$	m	Pow	$t_r$	m
500-15-0.5 e 700-8-0.5	-1	-1	-1	500	15	0.5	700	8	0.5
800-15-0.5 e 980-8-0.5	+1	-1	-1	800	15	0.5	980	8	0.5
500-60-0.5 e 700-12-0.5	-1	+1	-1	500	60	0.5	700	12	0.5
800-60-0.5 e 980-12-0.5	+1	+1	-1	800	60	0.5	980	12	0.5
500-15-1.5 e 700-8-1.5	-1	-1	+1	500	15	1.5	700	8	1.5
800-15-1.5 e 980-8-1.5	+1	-1	+1	800	15	1.5	980	8	1.5
500-60-1.5 e 700-12-1.5	-1	+1	+1	500	60	1.5	700	12	1.5
800-60-1.5 e 980-12-1.5	+1	+1	+1	800	60	1.5	980	12	1.5
650-37-1.0 e 840-10-1.0	0	0	0	650	37.5	1.0	840	10	1.0
650-37-1.0 e 840-10-1.0	0	0	0	650	37.5	1.0	840	10	1.0
650-37-1.0 e 840-10-1.0	0	0	0	650	37.5	1.0	840	10	1.0

#### 4.3. PROCESSO DE PREPARAÇÃO DOS CARVÕES ATIVADOS

A preparação do carvão ativado à base de lodo de esgoto foi composta de três etapas principais: uma visão geral da preparação de carvão ativado é mostrada na **Figura 12**.

A primeira etapa foi a de ativação química por impregnação. O processo de impregnação foi realizado utilizando o cloreto de zinco ( $ZnCl_2$ ) como agente de ativação sob diferentes proporções (m/m), conforme mostram as Tabelas 2 e 3. A ativação química foi realizada pesando-se em um recipiente uma determinada massa de Lodo de esgoto seco (granulometria baixo de 100 mesh) junto com o agente ativante ( $ZnCl_2$ ) e 5 ml de água, em seguida foi misturada até formar uma pasta homogênea. A pasta foi colocada num cadinho e secou-se em estufa durante 24 horas a  $70^\circ C$  e depois pirolisadas em temperaturas previamente estabelecidas conforme mostra a **Tabela 2**.



**Figura 12.** Fluxograma geral da preparação dos carvões ativados.

A segunda etapa compreendeu em submeter a pasta de lodo e  $ZnCl_2$  às condições de operacionais de pirólise. O conjunto de condições relacionadas à temperatura e tempo de ativação de pirólise para cada amostra é apresentado na **Tabela 2**. Os processos de pirólise foram realizados sob um fluxo de nitrogênio (gás inerte) com fluxo de 100 ml / min, e uma taxa de aquecimento constante de  $5^\circ C / min$  (pirólise convencional, ver **Tabela 2**). Para a

## **Capítulo Três: Parte experimental.**

pirólise assistida por microondas, as condições de síntese dos adsorventes foram estabelecidas variando a potência e tempo de permanência no reator sob potencia máxima (ver **Tabela 2**).

Para finalizar a preparação dos carvões ativados, a pasta carbonizada foi submetida a um processo de lixiviação ácida para remover ao máximo o  $ZnCl_2$  do material carbonizado. Para isto, as amostras foram lavadas com ácido clorídrico  $6,0 \text{ mol L}^{-1}$ . 8,0 g do material carbonizado foi adicionado a 150 mL de HCl  $6,0 \text{ mol L}^{-1}$  num balão de 250 ml; a mistura foi agitada num agitador magnético sob refluxo durante 3 h a  $75^\circ \text{C}$ . Posteriormente, a pasta foi resfriada e filtrada sob vácuo utilizando membranas de policarbonato. Após extensa lavagem com água destilada, o material sólido foi seco numa estufa a  $105^\circ \text{C}$  durante 5 horas, e então moído até um tamanho de partícula  $\leq 150 \text{ um}$ .

### 4.4. CARACTERIZAÇÃO QUÍMICA DOS PRECURSORES, CARVÕES ATIVADOS, HÍBRIDOS E COMPÓSITOS ADSORVENTES

#### 4.4.1. Análise elementar

A análise elementar é uma técnica útil que possibilita quantificar os grupos imobilizados nos suportes inorgânicos com o resultado do percentual dos elementos carbono, hidrogênio e nitrogênio, determinando dessa forma o grau de funcionalização dos materiais.

As medidas foram obtidas pelo menos em duplicata e realizadas em um analisador elementar de CHN da Perkin-Elmer, modelo 2400.

#### 4.4.2. Análise textural

A área superficial específica dos carvões ativados híbridos e compósitos foi determinada pela técnica de multipontos BET (Brunauer, Emmett e Teller), utilizando uma aparelhagem volumétrica apropriada para nitrogênio líquido a 77 K. As isotermas de adsorção e dessorção de nitrogênio foram empregadas para se obter a distribuição do tamanho de poros a 77 K (ponto de ebulição do nitrogênio líquido), usando o método de BJH (Barret, Joyner, e Halenda).

As amostras foram pré-tratadas a 473 K durante 24 h em atmosfera de nitrogênio, a fim de eliminar a umidade absorvida na superfície da amostra sólida. Os adsorventes foram então submetidos a 298 K num vácuo, atingindo uma pressão residual de  $10^{-4} \text{ Pa}$ .

## **Capítulo Três: Parte experimental.**

### 4.4.3. Análise termogravimétrica

A análise termogravimétrica (do inglês Thermogravimetric analysis - TGA) é uma técnica analítica utilizada para determinar a estabilidade térmica de um material e sua fração de componentes voláteis pelo acompanhamento da variação da massa que ocorre quando uma amostra é aquecida.

### 4.4.4. Análise morfológica

O microscópio eletrônico de varredura (MEV) é um equipamento versátil que permite a obtenção de informações estruturais e químicas de amostras diversas; neste trabalho de microscopia de varredura foi utilizada para o lodo de esgoto e para o material adsorvente. Um feixe fino de elétrons de alta energia incide na superfície da amostra onde, ocorrendo uma interação; parte do feixe é refletido e coletado por um detector que converte este sinal em imagem de ERE - imagem de elétrons retroespalhados - ou nesta interação a amostra emite elétrons produzindo a chamada imagem de ES (elétrons secundários). Ocorre também a emissão de raios- X que fornece a composição química elementar de um ponto ou região da superfície, possibilitando a identificação de praticamente qualquer elemento presente.

Os adsorventes foram analisados por microscopia de varredura eletrônica (MEV) utilizando um microscópio eletrônico marca Jeol, modelo JSM 6060, com uma tensão de 5 a 20 KV e ampliações das imagens variando de 500 a 10.000 vezes.

### 4.4.5. Espectroscopia de infravermelho

A espectroscopia de infravermelho (do inglês infrared spectroscopy - IR) é um tipo de espectroscopia de absorção a qual usa a região do infravermelho do espectro eletromagnético. Os espectros no infravermelho com transformada de Fourier (FTIR) dos carvões produzidos a partir do lodo de esgoto, dos materiais híbridos e compósitos foram obtidos utilizando um Espectrofotômetro modelo ALPHA da Bruker, com uma faixa espectral de 4000 a 400  $\text{cm}^{-1}$ , resolução de 4  $\text{cm}^{-1}$  a partir de amostras em pastilhas de 0,1% em KBr.

A absorção na região do infravermelho é causada por movimentos rotacionais e vibracionais dos grupos moleculares e ligações químicas de uma molécula. A espectroscopia vibracional na região do infravermelho dará informações quanto à presença de grupos

## **Capítulo Três: Parte experimental.**

funcionais na superfície dos materiais, o que subsidia a entender melhor sobre o fenômeno da adsorção através da interação entre o adsorvente e os adsorvatos.

### 4.4.6 Adsorção de vapores (Água e n-heptano)

Para a de adsorção de vapor, os adsorventes em pó foram secos em tubo de vidro de 5 ml a 70°C durante 24 h. As amostras foram resfriadas à temperatura ambiente num dessecador antes de se determinar o peso preciso (cerca de 0,5 g). O armazenamento de amostras em uma atmosfera de vapor de solvente saturado foi realizada em frascos de Erlenmeyer de tapar com uma junta de vidro esmerilado, usando 60 ml de solvente. O tubo de vidro contendo o adsorvente em pó foi colocado de tal maneira que não estivesse em contato com as paredes internas do erlenmeyer. As amostras foram removidas de dentro do erlenmeyer após 24 h. O ganho de peso durante o armazenamento foi usada para calcular a adsorção máxima de vapor.

### 4.4.7. Medida de potencial zeta

As medições de potencial zeta das partículas de carvões ativados foram realizadas em um equipamento *Zetasizer Nano (Nano-ZS)* acoplado a um titulador multiuso (*MPT-Z*), ambos do fabricante Malvern. As medições foram realizadas para diferentes valores de pH, visando a obtenção do pH que a carga da partícula apresenta o Ponto Iso-Elétrico (PIE). Na determinação do potencial zeta dos carvões ativados, empregou-se como eletrólito indiferente uma solução de 0,01 mmol L<sup>-1</sup> de KCl preparada com água deionizada. A suspensão coloidal em água foi preparada na adicionando 20 mg de CA em 100ml de cada solução ácida (HCl) e básica (NaOH). Foram feitas soluções independentes de 0,1 mol L<sup>-1</sup> de HCl e de 0,01 mol L<sup>-1</sup> de NaOH para ajuste de pH pelo titulador automático.

O valor de potencial zeta registrado representa a média de 3 valores medidos pelo aparelho o qual calcula a mobilidade eletroforética das partículas e converte esta para potencial zeta. Finalmente curvas de potencial zeta são construídas em função do pH para a determinação do ponto isoelétrico.

### 4.4.8. Soluções e reagentes

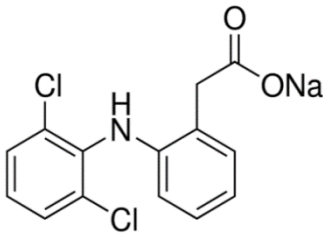
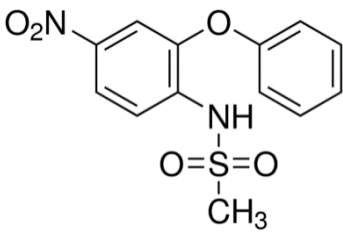
### Capítulo Três: Parte experimental.

As soluções estoque foram preparadas pela dissolução dos respectivos adsorvatos (fármacos e compostos fenólicos) precisamente pesados em água deionizada numa concentração de  $5.000 \text{ mg}^{-1}$ . A partir das soluções estoques dos corantes, foram preparados os padrões das curvas de calibração utilizando balões volumétricos e também foram realizadas todas as diluições necessárias para os experimentos.

As soluções de trabalho dos fármacos e compostos fenólicos foram obtidas por diluição serial das soluções estoque. Os ajustes de pH das soluções foram feitas com alíquotas de soluções de HCl e NaOH  $0,1 \text{ mol L}^{-1}$ , utilizando um pHmetro de Schott Lab 850.

Os fármacos utilizados nos experimentos foram o Diclofenaco de sódio (DCF) e nimesulida (NM), ambos obtidos da Sigma Aldrich e suas características estão apresentados na Tabela 3.

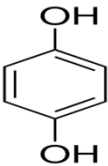
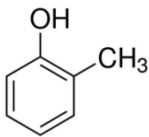
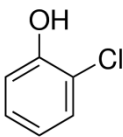
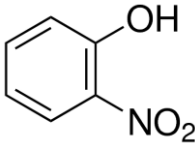
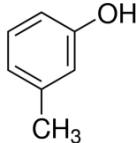
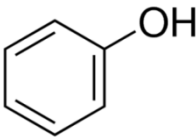
Tabela 3. Características químicas e estruturais dos fármacos utilizados neste trabalho.

Diclofenaco (DFC)	Nimesulida (NM)
	
CAS 15307-79-6	CAS 21803-78-2
$\text{C}_{12}\text{H}_{10}\text{Cl}_2\text{NNaO}_2$	$\text{C}_{13}\text{H}_{12}\text{N}_2\text{O}_5\text{S}$
$318.13 \text{ g. mol}^{-1}$	$308.31 \text{ g. mol}^{-1}$
$\text{LogK}_{\text{ow}} = 3.91$	$\text{LogK}_{\text{ow}} = 2.22$
$\lambda_{\text{max}} = 285 \text{ nm}$	$\lambda_{\text{max}} = 392 \text{ nm}$

Os compostos fenólicos utilizados neste estudo foram fornecidos por Sigma-Aldrich e usados sem purificação. A Tabela 4 mostra as propriedades dos compostos fenólicos utilizados para os testes de adsorção em carvões ativados. Ao todo foram utilizados para os testes de adsorção seis fenóis, m-cresol, fenol, o-cresol, 2-cloro fenol, 2-nitro fenol e hidroquinona.

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Tabela 4. Características químicas e estruturais dos compostos fenólicos utilizados neste trabalho.

Hidroquinona	o-Cresol	2-clorofenol	2-Nitrofenol	m-Cresol	Fenol
					
CAS 123-21-9 $C_6H_4-1,4(OH)_2$ $110.11 \text{ g mol}^{-1}$ $\text{LogK}_{ow} = 0.59$ $\text{pKa} = 9.98$ $\lambda_{max} = 288 \text{ nm}$	CAS 95-48-7 $CH_3C_6H_4OH$ $326.43 \text{ g mol}^{-1}$ $\text{LogK}_{ow} = 1.95$ $\text{pKa} = 10.37$ $\lambda_{max} = 270 \text{ nm}$	CAS 95-57-8 $C_6H_5ClO$ $128.56 \text{ g mol}^{-1}$ $\text{LogK}_{ow} = 2.15$ $\text{pKa} = 7.97$ $\lambda_{max} = 273 \text{ nm}$	CAS 88-75-5 $O_2NC_6H_4OH$ $139.11 \text{ g mol}^{-1}$ $\text{LogK}_{ow} = 1.79$ $\text{pKa} = 6.63$ $\lambda_{max} = 278 \text{ nm}$	CAS 108-39-4 $CH_3C_6H_4OH$ $139.11 \text{ g mol}^{-1}$ $\text{LogK}_{ow} = 1.96$ $\text{pKa} = 10.13$ $\lambda_{max} = 271 \text{ nm}$	CAS 108-95-2 $C_6H_5OH$ $94.11 \text{ g mol}^{-1}$ $\text{LogK}_{ow} = 1.46$ $\text{pKa} = 10.02$ $\lambda_{max} = 269 \text{ nm}$

#### 4.5. TESTES DE ADSORÇÃO

##### 4.5.1. Estudos cinéticos

A cinética de adsorção descreve a velocidade com qual o adsorbato é adsorvido pelo adsorvente com relação ao tempo, o que é de grande importância quando se deseja projetar um sistema de tratamento de efluentes por adsorção que tenha eficácia. O tempo de contato para que seja alcançado o equilíbrio de adsorção será determinado através de experimentos de adsorção de cada adsorbato em função do tempo de contato.

Para os estudos cinéticos, foram pesados 30,00 mg de cada adsorvente e colocados em contatos com 20,0 mL de solução contendo cada adsorbato com concentrações iniciais de  $70,0 \text{ mg L}^{-1}$  para o diclofenaco e nimesulida e  $500,0 \text{ mg L}^{-1}$  para o hidroquinona. A solução contendo os adsorventes e os adsorbatos foram deixados sob agitação a 50 rpm em temperatura de  $25^\circ\text{C}$  em períodos de 1,2,3,5,10, 15,20, 30, 40, 60, 90, 120, 150, 180, 240 e 300 min.

A cada intervalo de tempo, a solução residual após a adsorção foi quantificada usando UV / visível espectrofotômetro (T90 + espectrofotômetro de UV-VIS, PG Instruments, Londres, Reino Unido) aos respectivos comprimentos de onda (ver **Tabela 3 e 4**).

Com os dados cinéticos experimentais obtidos serão aplicados os modelos cinéticos de primeira e segunda ordem.



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### 4.5.2. Ensaio de adsorção

Alíquotas de 20,00 mL de DCF, NM (com concentrações iniciais variando de 5,00-500,0 mg L<sup>-1</sup>) e de compostos fenólicos (com concentrações iniciais variando de 5,00-2000,0 mg L<sup>-1</sup>) foram adicionadas aos diferentes tubos de plástico cônico (117 milímetros de altura, em 30 mm de diâmetro) contendo variadas quantidades de adsorventes (5,0 - 200,0 mg). Os frascos foram tapados e colocados num agitador GFL modelo 3015, e o sistema foi agitado entre 5 e 360 minutos. Em seguida, para separar o adsorvente a partir das soluções aquosas, as misturas foram centrifugadas utilizando uma centrífuga Fanem centrifugação (Heraeus Megafuge 16); quando necessário foram retiradas alíquotas de 1-5 ml do sobrenadante e diluídas.

A solução residual após a adsorção foi quantificada usando UV / visível espectrofotômetro (T90 + espectrofotômetro de UV-VIS, PG Instruments, Londres, Reino Unido) aos respectivos comprimentos de onda (ver **Tabela 3 e 4**). As quantidades adsorvidas dos adsorbatos  $q_e$  (mg g<sup>-1</sup>) foram calculadas pela equação (1).

$$q_e = \frac{V(C_o - C_e)}{M_C} \quad \text{Eq. 24}$$

Onde;

$q_e$  = Capacidade de adsorção de adsorbato por grama de carvão ativado;

$v$  = Volume da solução utilizada nos testes de adsorção;

$C_o$  = Concentração inicial do corante;

$C_E$  = Concentração após o teste de adsorção.

**Capítulo Quatro:** *The use of design of experiments for the evaluation of the production of surface rich activated carbon from sewage sludge via microwave and conventional pyrolysis*

# ***Capítulo Quatro***



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## Research Paper

# The use of design of experiments for the evaluation of the production of surface rich activated carbon from sewage sludge via microwave and conventional pyrolysis



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## HIGHLIGHTS

- Using of DOE for preparation of AC by conventional and microwave pyrolysis.
- The significant parameters in producing activated carbon were investigated.
- Conventional pyrolysis AC had better textural development than microwave AC.
- Temperature and holding time had significant influence on the  $S_{BET}$ .
- Reduction of production cost of activated carbon.

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## ABSTRACT

Experimental design and response surface methodology were used for the preparation and comparison of activated carbon produced from sewage sludge by two types of pyrolysis: conventional furnace and microwave. The preparation method was performed following a full fractional factorial design ( $2^3$ ), including pyrolysis temperature or power radiation, holding time and chemical activation agent, and specific surface area ( $S_{BET}$ ) of prepared activated carbon. The influence of these factors on the  $S_{BET}$  of obtained carbon was investigated using an analysis of variance. Samples made by conventional pyrolysis showed overall higher  $S_{BET}$  values than samples synthesised by the microwave method. The optimum parameters for the preparation of activated carbon using the conventional pyrolysis have been identified as: pyrolysis temperature of 500 °C, holding time of 15 min, and a ratio of  $ZnCl_2$ :sludge of 0.5. Microwave pyrolysis is found to be optimal when operating at 980 W for 12 min. Under these conditions,  $S_{BET}$  values of 679 and 501  $m^2g^{-1}$ , respectively, have been obtained. The analysis of nitrogen adsorption/desorption isotherms revealed the presence of micro and mesopores in the activated carbon. The most important significant factor, according statistical analysis, in the variance in  $S_{BET}$  for the conventional pyrolysis samples were the pyrolysis temperature and interaction between pyrolysis temperature, holding time and ratio of  $ZnCl_2$ :sludge were the most important factors. The highest impact parameters for the microwave method were found for the interaction between power radiation and ratio of  $ZnCl_2$ :sludge and the holding time.

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## 1. Introduction

The growing urbanisation of global society, coupled with increasingly stringent sludge reuse/disposal regulations and increasing

public pressure, is forcing both public and private sludge generators to evaluate their sludge management strategies [1,2]. Conventionally, waste sludge is disposed of via incineration, landfilling, and as soil conditioner in agriculture. However, in recent years, new applications for sewage sludge, such as production of ceramic materials [3,4] and activated carbon [5–7] have been explored.

Activated carbon is generally produced from natural starting materials (e.g. coconut shells) by pyrolysis under inert atmosphere at

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elevated temperatures. The temperature treatment can be conducted by conventional heating in a furnace, or by microwave-assisted pyrolysis. The main difference between conventional pyrolysis and the microwave-assisted method is the way the heat is generated. Microwaves supply energy directly to the carbon bed [8,9]. Energy transfer is not by conduction or convection as in conventional heating, but microwave energy is readily transformed into heat inside the particles by dipole rotation and ionic conduction [8,9]. Thus, it has the advantages of rapid temperature rise, uniform temperature distribution, and energy savings over conventional thermal methods [8,10]. However, current literature is not clear about which method produces adsorbents with higher specific surface areas ( $S_{\text{BET}}$ ). Different work comes to different conclusions about different starting materials; for instance, with oil palm shell as the starting material, conventional pyrolysis obtains higher  $S_{\text{BET}}$  than microwave [11]. Conversely, activated carbon prepared from olive pits obtained higher  $S_{\text{BET}}$  with the microwave-assisted heating process [12,13].

The properties, especially  $S_{\text{BET}}$ , of activated carbon depend on variables like feedstock type and source, pyrolysis temperature, radiation power, and holding time [13,14]. Because of these very controllable parameters, pyrolytic methods are highly versatile processes where it is possible to optimise these variables to get activated carbon with higher  $S_{\text{BET}}$  [13,14].

The properties of activated carbon such as  $S_{\text{BET}}$  can be improved using experimental design by response surface methodology (RSM). RSM is a very valuable tool for this purpose as it presents statistical models which can be used to understand the interactions between the parameters that have been optimised [15–17]. RSM has been applied widely in various processes for the optimisation of experimental conditions, and should prove useful for the preparation of activated carbon. As reported recently, RSM was applied in the production of AC using different precursors such as Turkish lignite [17], Albizia lebeck seed pods [18], Bamboo [19], Jatropha Hull [20], polycarbonate [21] and coconut shell [22].

To this point, it does not appear that RSM has been applied to study the comparison of the preparation of activated carbon from sludge sewage by conventional pyrolysis versus microwave-assisted pyrolysis.

This work aims to apply RSM to evaluate how microwave and conventional pyrolysis methods, and the pyrolysis conditions: pyrolysis temperature/applied microwave power, holding time, and

ratios of chemical agents, can be optimised for maximum effect on the  $S_{\text{BET}}$  of activated carbon from sewage sludge.

## 2. Materials and methods

### 2.1. Experimental design

In this work, a  $2^3$  full factorial design with 3 central points was studied. The factors used for the production of activated carbon from sewage sludge were studied with standard RSM in order to identify and optimise the effective process parameters. In addition, this method helps to analyse the interaction between these parameters [15,16]. With this method, a core factorial is created that forms a cube with sides that are two coded units in length (from  $-1$  to  $+1$ ); noted in the Table 1. Table 1 shows the ranges and the levels of the variables examined and their combinations in this study. The studied variables were: activation temperature or microwave power ( $X_1$ ), chemical impregnation ratio ( $X_2$ ), and holding time ( $X_3$ ). In order to minimise the effects of the uncontrolled factors, the experimental sequence was randomised, as can be seen in Table 1. It shows the number of runs and their respective parameter combinations to activated carbon samples made by conventional pyrolysis and microwave. It was assumed that the relationship between the three independent variables and the experimental  $S_{\text{BET}}$  data follow a linear equation, as expressed in Eq. (1):

$$R = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_4 X_1 X_2 + \beta_5 X_1 X_3 + \beta_6 X_2 X_3 + \beta_7 X_1 X_2 X_3 + \varepsilon \quad (1)$$

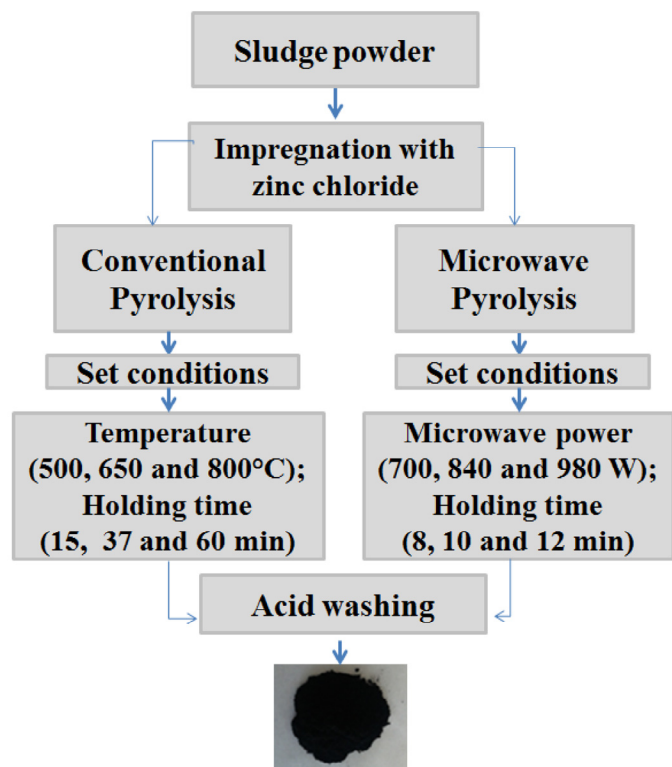
Where  $R$  is the predicted response;  $X_1$  to  $X_3$ , coded variables;  $\beta_0$ , the constant coefficient;  $\beta_1$  to  $\beta_3$ , the linear term coefficients;  $\beta_4$  to  $\beta_6$ , the interaction coefficients between two variables and  $\beta_7$ , the interaction coefficients between three variables.

### 2.2. Preparation of sludge-derived activated carbon

The raw material used for preparing the activated carbon was sewage sludge obtained from a municipal wastewater treatment plant in Porto Alegre, Brazil. First, the sludge was dried at  $105^\circ\text{C}$  for 24 h until no further weight loss could be detected. Subsequently, it was crushed with a grinder, and sieved to a size range

**Table 1**  
Design of experiments for preparation of activated carbon by conventional and microwave pyrolysis.

Factor	Name	Conventional			Microwave				
		Variable level							
		$-1$	$0$	$+1$	$-1$	$0$	$+1$		
		$-1$	$0$	$+1$	$-1$	$0$	$+1$		
X1	Temperature and power	500	650	800	700	840	980		
X2	Hold time	15	37.5	60	8	10	12		
X3	Ratio: $\text{ZnCl}_2/\text{sludge}$	0.5	1.0	1.5	0.5	1.0	1.5		
Experiments samples	Coded variables			Conventional			Microwave		
	$T_r$	$t_r$	m	$T_r$	$t_r$	m	Pow	$t_r$	m
500-15-0.5 and 700-8-0.5	$-1$	$-1$	$-1$	500	15	0.5	700	8	0.5
800-15-0.5 and 980-8-0.5	$+1$	$-1$	$-1$	800	15	0.5	980	8	0.5
500-60-0.5 and 700-12-0.5	$-1$	$+1$	$-1$	500	60	0.5	700	12	0.5
800-60-0.5 and 980-12-0.5	$+1$	$+1$	$-1$	800	60	0.5	980	12	0.5
500-15-1.5 and 700-8-1.5	$-1$	$-1$	$+1$	500	15	1.5	700	8	1.5
800-15-1.5 and 980-8-1.5	$+1$	$-1$	$+1$	800	15	1.5	980	8	1.5
500-60-1.5 and 700-12-1.5	$-1$	$+1$	$+1$	500	60	1.5	700	12	1.5
800-60-1.5 and 980-12-1.5	$+1$	$+1$	$+1$	800	60	1.5	980	12	1.5
650-37-1.0 and 840-10-1.0	$0$	$0$	$0$	650	37.5	1.0	840	10	1.0
650-37-1.0 and 840-10-1.0	$0$	$0$	$0$	650	37.5	1.0	840	10	1.0
650-37-1.0 and 840-10-1.0	$0$	$0$	$0$	650	37.5	1.0	840	10	1.0



**Fig. 1.** Scheme of preparation steps of the activated carbon made by conventional and microwave pyrolysis and varied parameters.

below 250  $\mu\text{m}$ . An overview of preparation of activated carbon is showed in the Fig. 1.

The preparation of the sludge-based activated carbon was comprised of three main steps:

- 10.0 g of dried, powdered sewage sludge was mixed with  $\text{ZnCl}_2$  at various  $\text{ZnCl}_2$ :sludge ratios (see Table 1). Afterwards, 5.0 mL of water was added, and thoroughly mixed to obtain a homogeneous paste. The paste was placed in a crucible and dried at room temperature for 24 h.
- Temperature and activation time of pyrolysis for each sample is listed in Table 1. Pyrolysis processes were performed under a steady-state flow of nitrogen (inert) gas with a flow rate of 100 mL/min, and at a constant heating rate of 5  $^\circ\text{C}/\text{min}$  (conventional furnace) or set to a constant power output (microwave-assisted pyrolysis, see Table 1).
- To complete the chemical activation by leaching the remaining  $\text{ZnCl}_2$  out of the pyrolysed carbon, and in order to enhance the specific area of the AC, the samples were washed with 6.0 mol  $\text{L}^{-1}$  HCl [23]. For this, 8.0 g of AC was added to 150 mL of 6 mol  $\text{L}^{-1}$  HCl in a 250 mL flask; the mixture was stirred on a magnetic stirrer under reflux for 3 h at 75  $^\circ\text{C}$ . Subsequently, the slurry was cooled down and vacuum filtered through 0.45  $\mu\text{m}$  polycarbonate membranes. After extensive washing with distilled water, the solid material was oven dried at 105  $^\circ\text{C}$  for 5 hours, and hand milled to a particle size  $\leq 150 \mu\text{m}$ .

### 2.3. Sample nomenclature

The pyrolysed materials investigated in this study are listed in Table 1. The first number in the sample name refers to the temperature or the power used in the pyrolysis, followed by the holding

time, and ratio of  $\text{ZnCl}_2$ :sludge. For example, “500-15-0.5” was prepared using conventional pyrolysis at 500  $^\circ\text{C}$ , with 15 minutes of holding time, and a weight ratio of 0.5:1.0 of  $\text{ZnCl}_2$ :sludge. “980-12-1.5” was prepared with microwave pyrolysis at 980 W of power, with 12 minutes of holding time, and a weight ratio of 1.5:1.0 of  $\text{ZnCl}_2$ :sludge.

An overview of the conditions under which the samples of sewage sludge were pyrolysed is presented in Table 1.

Where “T” is the pyrolysis temperature ( $^\circ\text{C}$ ), “P” is the power radiation, “t” is the holding time and “Ratio” is the ratio of  $\text{ZnCl}_2$ :sludge.

The specific surface area ( $S_{\text{BET}}$ ) was the parameter chosen as a “response”, in order to characterise the activated carbon product.

### 2.4. Characterisation of the activated carbon

For nitrogen adsorption/desorption experiments, the AC was crushed into a fine powder ( $<250 \mu\text{m}$ ) for analysis in order to diminish diffusion limitations that can occur for larger particles. Nitrogen adsorption isotherms were recorded with a commercial system (Belsorp-Mini, Bel Japan Inc.) at 77 K after drying for 3 h at 393 K under reduced pressure ( $<2 \text{ mbar}$ ). The  $S_{\text{BET}}$  were determined using the method of Brunauer, Emmett, and Teller (BET) [24]. The pore size distributions were calculated from the desorption branch of the isotherms based on the Barrett-Joyner-Halenda (BJH) model [25].

Elemental (C, H, N) analyses of samples were performed on a CHNOS Elemental Analyser (Elementar, Vario EL III, Germany). The yields of ash in sludge and AC were analysed by burning them in a muffle furnace at 600  $^\circ\text{C}$  for 30 min [26,27].

## 3. Results and discussion

### 3.1. Elemental analysis of sewage sludge and activated carbon

An elemental analysis was used to determine the carbon, hydrogen, and nitrogen composition of the sample. Oxygen composition was determined by subtracting the sum of the percentages of carbon, hydrogen, nitrogen, and ashes from the 100% total [11,26,27]. Elemental analyses and ash contents of raw sewage sludge and the activated carbon prepared with the lowest and highest surface areas by the microwave (980-8-1.5 and 980-12-0.5) and conventional method (800-15-1.5 and 500-15-0.5) are shown in Table 2.

The CHN analysis clearly shows little difference in the carbon content on the adsorbents made from conventional or microwave-assisted pyrolysis. This suggests that both types of pyrolysis work well for activated carbon production.

Although similar for all samples, relative C content was slightly reduced at higher [conventional] pyrolysis temperatures and increased holding times (microwave-assisted).

**Table 2**  
Elemental analysis of sewage sludge and activated carbon with lowest and highest specific surface area of both kind of pyrolysis.

	Ash <sup>a</sup>	Elemental composition <sup>b</sup> (%)			
		C	H	N	O <sup>c</sup>
Sewage sludge	46.24	32.68	5.12	6.17	9.79
Conventional heating					
500-15-0.5	52.36	36.40	1.73	3.24	6.27
800-15-1.5	61.09	31.32	1.07	1.56	4.96
Microwave-assisted					
980-12-0.5	57.85	32.02	2.10	2.70	5.33
980-8-1.5	51.73	34.46	2.57	3.99	7.25

<sup>a</sup> On dry basis.

<sup>b</sup> On dry and ash free basis.

<sup>c</sup> By difference,  $\text{O} = 100\% - (\text{C} + \text{H} + \text{N} + \text{Ash})$ .

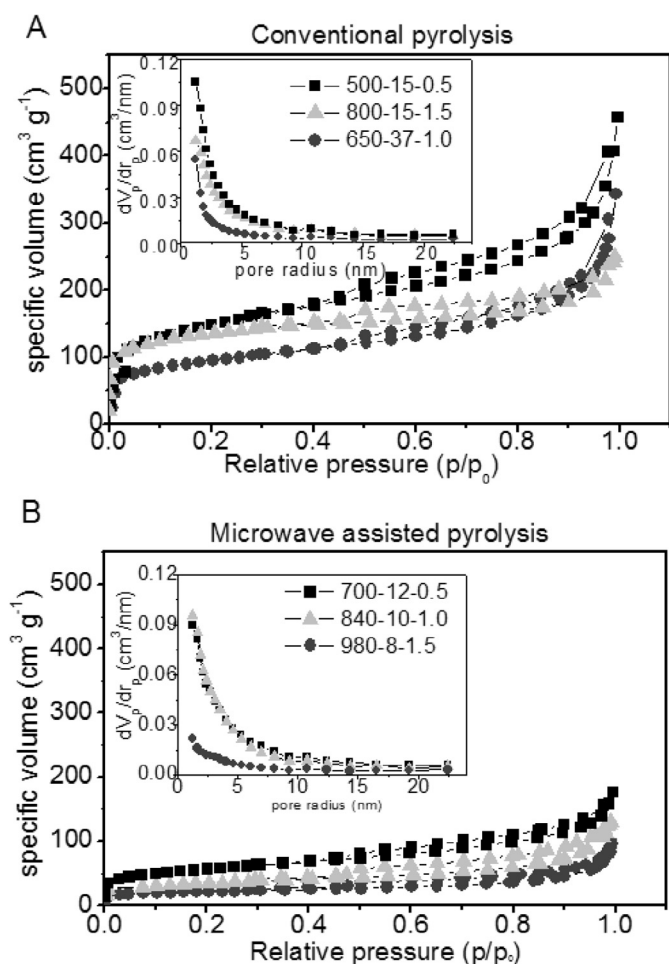


Fig. 2. Nitrogen adsorption/desorption isotherms for activated carbon made by conventional (A) and microwave (B) pyrolysis and their corresponding BJH plots.

Additionally, it can be shown that a decrease in hydrogen contents (from sewage sludge at 5.12% to 1.07–1.73% and 2.10–2.57% for conventional and microwave pyrolysis, respectively), due to the rupturing of molecular chains at high temperatures [27]. Nitrogen and oxygen content displayed a similar trend, with the sludge losing nitrogen and oxygen during pyrolysis. As expected, microwave and conventional pyrolysis favours the elimination of nitrogenous and hydrogen compounds as volatile gases [26]. The loss of oxygen content (in addition to other volatiles) suggest that a large number of functional groups were lost during pyrolysis [11].

### 3.2. Porosity – comparisons between conventional and microwave method

The comparison of microwave and conventional pyrolysis was performed in order to determine which method produces activated carbon with higher  $S_{\text{BET}}$ , which were determined for all samples by nitrogen adsorption–desorption isotherms. Fig. 2A and B show the isotherms of three selected samples from each pyrolysis method (other samples show similar isotherms).

All pyrolysed samples can be assigned a type IV isotherm according to International Union of Pure and Applied Chemistry (IUPAC) classification. Type IV isotherms possess a hysteresis loop, representing capillary condensation, indicating the presence of mesopores

[28–30]. However, it should be noted that the adsorbed  $\text{N}_2$  volumes are different, depending on the pyrolysis method applied (Fig. 2A and B). The range of nitrogen volumes adsorbed by activated carbon produced by conventional pyrolysis was slightly more than double ( $227\text{--}458\text{ cm}^3\text{ g}^{-1}$ ) those produced by microwave ( $91\text{--}187\text{ cm}^3\text{ g}^{-1}$ ).

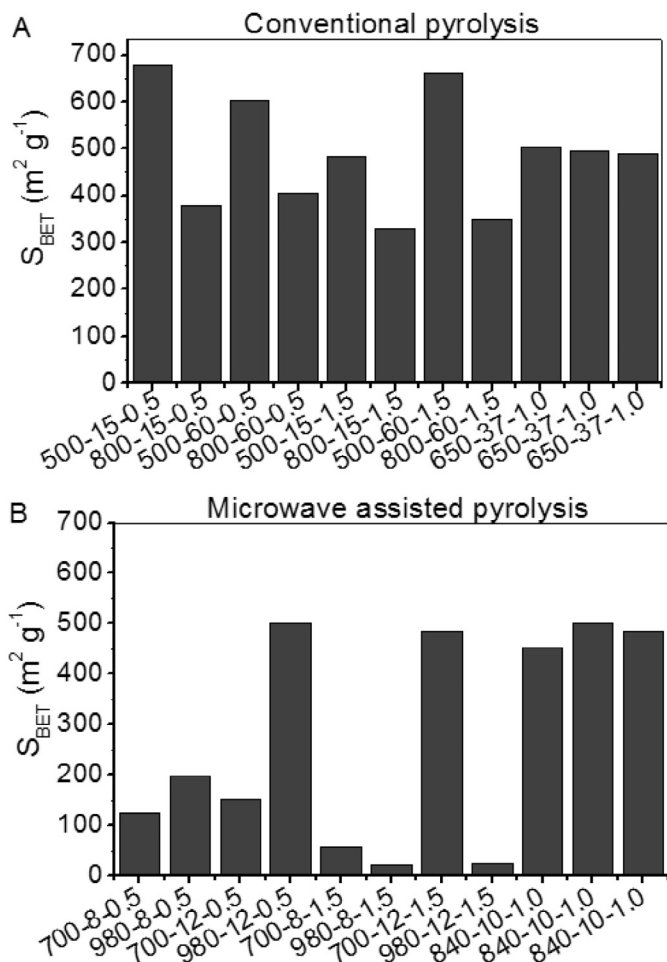
According to the standard adsorption classification of IUPAC, micropores have diameters lower than 2 nm, mesopores have diameters between 2 and 50 nm, and macropores are higher than 50 nm. All samples produced by both pyrolysis processes have micropores and mesopores, as illustrated in the BJH plots (Fig. 2A and B).

Structural heterogeneity and solid internal structure can be represented by characterisation of the pore size distribution [15]. The pore size distributions derived from the BJH plots of the conventional and microwave samples are shown in Fig. 2A and B, respectively. The pyrolysis conditions of each method appear to affect the pore structure of the activated carbon, in addition to the method used (see Fig. 2A and B). By increasing the temperature, the samples pyrolysed by conventional means showed a sharp peak in the range of large micropores or small mesopores. Activated carbon produced at higher temperatures, according to the BJH plots, possessed homogeneous, small mesopores.

The creation of large micropores and small mesopores, increased with the sample 500-15-0.5, which is in good agreement with the increase in adsorbed specific volume of  $\text{N}_2$  according to the isotherm of nitrogen (see Fig. 2A) for the conventional method. The microwave activated carbons also demonstrated a relatively broad peak in the micropore and mesopore range (see Fig. 2B). However, the AC samples obtained via microwave heating show  $S_{\text{BET}}$  and specific volume of pores rather smaller than the AC obtained via conventional pyrolysis. The microwave radiation has a strong influence on AC structure. AC processed by microwave heating has a different pore structure; a smaller surface area allocated to micropores, and a higher bulk density than the conventional method [31]. This difference might be the result of radiation action on the decomposition kinetics of the organic compounds, leading to a more condensed/dense network [31] that decreases the  $S_{\text{BET}}$  in comparison to AC produced by conventional pyrolysis. However, it should be noted that the samples produced via both methods show approximately the same textural properties. This implies that the quick, volumetric heating provided by the microwave technique promotes the development of pores in a shorter amount of time than conventional pyrolysis, which saves energy.

Fig. 3 shows the  $S_{\text{BET}}$  of all activated carbon samples, and it can be seen that the  $S_{\text{BET}}$  derived from conventional pyrolysis were higher than the  $S_{\text{BET}}$  of AC made by microwave-assisted pyrolysis over the whole set of conditions. The highest  $S_{\text{BET}}$  was found for a sample made by conventional method ( $679\text{ m}^2\text{ g}^{-1}$ ), which is about 35.52% higher than the highest  $S_{\text{BET}}$  of a sample made by microwave pyrolysis ( $501\text{ m}^2\text{ g}^{-1}$ ). These results show that, under these experimental conditions, conventional pyrolysis was more efficient at generating high  $S_{\text{BET}}$  values than the microwave-assisted pyrolysis. It remains possible that the differences may have arisen if the holding time was not high enough to promote the total carbonisation of the samples. However, not all samples pyrolysed for 12 min show high  $S_{\text{BET}}$ .

A microwave activation time shorter than that employed for conventional activation was chosen for the following reasons: in light of a previous study on sludge where the materials exhibited the highest ash content at an activation time of 15 min (at conditions established in this study), and consequently lower  $S_{\text{BET}}$ . Although, in the literature the activation times for the microwave pyrolysis differ from 30 s to 30 min, the precursors can influence the decomposition behaviour such that each precursor has its own optimal activation time [32–35].



**Fig. 3.** Specific surface areas of activated carbon made by conventional (A) and microwave assisted pyrolysis (B).

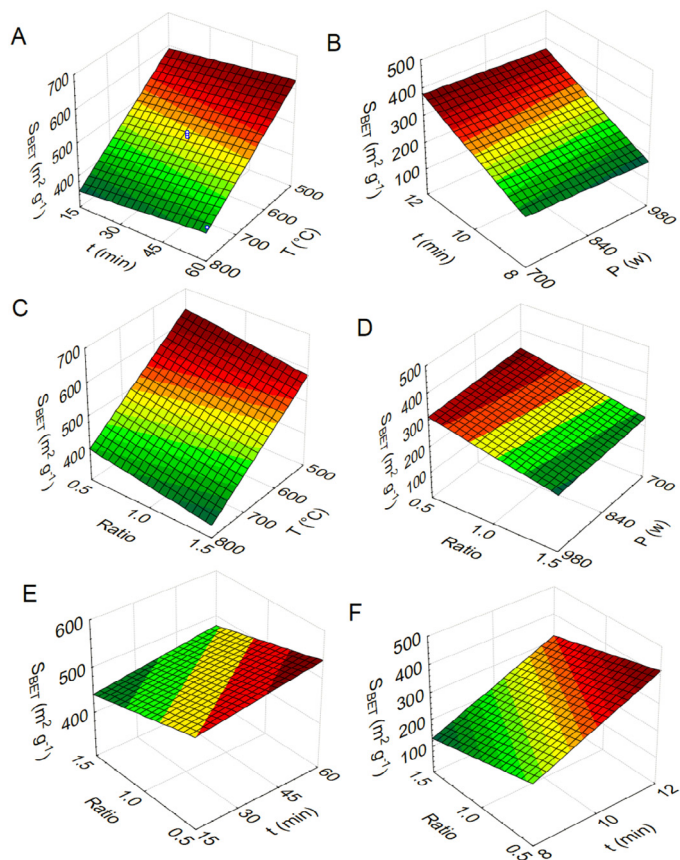
### 3.3. Analysis of the response surface plots and statistical analysis

The results of the  $S_{BET}$  from the activated carbon pyrolysed by conventional pyrolysis and microwave assisted were analysed with an ANOVA for a  $2^3$  factorial design and also for the response surface plots.

Fig. 4 shows the effect of the variables on the response ( $S_{BET}$ ) using 3D response surface graphs, obtained by combination of the various pyrolysis parameters (Table 1) and the resulting  $S_{BET}$  values (Fig. 4A–F).

Concerning activated carbon made by conventional pyrolysis, Fig. 4A shows interactions between holding time and pyrolysis temperature, and it is observed that the highest  $S_{BET}$  values are located in the region defined by lower pyrolysis temperatures. For activated carbon samples derived from microwave pyrolysis, the best  $S_{BET}$  results were obtained with a higher holding time (see Fig. 4B). Fig. 4C demonstrates the interactions between the ratio of  $ZnCl_2$ :sludge and the pyrolysis temperature;  $S_{BET}$  values increase while both parameters drop. On the other hand, samples produced with microwave-assisted pyrolysis showed that  $S_{BET}$  values were largely unaffected by both parameters (see Fig. 4D).

Fig. 4 illustrates the behaviour of the studied variables on the  $S_{BET}$  response; however, it is not possible to understand which variables were more important in terms of their interactions and how each one influenced the  $S_{BET}$  response. For this purpose, Pareto Charts have been showed and analysed. Fig. 5A and B presents the Pareto

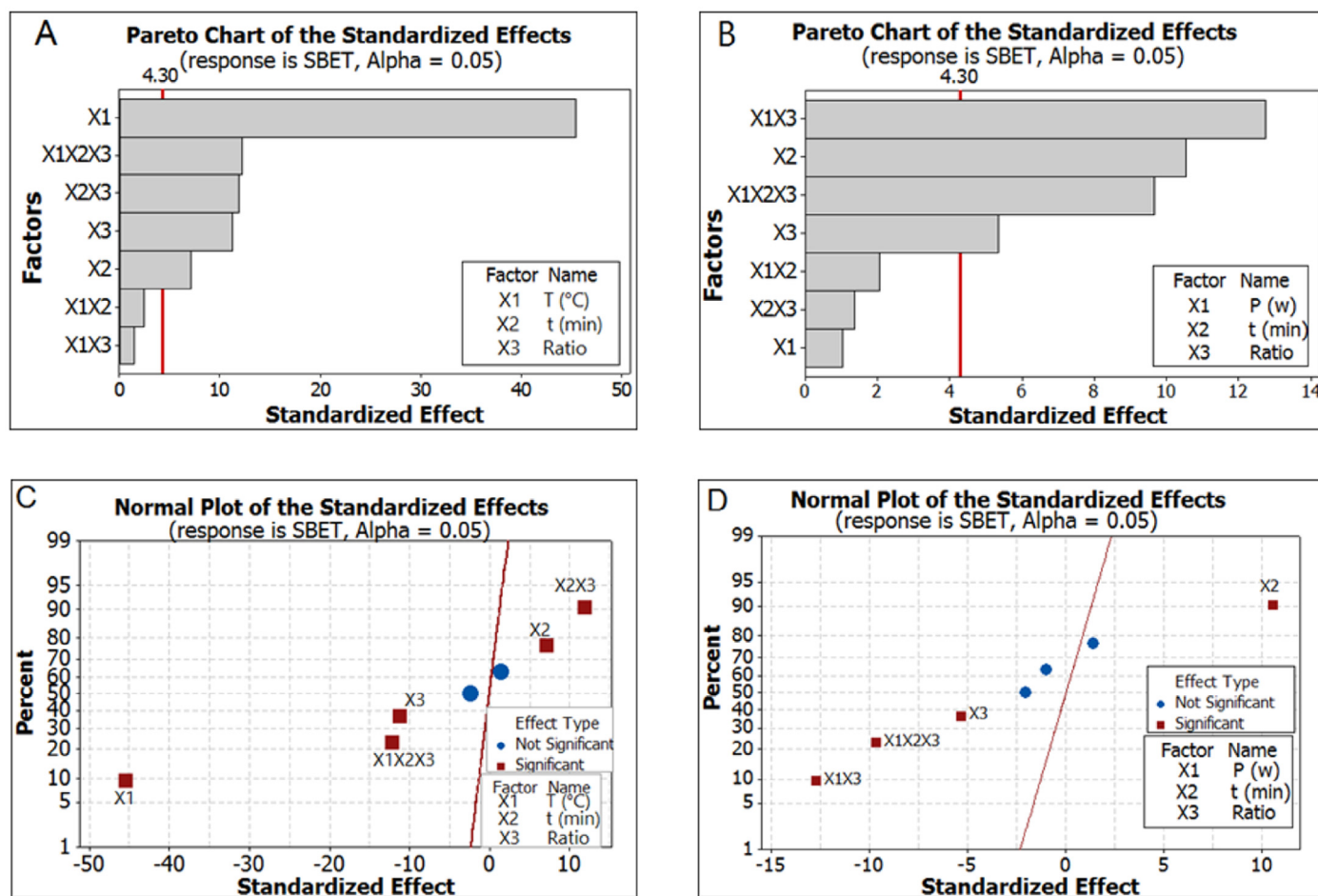


**Fig. 4.** (A) 3D response surface: Interactive effects of varied holding time and pyrolysis temperature ( $^{\circ}C$ ) on response  $S_{BET}$ . (B) 3D response surface: Interactive effects of varied ratio of  $ZnCl_2$ :sludge and pyrolysis temperature on response  $S_{BET}$ . (C) 3D response surface: Interactive effects of varied ratio of  $ZnCl_2$ :sludge and holding time (minutes) on response  $S_{BET}$ . (D) 3D response surface: Interactive effects of varied holding time and power radiation on response  $S_{BET}$ . (E) 3D response surface: Interactive effects of varied ratio of  $ZnCl_2$ :sludge and power radiation on response  $S_{BET}$ . (F) 3D response surface: Interactive effects of varied ratio of  $ZnCl_2$ :sludge and holding time on response  $S_{BET}$ .

Charts for standardised effects at  $p = 0.05$ , for activated carbon made by conventional and microwave pyrolysis, respectively. In addition, normal probability plots of standardised effects at  $p = 0.05$ , for activated carbon made by conventional and microwave pyrolysis, respectively, are shown in Fig. 5C and D. The bars visualise the variables ( $X1$ – $X3$ ) and their interactions (e.g.  $X1X2X3$ ). In this diagram, all bars that are located to the right of the vertical dashed line are significant, which means that the variables and/or their interactions influenced the  $S_{BET}$  response at a minimum statistically significant level of 95% confidence.

The results presented in Fig. 5A and B and Table 3 indicate that for activated carbon made by conventional pyrolysis, the most important factors influencing the  $S_{BET}$  values were (in descending order): pyrolysis temperature ( $X1$ ), the interaction between pyrolysis temperature with holding time and ratio of  $ZnCl_2$ :sludge ( $X1X2X3$ ), followed by holding time and ratio of  $ZnCl_2$ :sludge ( $X2X3$ ), ratio of  $ZnCl_2$ :sludge ( $X3$ ) and holding time ( $X2$ ). The most important factors influencing the  $S_{BET}$  values for microwave pyrolysis samples were, in descending order: interactions between power and ratio of  $ZnCl_2$ :sludge ( $X1X3$ ), holding time ( $X2$ ), interactions between power radiation, holding time and ratio of  $ZnCl_2$ :sludge ( $X1X2X3$ ), and the ratio of  $ZnCl_2$ :sludge ( $X3$ ).

The Pareto chart assists in ascertaining which of the factors and its interactions are most important [36]. However, to complement this analysis, it is important to plot the normal probability of



**Fig. 5.** (A,B) Pareto plots of standardised effects at  $p = 0.05$ , for activated carbon made by conventional and microwave pyrolysis, respectively. (C,D) Normal plots of standardised effects at  $p = 0.05$ , for activated carbon made by conventional and microwave pyrolysis, respectively. The dotted line at 50% divides the negative effects from the positive ones.

standardised effects at  $p = 0.05$  for activated carbon made by conventional and microwave pyrolysis (Fig. 5C and D). The fit line indicates the values expected to be obtained when the parameters would have no effect. Significant effects are shown with their labels and situated a certain distance to the left or right of the fit line showing negative (when the points are situated left to fit line) or positive values (when the points are situated right to fit line) of the standardised effect. Positive values for effects mean that an increase in their levels lead to an increase in the  $S_{BET}$  of the activated carbon; negative values lower the  $S_{BET}$  with increasing level.

**Table 3**  
Estimated effects and coefficients for  $S_{BET}$  at 95% of probability.

Term	Kind of pyrolysis					
	Conventional pyrolysis			Microwave assisted		
	Effect	Coeff	SE Coeff	Effect	Coeff	SE Coeff
Constant		486.1	2.654		195.4	9.028
X1	-241.2	-120.6	2.654	-18.7	-9.4	9.028
X2	37.7	18.9	2.654	190.2	95.1	9.028
X3	-59.8	-29.9	2.654	-96.8	-48.4	9.028
X1X2	-12.8	-6.4	2.654	-37.2	-18.6	9.028
X1X3	7.7	3.9	2.654	-230.3	-115.1	9.028
X2X3	62.7	31.4	2.654	24.8	12.4	9.028
X1X2X3	-64.8	-32.4	2.654	-174.7	-87.4	9.028

Note: Microwave assisted pyrolysis –  $R^2_{Adj} = 0.9857$ ; Conventional pyrolysis –  $R^2_{Adj} = 0.9961$ .

Variables having a negative effect were X1, X3, and X1X2X3 for samples derived from conventional pyrolysis, and X1X3, X1X2X3, and X3 for samples made using the microwave method. The variables with positive effects on the activated carbon synthesis were X2X3 (conventional method), and X2 (conventional and microwave). The optimal conditions for  $S_{BET}$  of activated carbon were extracted by comparing the observed values with the values predicted by the model. Fig. 6A and B presents the residuals versus fit values for the production of activated carbon by conventional and microwave pyrolysis, respectively. This figure shows how closely the set of observed values follows a theoretical distribution. Generally, in both cases, experimental points are reasonably aligned suggesting a normal distribution. This suggests that the model used in the statistical analysis was appropriate, and can be used to predict the set of conditions leading to the best results (response  $S_{BET}$ ).

#### 3.4. Analysis of variance (ANOVA)

A systematic study using RSM has been carried out to justify the adequacy of the model used in the analysis of pyrolysis process variables. Table 3 shows the results of fitting Eq. (1) to the experimental data by linear regression analysis, and those obtained from evaluating the fitness of the model by means of ANOVA together with the adjusted determination coefficient ( $R^2_{Adj}$ ).

The ANOVA tests show that the models for  $S_{BET}$  were statistically significant at a 95% confidence level ( $p \leq 0.05$ ); their lack-of-fit



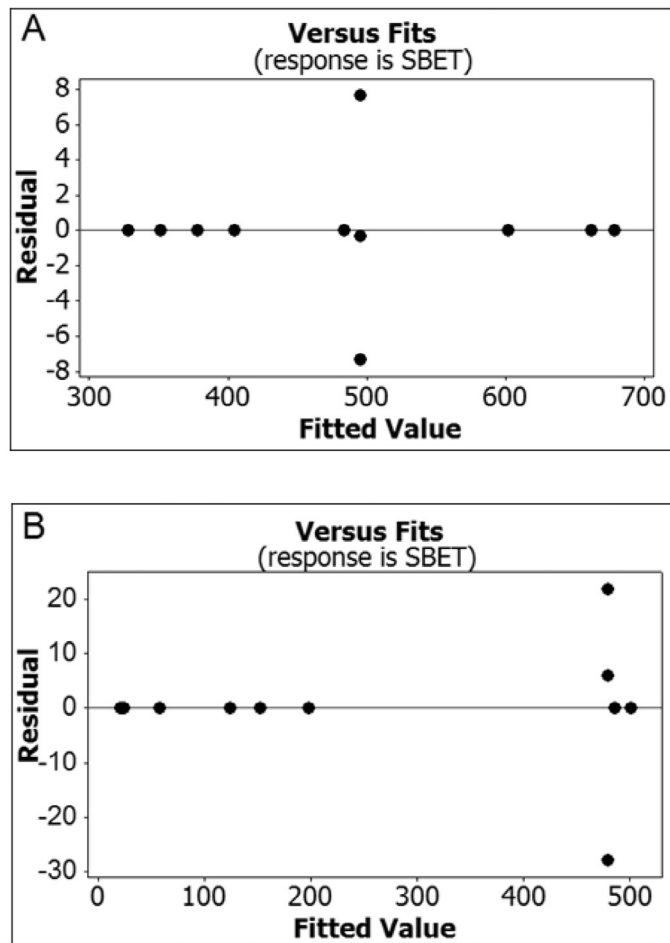


Fig. 6. Residuals versus fit values plot from activated carbon synthesised by conventional pyrolysis (A) and by microwave pyrolysis (B).

was found not to be statistically significant at a 95% confidence level ( $p > 0.05$ ) (see Table 3). For regression analysis, the model was simplified (reduced by rejection of non-significant factors X1X2 and X1X3 for conventional pyrolysis and X1, X1X2, and X2X3 for microwave assisted pyrolysis) and the best fit model equations which describe the  $S_{BET}$  values of the activated carbon made by conventional and microwave pyrolysis are given by Eqs. (2)–(5), respectively:

$$S_{BET} (Conventional) = A_0 + A_1X1 + A_2X2 + A_3X3 + A_6X2X3 + A_7X1X2X3 \quad (2)$$

$$S_{BET} (Conventional) = 486.1 - 120.6T + 18.9t - 29.9Ratio + 31.4t.Ratio - 32.4TtRatio \quad (3)$$

$$S_{BET} (microwave) = A_0 + A_2X2 + A_3X3 + A_5X1X3 + A_7X1X2X3 \quad (4)$$

$$S_{BET} (microwave) = 195.4 + 95.1t - 48.4ratio - 115.1PRatio - 87.4PtRatio \quad (5)$$

The quality of the fit of the model was checked by the  $R^2_{Adj}$  between the experimental and model-predicted values of the response variable (Fig. 6A and B). To strengthen the arguments for the quality of our statistical analysis, Table 4 summarises the sum of squares used to estimate the factors effect and the F-ratios (defined as the ratio of the respective mean-square-effect and the mean-square-error). Furthermore, because the factors in this study have two levels, each ANOVA main effect and interaction effects have one degree of freedom [37].

Table 4

Analysis of Variance for  $S_{BET}$  from microwave and conventional pyrolysis.

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Microwave assisted						
Main effects	3	91814	91814	30605	46.94	0.021
2-Way interactions	3	110030	110030	36677	56.25	0.018
3-Way interactions	1	61075	61075	61075	93.67	0.011
Curvature	1				269.19	0.004
Residual error	2	1304	1304	652		
Pure error	2	1304	1304	652		
Total	10	439736				
Conventional pyrolysis						
Main effects	3	126393	126393	42131	747.89	0.001
2-Way interactions	3	8320	8320	2773	49.23	0.020
3-Way interactions	1	8385	8385	8385	148.85	0.007
Curvature	1	185	185	185	3.28	0.212
Residual error	2	113	113	56		
Pure error	2	113	113	56		
Total	10					

Note: Microwave assisted pyrolysis –  $R^2_{Adj} = 0.9857$ ; Conventional pyrolysis –  $R^2_{Adj} = 0.9961$ .

Whereby the p value is defined as the lowest level of significance leading to rejection of the null hypothesis, it would appear that the main effect of each factor and the interaction effects are statistically significant at  $p < 0.05$  [36,37]. The results further strengthen the statistical significance of the studied factors and their interaction. Additionally, the values of  $R^2_{Adj} = 98.57\%$  for microwave method and  $R^2_{Adj} = 99.61\%$  for conventional method confirm the accuracy of the model.

#### 4. Conclusions

In order to achieve the best conditions for the production of activated carbon with high surface area from sewage sludge, a full  $2^3$  factorial design was employed for screening the factors that would influence the overall optimisation of the pyrolysis procedure by microwave and conventional methods. The activated carbon produced had a mixture of micro- and mesopores.

The optimum conditions for preparation of activated carbon by the microwave method was of 980 W power, a holding time of 12 min, and ratio of  $ZnCl_2$ :sludge of 0.5. Under these conditions, an  $S_{BET}$  of  $501 \text{ m}^2 \text{ g}^{-1}$  was obtained. Optimum conditions for conventional furnace pyrolysis were a pyrolysis temperature of  $500 \text{ }^\circ\text{C}$ , a holding time of 15 min, and ratio of  $ZnCl_2$ :sludge of 0.5. Under these conditions, a  $S_{BET}$  of  $679 \text{ m}^2 \text{ g}^{-1}$  was achieved.

The factor that most strongly influenced the  $S_{BET}$  values was the temperature (X1, negatively) for conventional furnace heating. On the other hand, for microwave assisted pyrolysis the holding time (X2) was the most important positive factor, followed by the interaction between temperature and ratio of  $ZnCl_2$ :sludge (X1X3, negative) in the response.

The data obtained for the two methods using sewage sludge as a starting material showed that conventional pyrolysis is preferable to the AC produced by microwave-assisted pyrolysis because activated carbon with higher specific areas were generated, and the accuracy of the model was slightly higher, according to  $R^2_{Adj}$ , with values of 0.9961 and 0.9857 for conventional and for microwave methods, respectively.

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## References

- [1] V.K. Tyagi, S.-L. Lo, Sludge: a waste or renewable source for energy and resources recovery?, *Renew. Sust. Energy Rev.* 25 (2013) 708–728.
- [2] Y. Liu, J.H. Tay, Strategy for minimization of excess sludge production from the activated sludge process, *Biotechnol. Adv.* 19 (2001) 97–107.
- [3] A.M. Szöke, M. Muntean, O. Dumitrescu, S. Mészáros, Studies on building ceramics manufacturing by incorporating dried sludge, *Environ. Eng. Manage. J.* 13 (2014) 15–20.
- [4] T. Yuanyuan, C. Liu, K. Shiha, Beneficial metal stabilization mechanisms using simulated sludge incineration ash for ceramic products, *J. Chem. Technol. Biotechnol.* 89 (2014) 536–543.
- [5] E. Agrafioti, B. Bouras, D. Kalderis, E. Diamadopoulou, Biochar production by sewage sludge pyrolysis, *J. Anal. Appl. Pyrol.* 101 (2013) 72–78.
- [6] L. Kong, Y. Xiong, S. Tian, R. Luo, C.H.H. Huang, Preparation and characterization of a hierarchical porous char from sewage sludge with superior adsorption capacity for toluene by a new two-step pore-fabricating process, *Bioresour. Technol.* 146 (2013) 457–462.
- [7] F. Lia, B. Yana, Z. Zhang, L. Zhang, T. Lei, Effect of activator on the structure and desulphurization efficiency of sludge-activated carbon, *Environ. Technol.* 35 (2014) 2572–2581.
- [8] Q.H. Lina, H. Cheng, G.Y. Chena, Preparation and characterization of carbonaceous adsorbents from sewage sludge using a pilot-scale microwave heating equipment, *J. Anal. Appl. Pyrol.* 93 (2012) 113–119.
- [9] J.A. Menéndez, A. Arenillas, B. Fidalgo, Y. Fernández, L. Zubizarreta, E.G. Calvo, et al., Microwave heating processes involving carbon materials, *Fuel Process. Technol.* 91 (2010) 1–8.
- [10] Q.S. Liu, T. Zheng, N. Li, P. Wang, G. Abulikemu, Modification of bamboo-based activated carbon using microwave radiation and its effects on the adsorption of methylene blue, *Appl. Surf. Sci.* 256 (2010) 3309–3315.
- [11] R.H. Hesas, A. Arami-Niya, W.M.A.W. Daud, J.N. Sahu, Comparison of oil palm shell-based activated carbons produced by microwave and conventional heating methods using zinc chloride activation, *J. Anal. Appl. Pyrol.* 104 (2013) 176–184.
- [12] X. Wang, X. Liang, Y. Wang, X. Wang, M. Liu, D. Yin, et al., Adsorption of Copper (II) onto activated carbons from sewage sludge by microwave-induced phosphoric acid and zinc chloride activation, *Desalination* 278 (2011) 231–237.
- [13] D. Angin, E. Altintig, T.E. Köse, Influence of process parameters on the surface and chemical properties of activated carbon obtained from biochar by chemical activation, *Bioresour. Technol.* 148 (2013) 542–549.
- [14] A.C. Lua, T. Yang, J. Guo, Effects of pyrolysis conditions on the properties of activated carbons prepared from pistachio-nut shells, *J. Anal. Appl. Pyrol.* 72 (2004) 279–287.
- [15] D.C. Montgomery, *Design and Analysis of Experiments*, Fifth ed., John Wiley & Sons, New York, 2001.
- [16] G.E.P. Box, W.G. Hunter, J.S. Hunter, *Statistics for Experimenters: An Introduction to Design, Data Analysis and Model Building*, Second ed., John Wiley & Sons, New York, 1978.
- [17] F. Karacan, U. Ozden, S. Karacan, Optimization of manufacturing conditions for activated carbon from Turkish lignite by chemical activation using response surface methodology, *Appl. Therm. Eng.* 27 (2007) 1212–1218.
- [18] J.A. Muthanna, K.T. Samar, Optimization of microwave preparation conditions for activated carbon from Albizialebeck seed pods for methylene blue dye adsorption, *J. Anal. Appl. Pyrol.* 105 (2014) 199–208.
- [19] P.G. González, T. Hernández-Quiroz, L. García-González, The use of experimental design and response surface methodologies for the synthesis of chemically activated carbons produced from bamboo, *Fuel Process. Technol.* 127 (2014) 133–139.
- [20] X. Duan, J. Peng, C. Srinivasakannan, L. Zhang, H. Xia, K. Yang, et al., Process optimization for the preparation of activated carbon from Jatropha Hull using response surface methodology, *Ener. Source* 33 (2011) 2005–2017.
- [21] L. Zhanyong, K. Wang, J. Song, Q. Xu, N. Kobayashi, Preparation of activated carbons from polycarbonate with chemical activation using response surface methodology, *J. Mat. Cycles Waste Manage.* 16 (2014) 359–366.
- [22] M.K.B. Gratuio, T. Panyathanmaporn, R.A. Chumnanklang, N. Sirinuntawittaya, A. Dutta, Production of activated carbon from coconut shell: optimization using response surface methodology, *Bioresour. Technol.* 99 (2008) 4887–4895.
- [23] M.C. Ribas, M.A. Adebayob, L.D.T. Prola, E.C. Lima, R. Cataluña, L.A. Feris, et al., Comparison of a homemade cocoa shell activated carbon with commercial activated carbon for the removal of reactive violet 5 dye from aqueous solutions, *Chem. Eng. J.* 248 (2014) 315–326.
- [24] S. Brunauer, P.H. Emmett, E. Teller, Adsorption of gases in multimolecular layers, *J. Am. Chem. Soc.* 60 (1938) 309.
- [25] E.P. Barrett, G. Joyner, P.P. Halend, The determination of pore volume and area distributions in porous substances. I. Computations from nitrogen isotherms, *J. Am. Chem. Soc.* 73 (1951) 373–380.
- [26] L. Leng, X. Yuana, H. Huang, J. Shao, H. Wang, X. Chend, et al., Bio-char derived from sewage sludge by liquefaction: characterization and application for dye adsorption, *Appl. Surf. Sci.* 346 (2015) 223–231.
- [27] A.V. Maldhure, J.D. Ekhe, Preparation and characterizations of microwave assisted activated carbons from industrial waste lignin for Cu(II) sorption, *Chem. Eng. J.* 168 (2011) 1103–1111.
- [28] P.B. Balbuenat, K.E. Gubbins, Theoretical interpretation of adsorption behavior of simple fluids in slit pores, *Langmuir* 9 (1993) 1801–1814.
- [29] K.S.W. Sing, D.H. Everett, R.A.W. Haul, L. Moscou, R.A. Pierotti, J. Rouquérol, et al., Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity (recommendations 1984), *Pure Appl. Chem.* 57 (1985) 603–619.
- [30] T. Prenzel, T.L.M. Guedes, F. Schluter, M. Wilhelm, K. Rezwani, Tailoring surfaces of hybrid ceramics for gas adsorption – from alkanes to CO<sub>2</sub>, *Sep. Purif. Technol.* 129 (2014) 80–89.
- [31] G.M. Neves, F.R.S. Lenza, W.L. Vasconcelos, Evaluation of the influence of microwaves in the structure of Silica gels, *Mater. Res.* 5 (2002) 447–451.
- [32] E. Yagmur, M. Ozmak, Z. Aktas, A novel method for production of activated carbon from waste tea by chemical activation with microwave energy, *Fuel* 87 (2008) 3278–3285.
- [33] Q.-S. Liu, T. Zheng, P. Wang, L. Guo, Preparation and characterization of activated carbon from bamboo by microwave-induced phosphoric acid activation, *Ind. Crop. Prod.* 31 (2010) 233–238.
- [34] H. Deng, L. Yang, G. Tao, J. Dai, Preparation and characterization of activated carbon from cotton stalk by microwave assisted chemical activation – application in methylene blue adsorption from aqueous solution, *J. Hazard. Mater.* 166 (2009) 1514–1521.
- [35] Y. Ji, T. Li, L. Zhu, X. Wang, Q. Lin, Preparation of activated carbons by microwave heating KOH activation, *Appl. Surf. Sci.* 254 (2007) 506–512.
- [36] M.R.E. Carmona, M.P. Silva, G.S.F. Leite, Biosorption of chromium using factorial experimental design, *Process Biochem.* 40 (2005) 779–788.
- [37] T.T. Allen, H. Xiong, Pareto charting using multifield freestyle text data applied to Toyota Camry user reviews, *Appl. Sto. Models Bus. Ind.* 28 (2012) 152–163.

**Capítulo Quatro:** *Removal of phenolic compounds from aqueous solutions using sludge-based activated carbons prepared by conventional heating and microwave-assisted pyrolysis*

# ***Capítulo Cinco***

# Removal of Phenolic Compounds from Aqueous Solutions Using Sludge-Based Activated Carbons Prepared by Conventional Heating and Microwave-Assisted Pyrolysis

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**Abstract** Sludge-derived activated carbons (ACs) were prepared by conventional heating and microwave pyrolysis. The ACs were characterized using several analytical and functional techniques and used for removal of six phenolic compounds from aqueous solutions. The adsorbents exhibited similar features and possessed hydrophobic surfaces. The ACs were assigned mesoporous materials, with specific surface areas of up to 641 and 540 m<sup>2</sup> g<sup>-1</sup> for CAC-500 and MAC-980, respectively. The preliminary results indicated that phenol removal onto the ACs increased in the order: m-cresol < phenol < o-

cresol < 2-chlorophenol < 2-nitrophenol < hydroquinone. Hydroquinone exhibited the highest adsorption capacity and was chosen to continue the remaining part of the experimental work—kinetic and isotherm studies. The adsorption kinetic and isotherm data were well described by the Avrami fractionary order and Redlich–Peterson models, respectively. The maximum amounts ( $Q_{\max}$ ) of hydroquinone adsorbed at 25 °C were too high, reaching 1218.3 and 1202.1 mg g<sup>-1</sup> for CAC-500 and MAC-980, respectively. The mechanism of adsorption was proposed in this work, and it was suggested that donor–acceptor complex and  $\pi$ – $\pi$  interactions play major roles in the adsorption process. The adsorbents were also tested on simulated effluents. The two ACs displayed good efficiency for the treatment of industrial simulated effluents.

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**Keywords** Sewage sludge · Microwave and conventional heating · Activated carbons · Phenolic compounds · Hydroquinone · Adsorption mechanism · Simulated effluents

## 1 Introduction

The origin of phenolic compounds in the environment can be traced to industrial activities and natural phenomena (Davi and Gnudi 1999). Phenolic compounds, as pollutants, are associated with petrochemical and petroleum refineries, coal, cooking, polymer product, dye synthesis, wood processing plants, pharmaceuticals, and pesticides (Babich and Davis 1981; Davi and Gnudi 1999; Wang et al.

2014). Organic compounds, such as phenol groups, have caused increasing environmental concerns in recent years because they are a group of ubiquitous, persistent, and biologically active compounds with pronounced toxicities (Babich and Davis 1981; Wang et al. 2014; Ailijiang et al. 2016). Production and use of these products results in wastewaters containing phenolic groups that must be treated before being discharged into the environment (Qu et al. 2010; Torres et al. 2016; Ailijiang et al. 2016).

There are several methods for the removal of phenolic compounds from effluents, including: photocatalytic degradation (Sin et al. 2015; Wang et al. 2015), biological processes (Duana et al. 2016; Paisio et al. 2016), electrochemical oxidation (Muppalla et al. 2015), nanofiltration (Rueda-Márquez et al. 2015), coagulation (Wang et al. 2016), and the adsorption process (Zhang et al. 2015b). All of these techniques have advantages and disadvantages. Because of the very high cost and disposal problems, many of these techniques for treating phenolic compounds from wastewater are not widely used at a large scale (Hemmati et al. 2015). However, among these methods, adsorption has been proven to be one of the methods widely used for purification and separation technology.

Activated carbons are among the most effective adsorbents used for adsorption processes. Activated carbons possess high surface area per unit mass and exhibit high adsorption capacities for several adsorbates, including phenolic compounds. Activated carbon is generally produced from natural and/or waste materials by pyrolysis at elevated temperatures (Dos Reis et al. 2016c; Georgina et al. 2016). There are two kinds of pyrolysis, namely, conventional and microwave heating (Dos Reis et al. 2016c). The main difference between conventional pyrolysis and the microwave-assisted method is the way the heat is generated (Lina et al. 2012; Georgina et al. 2016). In conventional pyrolysis the heat source is located outside of the sample, and the heat is transferred to the particles by convection, conduction, and radiation mechanisms (Lina et al. 2012; Georgina et al. 2016). For the microwave method, the energy is directly supplied to the sample. Energy transfer is not by conduction or convection as in conventional heating, but microwave energy is readily transformed into heat inside of the particles by dipole rotation and ionic

conduction (Lina et al. 2012; Georgina et al. 2016; Dos Reis et al. 2016c).

Microwave heating has the advantages of a rapid preparation period, uniform temperature distribution, increased yield, and energy savings over the conventional thermal method which might reduce the cost of activated carbon (AC) preparation (Lina et al. 2012; Georgina et al. 2016). However, current literature is not clear about which method produces ACs with better textural properties and higher specific surface areas. Different work comes to different conclusions, but the literature shows that conventional pyrolysis has shown to be a little more efficient on that issue.

In order to verify the effect of both pyrolysis methods on the properties of activated carbons as well as their phenolic compound removal efficiency, two preparation methods were developed in this work for the preparation of activated carbon from sewage sludge.

Sewage sludge is a by-product of wastewater treatment systems and has high levels of organic matter. The sewage sludge generated from human activities has increased significantly in recent years due to industrialization, urbanization, and the necessity of compliance with the legal regulations of wastewater treatments. Several technological solutions have been explored for final disposal of sludge, among which stand out composting, incineration, and application in agriculture (Dos Reis et al. 2016a, b). However, in this work, the proposal was to use the sewage sludge for activated carbon production.

In the present work, two activated carbon activations were produced by conventional heating and microwave pyrolysis, and they were tested for the removal of six phenolic compounds from aqueous solutions. The main objectives were: (1) to determine the ability of conventional and microwave ACs to adsorb phenolic compounds from aqueous solutions; (2) to compare the efficiencies of both ACs for the removal of phenolic compounds; and (3) to study the effect of different operating parameters, such as the initial concentration of sorbate being adsorbed, temperature, and the initial pH value, on the adsorption processes. The activated carbons used in this work were analyzed using several analytical techniques to explore the structure, nature, and surfaces of the ACs.

## 2 Materials and Methods

### 2.1 Preparation of Adsorbents

The sewage sludge (SS) used in this work was sourced from a municipal wastewater treatment plant in Porto Alegre, RS, Brazil. It is an aerobic sludge from an activated sludge plant. The sludge was collected and dried at 105 °C for 24 h until constant weight loss. The sludge was subsequently crushed and sieved to particle size below 300 µm.

The sludge-based adsorbents were prepared using two different heating methods: conventional pyrolysis in a vertical electrical furnace and microwave-assisted heating. The sludge-based adsorbents were prepared using the procedure described by Dos Reis et al. (2016a), where a full factorial design for the preparation of ACs using both types of pyrolysis was reported. In this work, the best ACs, based on the highest specific surface area of each type of pyrolysis, were chosen, as earlier reported (Dos Reis et al. 2016a).

The pyrolyzed ACs investigated in this study are named as CAC-500 and MAC-980. CAC-500 means that the conventional activated carbon was pyrolyzed using a conventional furnace at 500 °C for 1 h under inert atmosphere, and MAC-980 was pyrolyzed by microwave-assisted heating process at 980 W for 12 min under inert atmosphere. An overview of the preparation of the ACs is presented in Fig. 1.

### 2.2 Characterization of Adsorbents

Nitrogen adsorption isotherms were recorded on a commercial system (Belsorp-Mini, Bel Japan Inc.) at -196 °C after drying the samples for 3 h at 120 °C under reduced pressure (<2 mbar). Specific surface areas of the ACs were determined using the Brunauer, Emmett, and Teller method.

The CHN elemental analyses of the adsorbent materials were performed using a CHN Perkin Elmer M CHNS/O Analyzer, model 2400.

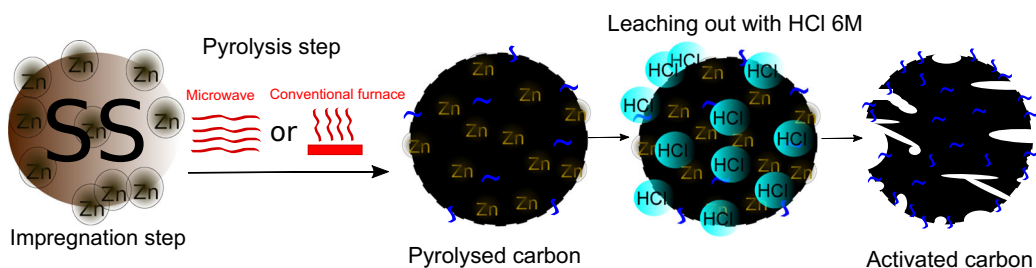
Surface morphologies and basic elements were observed with scanning electron microscopy (SEM) equipped with energy-dispersive X-ray spectroscopy (EDS; TESCAN 3, Sweden). Transmission electron microscopy (TEM) images were performed on a JEOL JEM-1200 ExII electron microscope.

The functional groups of the adsorbents were determined using Fourier transform infrared spectroscopy (FTIR; Bruker Spectrometer, alpha model) with the ATR (attenuated total reflectance) accessory. The spectrum was recorded with 64 cumulative scans over the range of 4000–400 cm<sup>-1</sup> with a resolution of 4 cm<sup>-1</sup>.

The zeta potential measurements of the adsorbents were determined by suspending 10.0 mg of each sample of ACs (CAC-500 and MAC-980) in 50 mL of 0.05 N NaCl to ensure constant ionic strength, and the pH was adjusted from 2 to 9 using HCl or NaOH solution. The suspensions were constantly agitated for 24 h, after which the zeta potential measurements were done on a ZetaPlus Zeta Potential Analyzer (Brookhaven Instruments Corporation).

Thermogravimetric analyses (TGA) of the samples were obtained on a TA Instruments model SDT Q600 (New Castle, USA) with a heating rate of 20 °C min<sup>-1</sup> at 100 mL min<sup>-1</sup> of synthetic air flow, wherein temperature was varied from 20 to 1000 °C (acquisition time of 1 point per 5 s) using 10.00–15.00 mg of solid.

For vapor adsorption experiments, the powdered samples were dried in 5-mL glasses at 70 °C for 24 h. The samples were cooled at room temperature in a desiccator before determining their accurate weight (approx. 0.5 g). Storage in an atmosphere of saturated solvent vapor was performed in Erlenmeyer flasks plugged with a ground glass joint using 60 mL of solvent (water and n-heptane). The powdered samples,



**Fig. 1** Scheme of preparation of AC materials

inside glasses, were placed in such a way that they were not in contact with the wall of the Erlenmeyer. The samples were removed from the Erlenmeyer flask after 24 h. The weight gain during storage was used to determine the maximal adsorption of the vapor.

### 2.3 Chemicals, Reagents, and Solutions

Deionized water was used to prepare all solutions. The phenolic compounds were supplied by Sigma-Aldrich and used without purification. Table 1 shows the properties of the phenolic compounds used in this study.

### 2.4 Batch Adsorption Studies

Aliquots of 20.00 mL of 100.00–1000.0 mg L<sup>-1</sup> concentrations of the phenolic compounds were added to 50.0-mL flat Falcon tubes containing 30 mg of adsorbents. The flasks were capped and placed horizontally in a thermostatic shaker model TE-240, and the system was agitated for time between 1 and 360 min. Afterwards, the samples were centrifuged to separate the adsorbents from the aqueous solutions using a Fanem

**Table 1** Chemical composition of the simulated industrial effluent

Phenolic compounds	Concentration (mg L <sup>-1</sup> )
Phenol	50.0
m-Cresol	10.0
o-Cresol	5.00
2-Chlorophenol	5.00
2-Nitrophenol	5.00
4-Nitrophenol	5.00
Bisphenol	5.00
Hydroquinone	5.00
Resorcinol	5.00
2-Naphtol	5.00
Humic acid	10.0
Potassium phosphate	20.0
Sodium carbonate	20.0
Sodium chloride	20.0
Potassium nitrate	20.0
Sodium sulfate	21.0
pH	7.0

centrifuge, and aliquots of 1–5 mL of the supernatants were properly diluted to 20.0–100.0 mL in calibrated flasks using deionized water.

The residual solutions of the phenolic compounds after adsorption were measured using a UV–Visible spectrophotometer (T90+ UV–Vis spectrophotometer, PG Instruments, London, UK) for their respective wavelengths (see Table 1).

The amounts of adsorbates adsorbed by both ACs and their percentages of removal were calculated using Eqs. 1 and 2, respectively.

$$q = \frac{C_0 - C_f}{m} \times V \quad (1)$$

$$\%Removal = 100 \times \frac{(C_0 - C_f)}{C_0} \quad (2)$$

where  $q$  is the amount of phenolic compound adsorbed by the adsorbent (in milligrams per gram);  $C_0$  is the initial phenolic compound concentration in contact with the adsorbent (in milligrams per liter);  $C_f$  is the phenolic compound concentration (in milligrams per liter) after the batch adsorption experiment;  $V$  is the volume of phenolic compound solution (in liters) in contact with the adsorbent; and  $m$  is the adsorbent mass (in grams).

### 2.5 Quality Assurance and Statistical Evaluation of Models

All the experiments were carried out three times to ensure reproducibility, reliability, and accuracy of data. The relative standard deviations of all measurements were <5%. Blanks were run in parallel and corrected if necessary (Lima et al. 2002). The solutions of the phenolic compounds were stored in glass bottles, which were previously cleaned by immersion in 1.4 mol L<sup>-1</sup> HNO<sub>3</sub> for 24 h, rinsed with deionized water, dried, and stored in clean closets (Lima et al. 1999).

Standard phenolic compound solutions (between 5.00 and 50.0 mg L<sup>-1</sup>), in parallel with a blank solution, were used for linear analytical calibration (Lima et al. 2003). The calibration curve was performed on the UV–Win software of the T90+ PG Instruments spectrophotometer. All of the analytical measurements were repeated three times, and the precisions of the standards were better than 3% ( $n = 3$ ). The detection limit of phenolic compounds was 0.14 mg L<sup>-1</sup>, with a signal/noise ratio of 3 (Lima et al. 1998). The standard phenolic

compound solution (50.0 mg L<sup>-1</sup>) was used as a quality control after every five measurements to ensure accuracy of the phenolic solutions (Lima et al. 2003).

Nonlinear methods with successive interactions calculated by the Levenberg–Marquardt method were used to fit the kinetic and equilibrium data. Similarly, interactions were evaluated using the Simplex method, which were based on the nonlinear fitting facilities of the Microcal Origin 9.0 software. A determination coefficient ( $R^2$ ), an adjusted determination coefficient ( $R^2_{adj}$ ), and the  $F_{error}$  were utilized to determine the accuracy of each fit (Calvete et al. 2010; Prola et al. 2013a, b).

Residual standard deviation is a measure of the difference between the theoretical and experimental amounts of phenolic compounds removed from aqueous solutions. Equations 3, 4, and 5 depict the respective  $R^2$ ,  $R^2_{adj}$ , and  $F_{error}$

$$R^2 = \left( \frac{\sum_i^n (q_{i,exp} - \bar{q}_{i,exp})^2 - \sum_i^n (q_{i,exp} - q_{i,model})^2}{\sum_i^n (q_{i,exp} - \bar{q}_{i,exp})^2} \right) \quad (3)$$

$$R^2_{adj} = 1 - (1 - R^2) \times \left( \frac{n-1}{n-p-1} \right) \quad (4)$$

$$SD = \sqrt{\left( \frac{1}{n-p} \right) \times \sum_i^n (q_{i,exp} - q_{i,model})^2} \quad (5)$$

where  $q_{i,model}$  is the individual theoretical  $q$  value predicted by the model;  $q_{i,exp}$  is the individual experimental  $q$  value;  $\bar{q}_{exp}$  is the average of experimental  $q$  values;  $n$  is the number of experiments; and  $p$  is the number of parameters in the model (Ribas et al. 2014; Calvete et al. 2010; Prola et al. 2013a, b).

### 2.6 Kinetic Models

The adsorption process is always supported by kinetic parameters. Knowing the adsorption kinetics, it is possible to design and conduct the adsorption process more effectively.

Pseudo-first-order, pseudo-second-order, Avrami fractional order, and intraparticle diffusion models were used to analyze the kinetic data. The mathematical equations for the pseudo-first-order, pseudo-second-order, Avrami

fractional order, and intraparticle diffusion models are shown in Eqs. 6, 7, 8, and (9), respectively.

$$q_t = q_e \times [1 - \exp(-k_1 \times t)] \quad (6)$$

$$q_t = q_e \frac{q_e}{[k_2(q_e) \times t + 1]} \quad (7)$$

$$q_t = q_e \{1 - \exp[-(k_{AV} \times t)]^{n_{AV}}\} \quad (8)$$

$$q_t = k_{id} \times \sqrt{t} + C \quad (9)$$

For more information about these models, please see [Supplementary Material](#) (Ho 2006; Liu and Liu 2008; Lopes et al. 2003).

### 2.7 Equilibrium Models

The Langmuir, Freundlich, and Redlich–Peterson models are represented in Eqs. 10, 11, and 12, respectively. These models were used to analyze the equilibrium data.

$$q_e = \frac{Q_{max} \times K_L \times C_e}{1 + K_L \times C_e} \quad (10)$$

$$q_e = K_F \times C_e^{1/n_F} \quad (11)$$

$$q_e = \frac{K_{RP} \times C_e}{1 + a_{RP} \times C_e^g} \quad (12)$$

Details of these models are presented in [Supplementary Material](#) (Freundlich 1906; Langmuir 1918; Redlich and Peterson 1959).

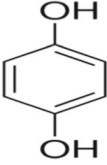
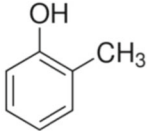
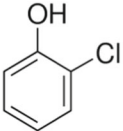
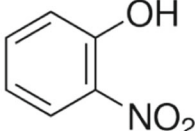
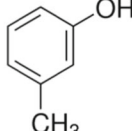
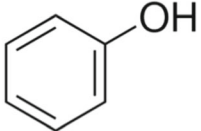
### 2.8 Simulated Effluents

The simulated effluents were prepared by mixing ten phenolic compounds, humic acid, and some inorganic salts that are associated with industrial effluents. The effluents were prepared using deionized water and the pH was adjusted to 7.0.

The concentrations of organic compounds and auxiliary chemicals are given in Table 2. The aim of using simulated effluents was to test the performance of adsorbents toward treatment of effluents, which are similar to real wastewater.



**Table 2** Chemical structures and characteristics of the adsorbates used in this study

Hydroquinone	o-Cresol	2-chlorophenol	2-Nitrophenol	m-Cresol	Phenol
					
CAS 123-21-9	CAS 95-48-7	CAS 95-57-8	CAS 88-75-5	CAS 108-39-4	CAS 108-95-2
C <sub>6</sub> H <sub>4</sub> -1,4(OH) <sub>2</sub>	CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> OH	C <sub>6</sub> H <sub>5</sub> ClO	O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> OH	CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> OH	C <sub>6</sub> H <sub>5</sub> OH
110.11 g mol <sup>-1</sup>	326.43 g mol <sup>-1</sup>	128.56 g mol <sup>-1</sup>	139.11 g mol <sup>-1</sup>	139.11 g mol <sup>-1</sup>	94.11 g mol <sup>-1</sup>
LogK <sub>ow</sub> = 0.59	LogK <sub>ow</sub> = 1.95	LogK <sub>ow</sub> = 2.15	LogK <sub>ow</sub> = 1.79	LogK <sub>ow</sub> = 1.96	LogK <sub>ow</sub> = 1.46
pKa = 9.98	pKa = 10.37	pKa = 7.97	pKa = 6.63	pKa = 10.13	pKa = 10.02
λ <sub>max</sub> = 288 nm	λ <sub>max</sub> = 270 nm	λ <sub>max</sub> = 273 nm	λ <sub>max</sub> = 278 nm	λ <sub>max</sub> = 271 nm	λ <sub>max</sub> = 269 nm

### 3 Results and Discussions

#### 3.1 Elemental, Thermogravimetric, and Vapor Analyses

The CHN elemental analysis was used to determine the compositions of carbon, hydrogen, and nitrogen in the samples. The composition of oxygen was determined by subtracting the sum of the percentages of carbon, hydrogen, nitrogen, and ashes from 100% (total) (Leng et al. 2015). Elemental analysis and ash contents of SS (the precursor), CAC-500, and MAC-980 are shown in Table 3.

The CHN analysis clearly shows a slight difference in the carbon contents in the adsorbents made from conventional and microwave-assisted pyrolysis. This suggests that the two types of pyrolysis are acceptable for the production of activated carbons. The CHN analysis results show that the oxygen content for sewage sludge decreased from 9.79 to 6.27% and 5.33% for CAC-500 and MAC-980, respectively, whereas the carbon content remained almost constant. The carbon content indicates that the aromatic structure becomes dominant after degradation in the presence of zinc chloride. The loss of

oxygen content (in addition to other volatile compounds) suggests that a large number of functional groups were lost during pyrolysis (Chen et al. 2015).

The results of the TGA of the two samples pyrolyzed by conventional and microwave-assisted heating are illustrated in Fig. 2. The profiles of TGA show a one-

**Table 3** Element analysis of SS and ACs and uptake values of *n*-heptane/water adsorption of the ACs

	Ash <sup>a</sup>	Elemental composition <sup>b</sup> (%)			
		C	H	N	O <sup>c</sup>
SS	46.24	32.68	5.12	6.17	9.79
CAC-500	52.36	36.40	1.73	3.24	6.27
MAC-980	57.25	32.02	2.10	2.70	5.93
Hydrophobicity features	<i>n</i> -heptane/water adsorption				
CAC-500		1.87			
MAC-980		1.36			

<sup>a</sup> On a dry basis

<sup>b</sup> On a dry and ash-free basis

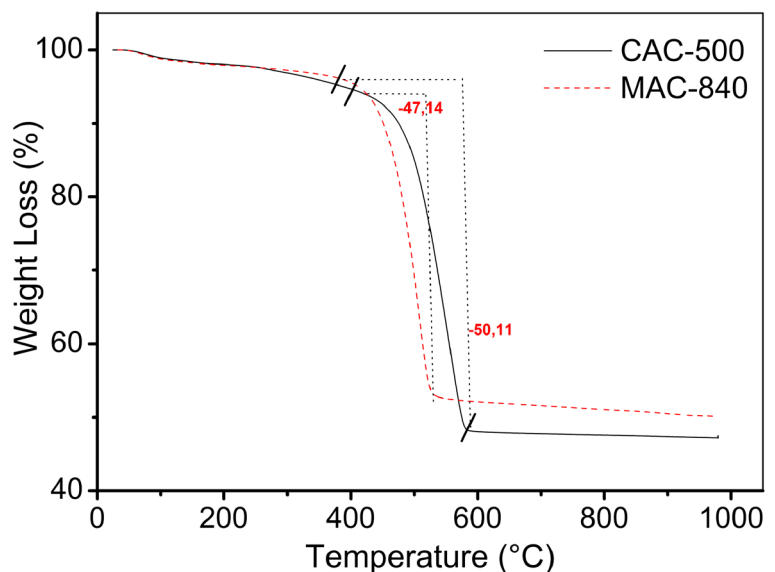
<sup>c</sup> By difference, O = 100% - (C + H + N + Ash)

stage weight loss in the thermal behavior of both samples. Below 400 °C, the weight loss is negligible for both samples. However, the samples have some differences in the heating process. For CAC-500, the total weight loss is 51.71% at 580 °C, but this value is 47.14% at 520 °C for MAC-980.

Looking through the TGA and CHN data, it is seen that the final weight loss is in line with the theoretical calculation value according to the CHN analysis. Figure 2 and Table 3 reveal that the weight loss is higher for the samples with higher carbon content; for instance, CAC-500 presents the highest carbon content and weight loss, followed by MAC-980.

The surface polarity of adsorbents, which are solutes that dissolve in solvents, is important for interactions with adsorbates (Prenzel et al. 2015). Solvent vapors of different polarities were used to characterize the surface of the adsorbents prepared in this study, as shown in Table 3 for both ACs. Table 3 shows the ratio of mass of n-heptane to water taken up by dried samples of the activated carbons. For both ACs, the uptakes of n-heptane (showing mainly dispersive interaction) were higher than the uptake of water (which is mainly polar); this demonstrates that the activated carbons have more hydrophobic surfaces. However, CAC-500 was 27.27% more hydrophobic than MAC-980 (see Table 2). This data totally agrees with the CHN and TGA analyses, which showed that CAC-500 has more carbon content than MAC-980, but nearly the same oxygen content. This is the reason why CAC-500 is more hydrophobic than MAC-980.

**Fig. 2** Thermogravimetric curves of CAC-500 and MAC-980 samples



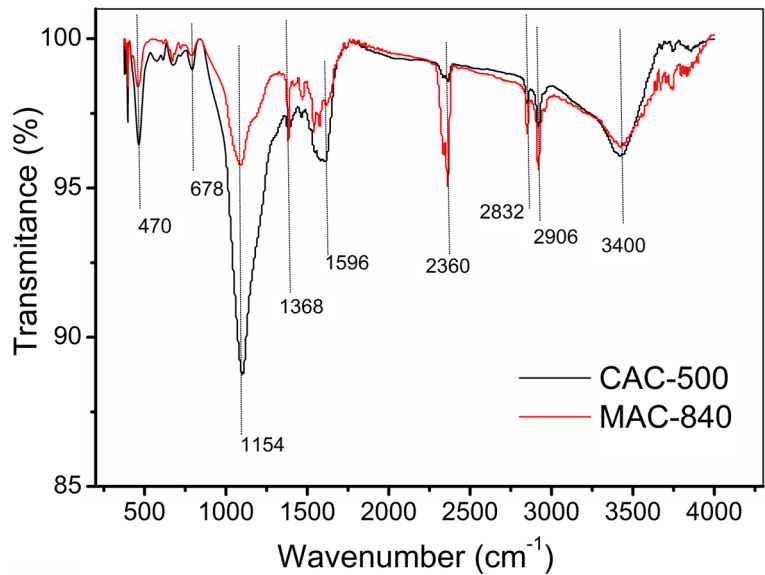
### 3.2 Surface Chemical Properties and Morphology

FTIR analysis was performed to obtain the chemical functional groups on the surface of the ACs; this analysis provides valuable information on the chemical compositions of the materials. The FTIR spectra of the CAC-500 and MAC-980 activated carbons are presented in Fig. 3. The spectra of the two samples are similar. The broad band at about 3450  $\text{cm}^{-1}$  is assigned to the O–H stretching vibration of the hydroxyl functional group, including hydrogen bonding. The intense band at about 2906  $\text{cm}^{-1}$  is attributed to the C–H stretching vibration. A series of complex bands are observed in the range of 1368–1596  $\text{cm}^{-1}$  for both samples, which could be attributed to functional groups such as lactone, carboxyl, aromatics, and nitrate groups (Ribas et al. 2014; Calvete et al. 2010; Prola et al. 2013b; Saucier et al. 2015).

The small band at 1380  $\text{cm}^{-1}$  could be assigned to C–H bending vibration (Chen et al. 2015; Dos Reis et al. 2016c). The strong absorption at 1154  $\text{cm}^{-1}$  could be assigned to the C–O stretching of alcohol and phenol and the Si–O stretching of silicates. The small FTIR band at 678  $\text{cm}^{-1}$  is assigned to aromatic out-of-plane C–H bending, while the band 677  $\text{cm}^{-1}$  is assigned to aromatic ring bending (Ribas et al. 2014; Calvete et al. 2010; Dos Reis et al. 2016c; Prola et al. 2013b; Saucier et al. 2015).

Therefore, it could be inferred that the heating process did not influence the surface groups of ACs. The major functional groups found in the carbon adsorbents include O–H (alcohols and phenols), aromatic rings, CO

**Fig. 3** FTIR analysis of CAC-500 and MAC-980 samples



(phenols and alcohols), Si–O (silicates), and CH (aromatics and aliphatics).

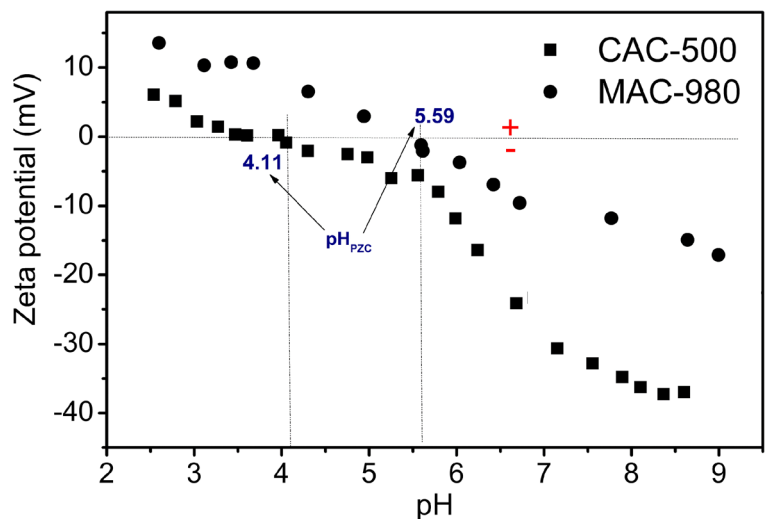
Figure 4 presents the zeta potentials of the CAC-500 and MAC-980 samples. The samples have positively charged surfaces at  $\text{pH} < 6$ . It is seen that the zeta potential of MAC-980 is lower than that of CAC-500. The point of zero charges ( $\text{pH}_{\text{PZC}}$ ) for CAC-500 and MAC-980 are 4.11 and 5.59, respectively (see Fig. 4). For pH values lower than  $\text{pH}_{\text{PZC}}$ , the adsorbent presents a positive surface charge (Thue et al. 2016).

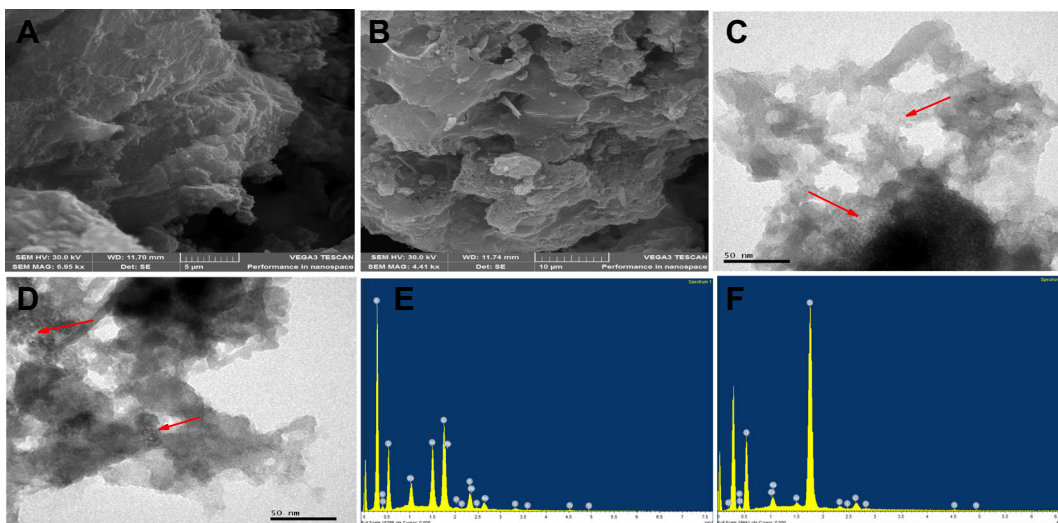
The zeta potentials of both samples were approx. 10 initially due to the presence of some ionic groups on the surface of the carbons, and then the potential value

decreased as the pH increased further (Zhang et al. 2015a). CAC-500 shows a higher negative zeta potential than MAC-980 (see Fig. 4). These data suggest that CAC-500 has better dispersibility in aqueous media; this observation might influence the performance of CAC-500 for the adsorption process (Zhang et al. 2015a).

SEM and TEM are among the most versatile techniques available for the examination and analysis of the microstructure morphology characterization, providing detailed surface information such as the shape and size of the particles. Figure 5a, b shows the SEM images of samples CAC-500 and MAC-980, respectively. For both samples, the roughness of their surface carbons is visible (see Fig. 5).

**Fig. 4** Zeta potential curves of CAC-500 and MAC-980 samples





**Fig. 5** SEM images of CAC-500 (a) and MAC-980 (b); TEM images of CAC-500 (c) and MAC-980 (d); and EDS spectra of CAC-500 (e) MAC-980 (f)

Also, the samples exhibit an almost identical morphology that is characterized by irregularly shaped pores with different size cavities. Figure 5a, b reveals that the cavities and the irregularities on the surfaces might be formed during the carbonization and leaching steps, which led to a relatively well-developed pore structure and a roughened surface. A comparison of both samples indicates that both methods of heating can produce activated carbons with well-developed porosity.

Further details of the CAC-500 and MAC-980 carbons are shown in the TEM images. Figure 5c, d shows that the inner structures of the carbon samples are viewed by the TEM. It is shown that the obtained ACs comprise a certain extent of agglomeration and irregular shapes. The TEM images identified a considerable porosity within the surfaces of the CAC-500 and MAC-980 samples comprising randomly oriented pores in different porous size scales (around 2–4 nm; see red arrows).

The EDS of samples CAC-500 and MAC-980 are seen in Fig. 5e, f, respectively. The EDS did not show differences in the content of the samples; it showed very heterogenic basic element contents with the presence of Si, Ti, O, K, Al, Na, N, Cl, and Zn for both carbons.

### 3.3 Surface Areas and Porosity

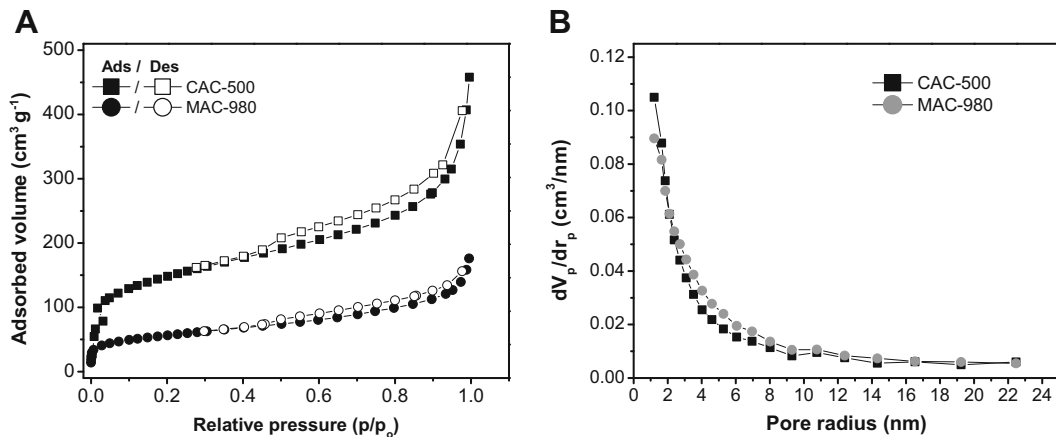
Among the main features of the adsorbents, the textural properties such as surface area and porosity are the most influential (Ozdemir et al. 2015; Thommes et al. 2015).

Good textural properties with high surface area are crucial for ACs because they reflect the adsorption capacity to some extent (Ozdemir et al. 2015). The textural characterization of an adsorbent (surface area, pore size, and total pore volume) can be determined by  $N_2$  adsorption/desorption isotherms.

The nitrogen adsorption–desorption isotherms of the carbons are shown in Fig. 6a. Both activated carbons exhibit type IV isotherms, which is characteristic of mesoporous materials with hysteresis loops (blank symbol), which is due to capillary condensation inside of the mesopores (Balbuenat and Gubbins 1993; Shang et al. 2015; Thommes et al. 2015). This type of loop is usually attributed to slit-shaped pores (Balbuenat and Gubbins 1993; Shang et al. 2015; Thommes et al. 2015). However, both activated carbons also presented a small microporous section, which can easily be seen in Fig. 6a, containing a vertical increase of adsorbed volume at low relative pressure ( $p/p_0 < 0.025$ ).

Figure 6b shows the Barrett–Joyner–Halenda (BJH) pore size distributions of the corresponding samples derived from the desorption data of their isotherms. Both samples showed similar pore size distributions with pores in the mesopore (2–3 nm) size range (see Fig. 6b).

According to the amount of adsorbed  $N_2$  volume, CAC-500 presented a higher value ( $458 \text{ cm}^3 \text{ g}^{-1}$ ) compared to MAC-980 ( $187 \text{ cm}^3 \text{ g}^{-1}$ ). It is clearly seen that samples with higher values of adsorbed  $N_2$  volume presented higher specific surface area.



**Fig. 6** Nitrogen adsorption–desorption isotherms (a) and BJH pore size distributions (b) of CAC-500 and MAC-980

Table 4 presents the data of the specific surface areas, mesopore areas, micropore areas, and total pore volume analyses. According to Table 4, it is seen that the pyrolysis of the sewage sludge without  $\text{ZnCl}_2$  impregnation (AC) resulted in very low surface area, an area of  $21.64 \text{ m}^2 \text{ g}^{-1}$ , as well as low micropore, mesopore, and total pore volume of  $15.607$ ,  $6.033 \text{ m}^2 \text{ g}^{-1}$ , and  $0.09687 \text{ m}^3 \text{ g}^{-1}$ , respectively. However, for sample ACZn, in which the sludge sample (SS) was blended with  $\text{ZnCl}_2$  and carbonized but not refluxed with  $6 \text{ M HCl}$ , it is noted that the surface area ( $1.14 \text{ m}^2 \text{ g}^{-1}$ ) is lower than those of the AC samples (see Table 4)—highlighting that the reflux step is in fact an important step for increasing the surface area; the reflux step is responsible for leaching the free zinc chloride from the carbonaceous material. The leaching process has great influence on the porosities of ACs; the specific surface areas of CAC-500 and MAC-980 are  $671.85$  and  $544.22 \text{ m}^2 \text{ g}^{-1}$ , respectively. The reflux step under acidic condition ( $6 \text{ M HCl}$ ) promoted an enormous increase in the mesopore areas of the samples, from  $0.2588 \text{ m}^2 \text{ g}^{-1}$  (ACZn) to  $289.82 \text{ m}^2 \text{ g}^{-1}$  (CAC-500) and  $262.55 \text{ m}^2 \text{ g}^{-1}$  (MAC-980). The same trend was observed for the micropore areas.

Activation of the adsorbent with  $\text{ZnCl}_2$  and the acid reflux step are effective in increasing the porosity of the ACs. A possible explanation for this could be as follows: in the carbonization process, usage of  $\text{ZnCl}_2$  promotes the extraction of water molecules from structures of the precursors at high temperatures, and  $\text{ZnCl}_2$  melts at  $>300 \text{ }^\circ\text{C}$  and diffuses to occupy the cavities; the acid reflux used during the final step then removes the  $\text{ZnCl}_2$  from the cavities (Shang et al. 2015). The entire process enhances good porosity development (Shang et al. 2015).

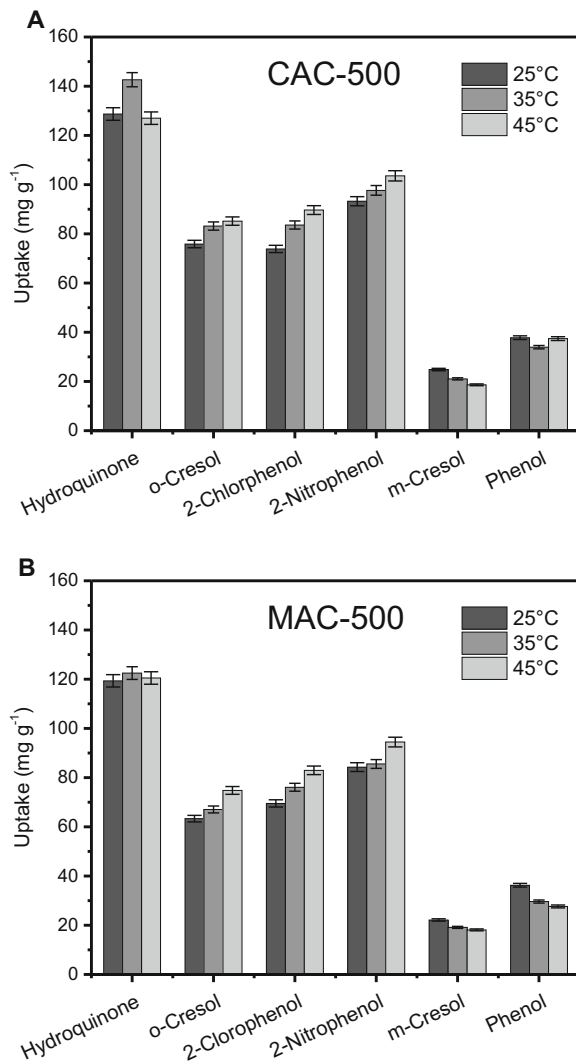
Regarding the pyrolysis type used for the sewage sludge studied, it is seen from Table 4 that conventional pyrolysis was more effective than the microwave heating process—due to the larger surface area, micropore and mesopore areas, and pore volume of CAC-500.

### 3.4 Preliminary Results of the Adsorption of Phenolic Compounds

Preliminary adsorption tests, using ACs (CAC-500 and MAC-980) for the removal of different phenolic compounds as adsorbates, were carried out and the results are summarized in Fig. 7a, b. Six phenolic compounds were tested (see Table 2) for adsorption at three different

**Table 4** Textural properties of AC, ACZn, CAC-500, and MAC-980

Parameters	AC	ACZn	CAC-500	MAC-980
Specific surface area ( $\text{m}^2 \text{ g}^{-1}$ )	21.64	1.124	671.85	554.22
BJH mesopore area ( $\text{m}^2 \text{ g}^{-1}$ )	6.033	0.2588	289.82	262.55
t-Plot micropore area ( $\text{m}^2 \text{ g}^{-1}$ )	15.607	0.8652	382.03	291.67
Total pore volume ( $\text{cm}^3 \text{ g}^{-1}$ )	0.09687	0.000462	0.6654	0.5921



**Fig. 7**  $Q_{\max}$  of the phenolic compounds for CAC-500 (a) and MAC-980 (b) at different temperatures (conditions: initial concentration, 200 mg L<sup>-1</sup>; adsorbent mass, 30 mg; contact time, 120 min; and temperatures of 25, 35, and 45 °C)

temperatures (see Fig. 7a, b). As seen in these figures, CAC-500 shows higher adsorption capacity than MAC-980 for all adsorbates, with little differences in adsorption capacities (see Fig. 7). This observation signifies that both samples were successfully employed for the adsorption of phenolic compounds. For both samples, the adsorption capacities and relative affinities of the phenols toward the surfaces of the adsorbents decrease in this order: hydroquinone > 2-nitrophenol > 2-chlorophenol > o-cresol > phenol > m-cresol.

The  $Q_e^{200}$  values (adsorptive amounts at an initial concentration of 200 mg L<sup>-1</sup>) for hydroquinone are

117.01 and 108.49 mg g<sup>-1</sup> for CAC-500 and MAC-980, respectively. Comparing the  $Q_e^{200}$  values of hydroquinone with those of o-cresol for CAC-500 and MAC-980, the values are higher for o-cresol; the values are 84.77 (CAC-500) and 76.61 mg g<sup>-1</sup> (MAC-980) and 27.5 and 29.39%, respectively. The  $Q_e^{200}$  values of CAC-500 and MAC-980 for o-cresol, 2-chlorophenol, phenol, and m-cresol are 68.14 and 63.58, 67.14 and 57.58, 34.36 and 32.96, and 22.58 and 20.13 mg g<sup>-1</sup>, respectively.

The sorption characteristics of all phenolic compounds and the differences between the  $Q_e^{200}$  values of the ACs are influenced by their physicochemical properties, such as water solubility and octanol–water partition coefficients (Arellano-Cárdenas et al. 2005; Dursun and Kalayci 2005). However, the order of affinity of phenolic compounds toward the surface of both carbons does not follow a logical pattern with respect to the properties of their compounds. For example, the acid dissociation constant ( $pK_a$ ) values do not correspondingly follow a logical pattern with the affinity of the adsorbates for the adsorbents. The  $pK_a$  values for hydroquinone, 2-nitrocresol, 2-chlorophenol, o-cresol, phenol, and m-cresol are 9.98, 6.63, 7.97, 10.37, 10.02, and 10.13, respectively. The same trend is observed for the hydrophilic–lipophilic balance (HLB), which measures the degree of the hydrophobicity or lipophilicity of a substance; the HLB values for hydroquinone, 2-nitrocresol, 2-chlorophenol, o-cresol, phenol, and m-cresol are 7.95, 8.15, 6.05, 5.57, 8.02, and 5.57, respectively. Therefore, the affinity for each phenolic compound cannot be successfully linked with their physicochemical properties such as  $pK_a$  and HLB—this suggests that several factors might play key roles in the interactions of the phenolic compounds with AC surfaces.

The effect of temperature on the removal of the phenolic compounds by CAC-500 and MAC-980 is also shown in Fig. 7a, b. For all phenolic compounds, the temperature did not cause an enormous influence on the  $Q_e^{200}$  values. For hydroquinone, the  $Q_e^{200}$  value at 25 °C of 117.02 mg g<sup>-1</sup> increased to 129.18 at 35 °C and decreased to 116.88 at 45 °C. 2-Nitrocresol, 2-chlorophenol, and o-cresol present the same trend; the  $Q_e^{200}$  values slightly increased when the temperature was increased from 25 to 45 °C.

On the other hand, for phenol and m-cresol, the  $Q_e^{200}$  values slightly decreased when the temperature was increased from 25 to 45 °C. When the adsorption capacity decreases as the temperature increases, the system is considered to be exothermic, but endothermic when the

adsorption capacity increases as the temperature increases. Therefore, the adsorption process for phenol and m-cresol is exothermic, but for hydroquinone, 2-nitrocresol, 2-chlorophenol, and o-cresol, the process is endothermic.

As the temperature does not highly influence the  $Q_e^{200}$  values, an increase in temperature from 25 °C can result in a very high operational cost of the process. Therefore, 25 °C was selected as an optimum temperature for the subsequent experiments in this work.

These preliminary adsorption results show that both materials have higher sorption capacities for phenolic compounds at all temperatures studied, but the best value of removal was attained by hydroquinone. Therefore, hydroquinone was chosen to continue the remaining part of the experimental work (kinetic and isotherm studies).

### 3.5 Adsorption Kinetics

In order to describe the rate of adsorbate taken up at the solid–liquid interface, pseudo-first-order, pseudo-second-order, Avrami fractionary order, and intraparticle diffusion equations were chosen. The adsorption kinetic curves of hydroquinone onto CAC-500 and MAC-980 are summarized in Supplementary Fig. 1, while the parameters are presented in Table 5.

As seen from Supplementary Fig. 1A (CAC-500), a fast adsorption was observed during the first 5 min, adsorbing 147.34 mg g<sup>-1</sup>, and 314.23 mg g<sup>-1</sup> at 90 min when equilibrium was reached. The same adsorption rate pattern was observed for MAC-980; at 5 min, the uptake value was 118.31 mg g<sup>-1</sup>, and at 90 min, equilibrium was achieved with an uptake value of 302.82 mg g<sup>-1</sup>.

As seen from Table 5, going by the  $R^2_{adj}$  and SD values, the kinetic data were best fitted by the Avrami fractionary kinetic model, which shows the highest  $R^2_{adj}$  values and the lowest SD values. The lowest value of error function (SD = 6.612 for CAC-500 and SD = 10.29 for MAC-980) means that the  $q$  predicted by the kinetic model (320.9 mg g<sup>-1</sup>) is closer to the  $q$  measured experimentally (319.55 mg g<sup>-1</sup> for CAC-500 and 308.93 mg g<sup>-1</sup> for MAC-980). This means a small difference between the theoretical  $q$  and experimental  $q$  values; therefore, the Avrami fractionary order model was the best to describe the hydroquinone adsorption onto CAC-500 and MAC-980.

To increase understanding of the adsorption process, an intraparticle diffusion equation was also used to fit the data.

**Table 5** Kinetic parameters of hydroquinone adsorption onto CAC-500 and MAC-980

	CAC-500	MAC-980
Pseudo-first order		
$k_1$ (min <sup>-1</sup> )	0.08835	0.06429
$q_e$ (mg g <sup>-1</sup> )	311.7	303.5
$R^2_{adj}$	0.9738	0.9760
SD (mg g <sup>-1</sup> )	15.95	15.41
Pseudo-second order		
$k_2$ (g mg <sup>-1</sup> min <sup>-1</sup> )	0.0004212	0.0002969
$q_e$ (mg g <sup>-1</sup> )	334.1	329.2
$R^2_{adj}$	0.9915	0.9841
SD (mg g <sup>-1</sup> )	9.072	12.54
Avrami fractionary order		
$k_N$ [h <sup>-1</sup> (g mg <sup>-1</sup> ) <sup><math>n-1</math></sup> ]	0.08532	0.06212
$q_e$ (mg g <sup>-1</sup> )	320.9	310.7
$N$	0.6595	0.7333
$R^2_{adj}$	0.9998	0.9893
SD (mg g <sup>-1</sup> )	6.612	10.29
Intraparticle diffusion		
$k_{id,2}$ (mg g <sup>-1</sup> min <sup>-0.5</sup> ) <sup>a</sup>	14.07	15.14

Conditions: temperature, 25 °C; pH, 7.0; mass of adsorbent, 30.0 mg

<sup>a</sup>Second stage

The plots of the intraparticle diffusion model are presented in Supplementary Fig. 1C, D; both CAC-500 and MAC-980 show similar adsorption kinetics behavior. It is observed that, for both samples, the plots can be divided into two stages of adsorption: the first stage corresponds to that of a sharp rise and the second stage to that of a plateau. The initial sharp rise portion, which corresponds to the fastest sorption stage, represents the intraparticle diffusion process. The second segment, which is followed by the attainment of equilibrium, is regarded as diffusion through smaller pores (Kumar and Gaur 2011; Thue et al. 2016). During the initial sharp rise stage, the diffusion of hydroquinone is restricted mainly by the pore structure of the ACs, and during the second stage, the diffusion is retarded and saturated until equilibrium is reached (Kumar and Gaur 2011; Thue et al. 2016).

An examination of the first point of the second portion shows that the minimum equilibrium contact time for hydroquinone adsorption is 45 min for both adsorbents. The contact time of 60 min for both adsorbents (CAC-500 and MAC-980) was used for the adsorption of hydroquinone. The contact time was increased to ensure that

equilibrium is attained at higher concentrations of hydroquinone.

### 3.6 Adsorption Isotherms

An adsorption isotherm describes the relationship between the amount of adsorbate adsorbed and the adsorbate concentration that remained in solution. Equilibrium isotherms are frequently applied to explain the experimental data of the adsorption equilibrium. The parameters of these models give insight into the adsorption mechanism, surface properties, and affinity of the adsorbents.

Supplementary Fig. 2 presents the curves of the nonlinear fittings of the Langmuir, Freundlich, and Redlich–Peterson models, while their parameters are summarized in Table 6.

On the basis of the SD values, the best fittings for CAC-500 and MAC-980 were obtained from the Freundlich model ( $SD = 46.353$  for CAC-500 and  $SD = 48.345$  for MAC-980), followed by the Langmuir model ( $SD = 113.49$  for CAC-500 and  $SD = 113.53$  for MAC-980) and then Redlich–Peterson ( $SD = 34.281$  for CAC-500 and  $SD = 34.056$  for MAC-980). SD

**Table 6** Isotherm parameters of hydroquinone adsorption using CAC-500 and MAC-980

	CAC-500	MAC-980
Langmuir		
$Q_{\max}$ (mg g <sup>-1</sup> )	1218.3	1202.1
$K_L$ (L mg <sup>-1</sup> )	0.0076811	0.0075821
$R^2_{\text{adj}}$	0.98312	0.98113
SD (mg g <sup>-1</sup> )	46.353	48.345
Freundlich		
$K_F$ (mg g <sup>-1</sup> (mg L <sup>-1</sup> ) <sup>-1/n<sub>F</sub></sup> )	78.731	76.679
$n_F$	2.5379	2.5281
$R^2_{\text{adj}}$	0.89881	0.89591
SD (mg g <sup>-1</sup> )	113.49	113.53
Redlich–Peterson		
$K_{RP}$ (L mg <sup>-1</sup> )	7.0211	6.6956
$A_{RP}$	0.084103	0.079958
$\beta_{RP}$	1.2544	1.2864
$R^2_{\text{adj}}$	0.99077	0.99035
SD (mg g <sup>-1</sup> )	34.281	34.056

Conditions: pH, 7.0; adsorbent mass, 30.0 mg; contact time, 120 min

values are used to explain the suitability of nonlinear models.

Redlich–Peterson was the best model for hydroquinone adsorption onto CAC-500 and MAC-980. The Redlich–Peterson isotherm model combines elements from both the Langmuir and Freundlich equations, and the mechanism of adsorption is a hybrid one and does not follow ideal monolayer adsorption.

The Langmuir model presented lower SD values compared with the Freundlich model (see Table 4). This suggests that some homogeneity in the surface or pores of both carbons might play a key role in hydroquinone adsorption. The maximum amounts ( $Q_{\max}$ ) of the Langmuir model for hydroquinone adsorbed at 25 °C were too high, reaching 1218.3 and 1202.1 mg g<sup>-1</sup> for CAC-500 and MAC-980, respectively.

### 3.7 Desorption Studies

The regeneration of the adsorbent is crucially important (in the adsorption process) for diminishing the costs in a wastewater treatment process (Ribas et al. 2014; Dos Reis et al. 2016c; He et al. 2014; Prola et al. 2013b; Saucier et al. 2015; Suresh et al. 2011). The regeneration of the activated carbons was examined through desorption experiments. As eluents on the hydroquinone desorption process, we used NaOH (1.0–5.0 M) and 10%EtOH + NaOH M and 50%EtOH + NaOH M. The results of the desorption process are summarized in Supplementary Fig. 3.

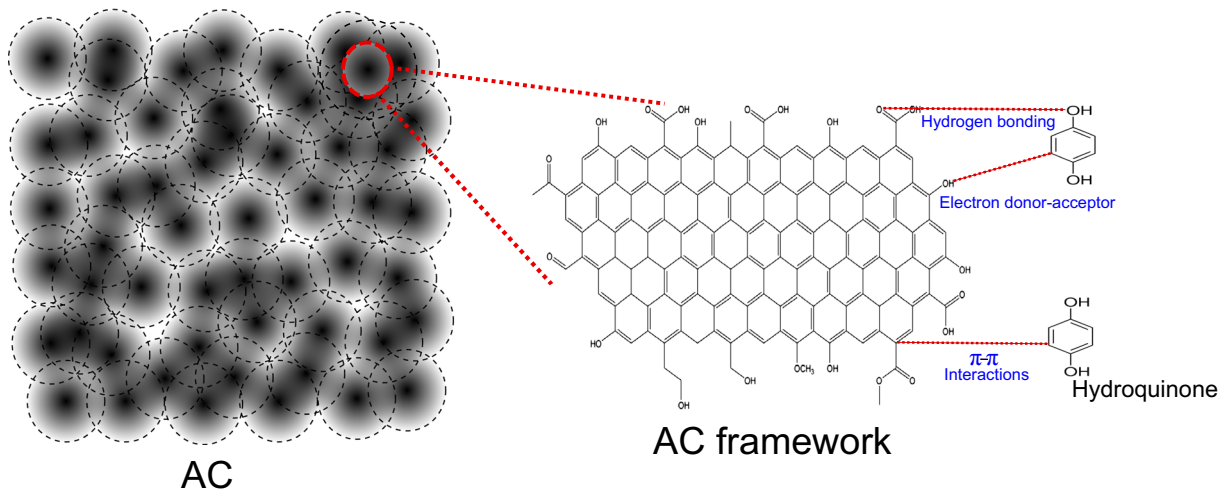
Pure NaOH solutions, up to 5 M, showed good desorption of hydroquinone (between 76.23 and 85.10). However, a mixture of EtOH (10 and 50%) + NaOH (5 M) presented an excellent desorption efficiency, desorbing more than 99.9% of hydroquinone from both adsorbents CAC-500 and MAC-500. The results show that the addition of EtOH obviously caused the enhancement of the amount of desorbed hydroquinone.

### 3.8 Adsorbent–Adsorbate Interactions

To better understand the possible mechanisms that might play key roles in phenolic compound adsorption on activated carbons, some mechanisms, such as electron donor–acceptor complex, dispersion interactions, and solvent effects (Dos Reis et al. 2016c; Saucier et al. 2015), are proposed (see Fig. 8).

The mechanism of electron donor–acceptor complex proposes that the aromatic rings of the hydroquinone act





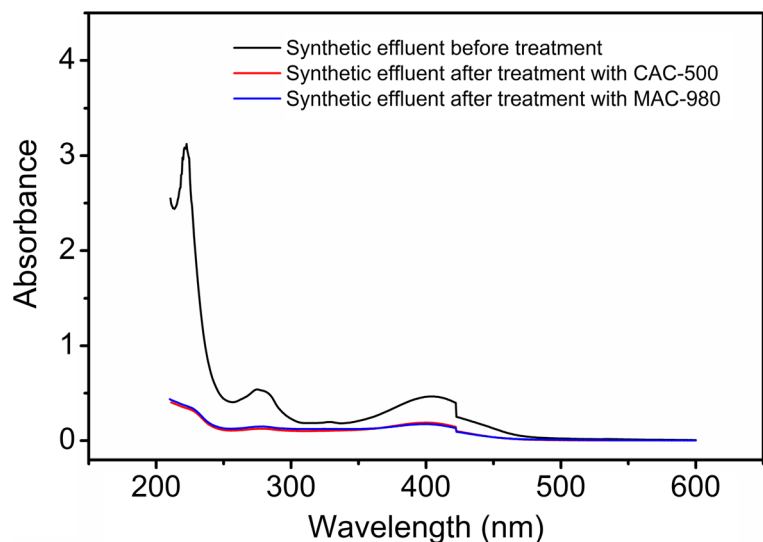
**Fig. 8** Proposed adsorption mechanism between ACs and hydroquinone

as the electron acceptors while the basic sites on the carbon surface serve as the donors (Dos Reis et al. 2016c; Liu et al. 2010; Rawajfih and Nsour 2006; Suresh et al. 2011). The hydroxyl group on the surfaces of CAC-500 and MAC-980 (see Fig. 3, FTIR results) is an electron-donating functional group which can increase the  $\pi$ -donating strength of the host aromatic ring. Thus,  $-\text{OH}$  can increase the adsorption affinity of the phenolic compounds onto the AC surfaces (Dos Reis et al. 2016c; Liu et al. 2010; Rawajfih and Nsour 2006; Suresh et al. 2011). However, this is not the only mechanism that could explain the adsorption process of phenolic compounds such as hydroquinone.

Another mechanism is the  $\pi$ - $\pi$  interactions. The aromatic rings of phenolic compounds interact with the aromatic groups of the ACs through  $\pi$ - $\pi$  interactions, which comprise charge transfer, dispersive force, and polar electrostatic components (Ribas et al. 2014; Thommes et al. 2015; Thue et al. 2016; Torres et al. 2016).

Phenolic compounds are hydrophobic (see Table 3), which causes good affinity between the adsorbates and adsorbents. Therefore, hydrophobic interaction is regarded as another important factor for the mechanism of the adsorption of phenolic compounds (Dos Reis et al. 2016c; Liu et al. 2010; Rawajfih and Nsour 2006; Suresh et al. 2011). In an aqueous solution, the

**Fig. 9** UV/Vis spectra of the simulated effluents before and after treatment with CAC-500 and MAC-980. See Table 1 for the composition of the effluents



adsorbate with higher hydrophobicity has a stronger tendency to be adsorbed and retained on the carbon surface or in the pores. As suggested by the solubility data (see Table 2), the hydrophobicities of the phenols used in this study are reinforced by an increase in the substitution degree, which is another reason for the enhanced adsorption of the substituted phenols.

### 3.9 Treatment of a Simulated Effluent of Phenolic Compounds

A simulated effluent containing ten phenolic compounds, humic acid, and some salts, prepared (see Table 1) with different compositions of phenolic compounds, was used to investigate the effectiveness and efficiency of CAC-500 and MAC-980 to remove phenols from simulated synthetic effluents; the results are shown in Fig. 9.

The UV–Vis spectra of the untreated effluents and the effluents treated with CAC-500 and MAC-980 were recorded from 200 to 600 nm (see Fig. 9). The areas under the absorption bands from 200 to 600 nm were used to monitor the percentage of the phenolic compound mixtures removed from the simulated effluents. Both CAC-500 and MAC-980 showed excellent performance on the treatment of simulated effluents. The percentages of removal of mixtures of phenolic compounds are 93.82 and 91.58% for CAC-500 and MAC-980, respectively.

These results are in accordance with the porosity and adsorption data, which revealed that the CAC-500 sample exhibited better textural features and higher sorption capacities than MAC-980. Based on the simulated effluent data, it is safe to say that both ACs could be excellently applied for the removal of phenolic compounds from simulated wastewaters as well as industrial effluents contaminated with phenols.

## 4 Conclusion

This study has demonstrated that high surface area activated carbons (ACs) can be prepared from two methods of pyrolysis (microwave and conventional thermal processes). Sorption of six phenolic compounds was investigated in the present study. The study has demonstrated that the adsorption of phenolic

compounds is influenced by their physicochemical properties. Among the six phenolic compounds, hydroquinone exhibited the highest affinity for both ACs (CAC-500 and MAC-980). Hydroquinone had the highest uptake values among the six phenolic compounds; therefore, it was chosen for further adsorption experiments on kinetic and equilibrium studies.

The Avrami fractionary order and Redlich–Peterson models best described the adsorption process. The maximum amounts ( $Q_{\max}$ ) of hydroquinone adsorbed at 25 °C were too high, reaching 1218.3 and 1202.1 mg g<sup>-1</sup> for CAC-500 and MAC-980, respectively. Both ACs showed excellent outcome in the treatment of simulated industrial effluents; they effectively removed 93.82% (CAC-500) and 91.58% (MAC-980) of a mixture of different organic compounds in a medium with high salt and sugar contents. A mechanism of adsorption was proposed in this work, and it was suggested that donor–acceptor complex and  $\pi$ – $\pi$  interactions play key roles in the adsorption process.

Based on the data of this work, it is possible to conclude that both kinds of pyrolysis (microwave and conventional methods) can produce high surface area and efficient activated carbons from sewage sludge.

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## References

- Ailijiang, N., Chang, J., Wu, Q., Li, P., Liang, P., Zhang, X., & Huang, X. (2016). Phenol degradation by suspended biomass in aerobic/anaerobic electrochemical reactor. *Water, Air, and Soil Pollution*, 227, 233. doi:10.1007/s11270-016-2924-x.
- Arellano-Cárdenas, S., Gallardo-Velázquez, T., Osorio-Revilla, G., López-Cortéz, M. S., & Gómez-Pere, B. (2005). Adsorption of phenol and dichlorophenols from aqueous solutions by porous clay heterostructure (PCH). *Journal of the Mexican Chemical Society*, 49, 287–291.
- Babich, H., & Davis, D. L. (1981). Phenol: a review of environmental and health risks. *Regulatory Toxicology and Pharmacology*, 1, 90–109.
- Balbuena, P. B., & Gubbins, K. E. (1993). Theoretical interpretation of adsorption behavior of simple fluids in slit pores. *Langmuir*, 9, 1801–1814.

- Calvete, T., Lima, E. C., Cardoso, N. F., Dias, S. L. P., & Ribeiro, E. S. (2010). Removal of brilliant green dye from aqueous solutions using home made activated carbons. *Clean: Soil, Air, Water*, 38, 521–532.
- Chen, H., Chen, D., & Hong, L. (2015). Influences of activation agent impregnated sewage sludge pyrolysis on emission characteristics of volatile combustion and De-NOx performance of activated char. *Applied Energy*, 156, 767–775.
- Davi, M. L., & Gnudi, F. (1999). Phenolic compounds in surface water. *Water Research*, 33, 3213–3219.
- Dos Reis, G. S., Adebayo, M. A., Lima, E. C., Sampaio, C. H., & Prola, L. D. T. (2016a). Activated carbon from sewage sludge for preconcentration of copper. *Analytical Letters*, 49, 541–555.
- Dos Reis, G. S., Sampaio, C. H., Lima, E. C., & Wilhelm, M. (2016b). Preparation of novel adsorbents based on combinations of polysiloxanes and sewage sludge to remove pharmaceuticals from aqueous solutions. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 497, 304–315.
- Dos Reis, G. S., Wilhelm, M., Silva, T. C. A., Rezwan, K., Sampaio, C. H., Lima, E. C., & Souza, S. M. A. G. U. (2016c). The use of design of experiments for the evaluation of the production of surface rich activated carbon from sewage sludge via microwave and conventional pyrolysis. *Applied Thermal Engineering*, 93, 590–597.
- Duana, L., Wanga, H., Suna, Y., & Xie, X. (2016). Biodegradation of phenol from wastewater by microorganism immobilized in bentonite and carboxymethyl cellulose gel. *Chemical Engineering Communications*, 203(7), 948–956.
- Dursun, A. Y., & Kalayci, C. S. (2005). Equilibrium, kinetic and thermodynamic studies on the adsorption of phenol onto chitin. *Journal of Hazardous Materials*, 123, 151–157.
- Freundlich, H. M. F. (1906). über die adsorption in lösungen. *Zeitschrift fuer Physikalische Chemie*, 57A, 385–470.
- Georgina, J., Dotto, G. L., Mazutti, M. A., & Foletto, E. L. (2016). Preparation of activated carbon from peanut shell by conventional pyrolysis and microwave irradiation-pyrolysis to remove organic dyes from aqueous solutions. *Journal of Environmental Chemical Engineering*, 4, 266–275.
- He, Q., Chen, Q., Lü, M., & Liu, X. (2014). Adsorption behavior of rhodamine B on UiO-66. *Chinese Journal of Chemical Engineering*, 22, 1285–1290.
- Hemmati, M., Nazari, N., Hemmati, A. S., & Shirazian, S. (2015). Phenol removal from wastewater by means of nanoporous membrane contactors. *Journal of Industrial and Engineering Chemistry*, 21, 1410–1416.
- Ho, Y. S. (2006). Review of second-order models for adsorption systems. *Journal of Hazardous Materials*, 136, 681–689.
- Kumar, D., & Gaur, J. P. (2011). Chemical reaction- and particle diffusion-based kinetic modeling of metal biosorption by a *Phormidium* sp.-dominated cyanobacterial mat. *Bioresource Technology*, 102, 633–640.
- Langmuir, I. (1918). The adsorption of gases on plane surfaces of glass, mica and platinum. *Journal of the American Chemical Society*, 40, 1361–1403.
- Leng, L., Yuana, X., Huang, H., Shao, J., Wanga, H., Chen, X., & Zeng, G. (2015). Bio-char derived from sewage sludge by liquefaction: characterization and application for dye adsorption. *Applied Surface Science*, 346, 223–231.
- Lima, E. C., Fenga, P. G., Romero, J. R., & de Giovanni, W. F. (1998). Electrochemical behaviour of [Ru(4,4'-Me<sub>2</sub>bpy)<sub>2</sub>(PPh<sub>3</sub>)(H<sub>2</sub>O)](ClO<sub>4</sub>)<sub>2</sub> in homogeneous solution and incorporated into carbon paste electrodes: application to oxidation of benzylic compounds. *Polyhedron*, 17, 313–318.
- Lima, E. C., Barbosa-Jr, F., Krug, F. J., & Guaita, U. (1999). Tungsten–rhodium permanent chemical modifier for lead determination in digests of biological materials and sediments by electrothermal atomic absorption spectrometry. *Journal of Analytical Atomic Spectrometry*, 14, 1601–1605.
- Lima, E. C., Barbosa, R. V., Brasil, J. L., & Santos, A. H. D. P. (2002). Evaluation of different permanent modifiers for the determination of arsenic, cadmium and lead in environmental samples by electrothermal atomic absorption spectrometry. *Journal of Analytical Atomic Spectrometry*, 17, 1523–1529.
- Lima, E. C., Brasil, J. L., & Santos, A. H. D. P. (2003). Evaluation of Rh, Ir, Ru, W-Rh, W-Ir, and W-Ru as permanent modifiers for the determination of lead in ashes, coals, sediments, sludges, soils, and freshwaters by electrothermal atomic absorption spectrometry. *Analytica Chimica Acta*, 484, 233–242.
- Lina, Q. H., Cheng, H., & Chena, G. Y. (2012). Preparation and characterization of carbonaceous adsorbents from sewage sludge using a pilot-scale microwave heating equipment. *Journal of Analytical and Applied Pyrolysis*, 93, 113–119.
- Liu, Y., & Liu, Y. J. (2008). Review: biosorption isotherms, kinetics and thermodynamics. *Separation and Purification Technology*, 61, 229–242.
- Liu, Q.-S., Zheng, T., Wang, P., Jiang, J.-P., & Li, N. (2010). Adsorption isotherm, kinetic and mechanism studies of some substituted phenols on activated carbon fibers. *Chemical Engineering Journal*, 157, 348–356.
- Lopes, E. C. N., dos Anjos, F. S. C., Vieira, E. F. S., & Cestari, A. R. (2003). An alternative Avrami equation to evaluate kinetic parameters of the interaction of Hg(II) with thin chitosan membranes. *Journal of Colloid and Interface Science*, 263, 542–547.
- Muppalla, R., Jewrajka, S. K., & Reddy, A. V. R. (2015). Fouling resistant nanofiltration membranes for the separation of oil-water emulsion and micropollutants from water. *Separation and Purification Technology*, 143, 125–134.
- Ozdemir, I., Şahin, M., Orhan, R., & Erdem, M. (2015). Preparation and characterization of activated carbon from grape stalk by zinc chloride activation. *Fuel Processing Technology*, 125, 200–206.
- Paisio, C. E., Talano, M. A., Gonzalez, O. S., Magallanes-Noguera, C., Kurina-Sanzb, M., & Agostinia, E. (2016). Biotechnological tools to improve bioremediation of phenol by *Acinetobacter* sp. RTE1.4. *Environmental Technology*, 37, 2379–2390.
- Prenzel, T., Guedes, T. L. M., Schlüter, F., Wilhelm, M., & Rezwan, K. (2015). Tailoring surfaces of hybrid ceramics for gas adsorption—from alkanes to CO<sub>2</sub>. *Separation and Purification Technology*, 129, 80–89.
- Prola, L. D. T., Acayanka, E., Lima, E. C., Umpierrez, C. S., Vagheti, J. C. P., Santos, W. O., Laminsi, S., & Djifon, P. T. (2013a). Comparison of *Jatropha curcas* shells in natural form and treated by non-thermal plasma as biosorbents for removal of Reactive Red 120 textile dye from aqueous solution. *Industrial Crops and Products*, 46, 328–340.
- Prola, L. D. T., Machado, F. M., Bergmann, C. P., de Souza, F. E., Gally, C. R., Lima, E. C., Adebayo, M. A., Dias, S. L., & Calvete, T. (2013b). Adsorption of Direct Blue 53 dye from aqueous solutions by multi-walled carbon nanotubes and activated carbon. *Journal of Environmental Management*, 130, 166–175.

- Qu, X., Tian, M., Liao, B., & Chen, Z. (2010). Enhanced electrochemical treatment of phenolic pollutants by an effective adsorption and release process. *Electrochimica Acta*, 55, 5367–5374.
- Rawajfih, Z., & Nsour, N. (2006). Sorption of phenol and 4-chlorophenol onto pumice treated with cationic surfactant. *Journal of Colloid and Interface Science*, 298, 39–49.
- Redlich, O., & Peterson, D. L. (1959). A useful adsorption isotherm. *The Journal of Chemical Physics*, 63, 1024–1027.
- Ribas, M. C., Adebayo, M. A., Prola, L. D. T., Lima, E. C., Cataluña, R., Feris, L. A., Puchana-Rosero, M. J., Machado, F. M., Pavan, F. A., & Calvete, T. (2014). Comparison of a homemade cocoa shell activated carbon with commercial activated carbon for the removal of reactive violet 5 dye from aqueous solutions. *Chemical Engineering Journal*, 248, 315–326.
- Rueda-Márquez, J. J., Pintado-Herrera, M. G., Martín-Díaz, M. L., Acevedo-Merino, A., & Manzano, M. A. (2015). Combined AOPs for potential wastewater reuse or safe discharge based on multi-barrier treatment (microfiltration-H<sub>2</sub>O<sub>2</sub>/UV-catalytic wet peroxide oxidation). *Chemical Engineering Journal*, 270, 80–90.
- Saucier, C., Adebayo, M. A., Lima, E. C., Cataluña, R., Thue, P. S., Prola, L. D. T., Puchana-Rosero, M. J., Machado, F. M., Pavan, F. A., & Dotto, G. L. (2015). Microwave-assisted activated carbon from cocoa shell as adsorbent for removal of sodium diclofenac and nimesulide from aqueous effluents. *Journal of Hazardous Materials*, 289, 18–27.
- Shang, H., Lu, Y., & Zhao, F. (2015). Preparing high surface area porous carbon from biomass by carbonization in a molten salt medium. *RSC Advances*, 5, 75728–75734.
- Sin, J.-C., Lam, S.-M., Lee, K. T., & Mohamed, A. R. (2015). Preparation of cerium-doped ZnO hierarchical micro/nanospheres with enhanced photocatalytic performance for phenol degradation under visible light. *Journal of Molecular Catalysis A: Chemical*, 409, 1–10.
- Suresh, S., Srivastava, V. C., & Mishra, I. M. (2011). Study of catechol and resorcinol adsorption mechanism through granular activated carbon: characterization, pH and kinetic study. *Separation Science and Technology*, 46, 1750–1766.
- Thommes, M., Kaneko, K., Neimark, A. V., Olivier, J. P., Rodriguez Reinoso, F., Rouquerol, J., & Sing, K. S. W. (2015). Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report). *Pure and Applied Chemistry*, 87, 1051–1069.
- Thue, P. S., Adebayo, M. A., Lima, E. C., Sieliechi, J. M., Machado, F. M., Dotto, G. L., Vaghetti, P. S., & Dias, S. L. P. (2016). Preparation, characterization and application of microwave-assisted activated carbons from wood chips for removal of phenol from aqueous solution. *Journal of Molecular Liquids*, 223, 1067–1080.
- Torres, J. A., Chagas, P. M. B., Silva, M. C., dos Santos, C. D., & Corrêaa, A. D. (2016). Evaluation of the protective effect of chemical additives in the oxidation of phenolic compounds catalysed by peroxidase. *Environmental Technology*, 37, 1288–1295.
- Wang, H., Guan, Q., Li, J., & Wang, T. (2014). Phenolic wastewater treatment by an electrocatalytic membrane reactor. *Catalysis Today*, 236, 121–126.
- Wang, Y., Zhou, L., Duan, X., Sun, H., Tin, E. L., Jin, W., & Wang, S. (2015). Photochemical degradation of phenol solutions on Co<sub>3</sub>O<sub>4</sub> nanorods with sulfate radicals. *Catalysis Today*, 258, 576–584.
- Wang, B., Shui, Y., Ren, H., & He, M. (2016). Research of combined adsorption-coagulation process in treating petroleum refinery effluent. *Environmental Technology*. doi:10.1080/09593330.2016.1197319.
- Zhang, B., Li, F., Wu, T., Sun, Y., & Li, Y. (2015a). Adsorption of p-nitrophenol from aqueous solutions using nanographite oxide. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 464, 78–88.
- Zhang, D., Huo, P., & Liu, W. (2015b). Behavior of phenol adsorption on thermal modified activated carbon. *Chinese Journal of Chemical Engineering*, 24, 446–452.

## Supplementary Material for the Article

### **Removal of phenolic compounds from aqueous solutions using sludge-based activated carbons prepared by conventional heating and microwave-assisted pyrolysis**

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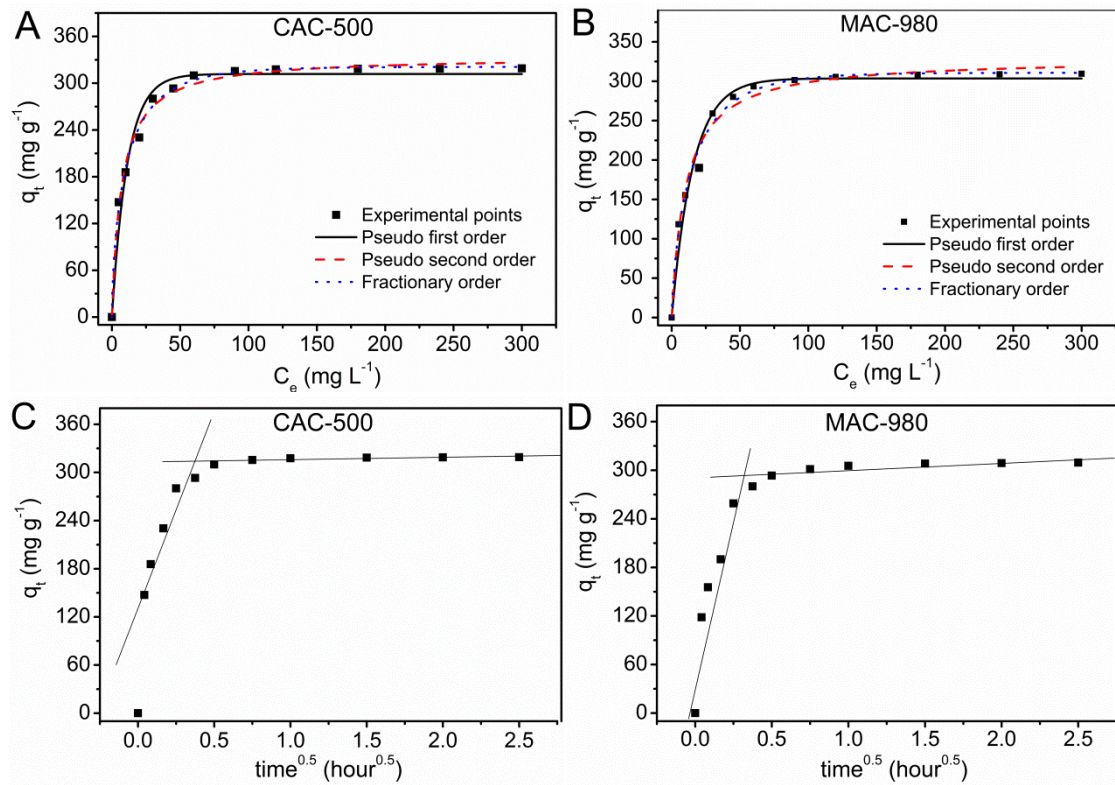
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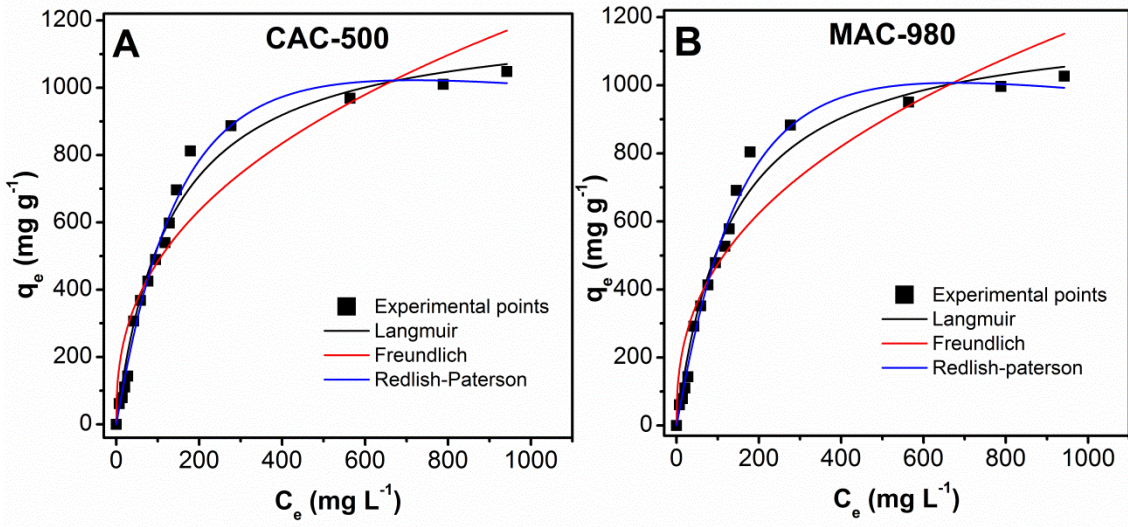
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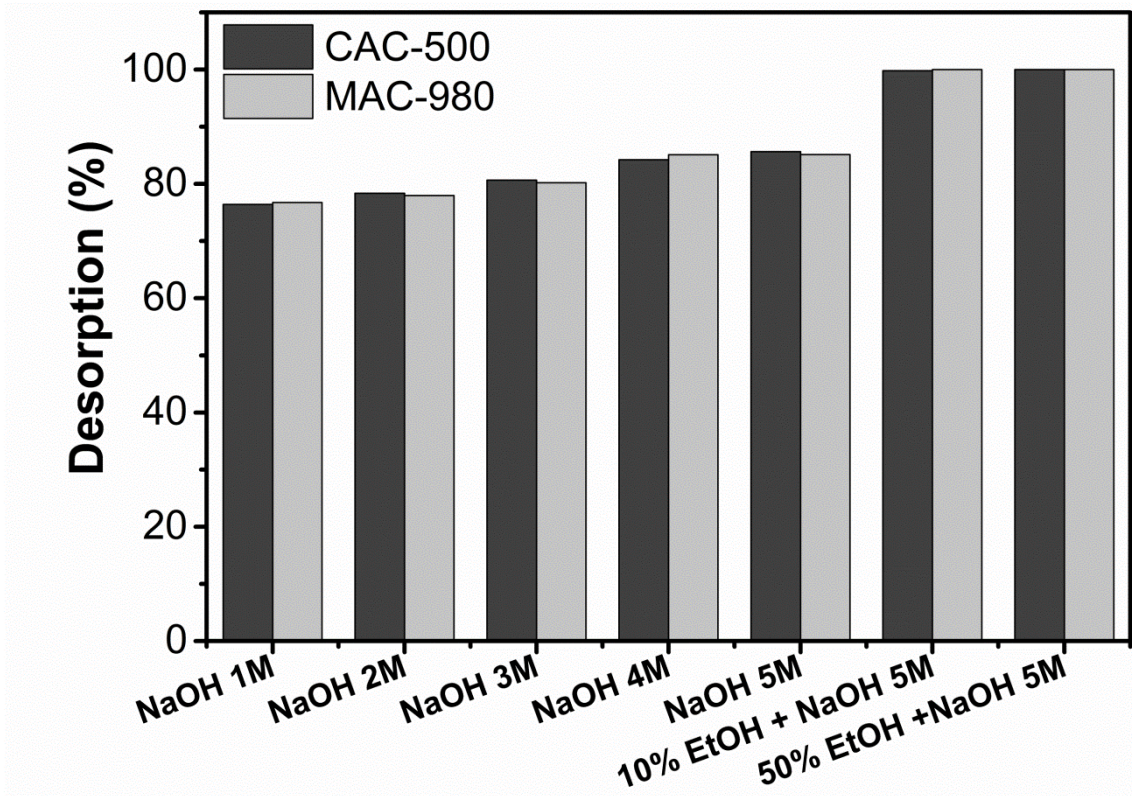
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**Supplementary Fig. 1** - Adsorption kinetic models fitting in the adsorption of hydroquinone onto CAC-500 (A) and MAC-980 (B) and Intra-particle diffusion model for CAC-500 (C) and MAC-980 (D).



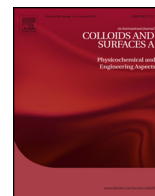
Supplementary Fig. 2 - Adsorption isotherm models fitting in the adsorption of hydroquinone by activated carbons.



Supplementary Fig. 3 - Desorption amount of hydroquinone by activated carbons.



# ***Capítulo Seis***



## Preparation of novel adsorbents based on combinations of polysiloxanes and sewage sludge to remove pharmaceuticals from aqueous solutions



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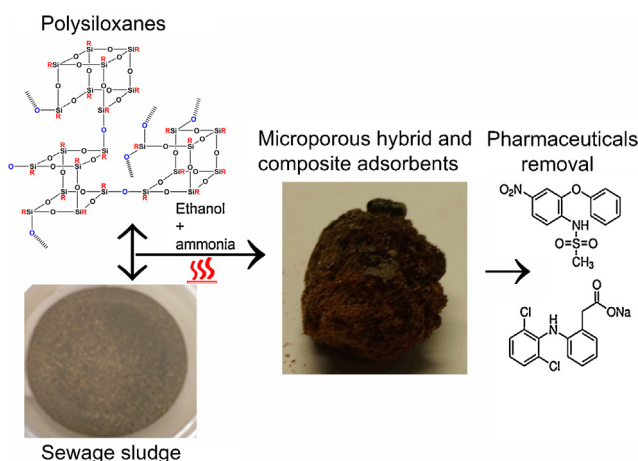
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### HIGHLIGHTS

- Novel adsorbents were prepared by mixing polysiloxanes and sewage sludge.
- The microporous adsorbents have high  $S_{\text{BET}}$  up to  $\sim 641 \text{ m}^2/\text{g}$ .
- Surface characteristic is adjustable by varying the polysiloxane/sewage sludge ratio.
- Adsorption of pharmaceuticals is controlled by  $S_{\text{BET}}$  and surface characteristics.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Novel adsorbents were developed by varying the ratios of polysiloxanes and sewage sludge. The adsorbents were synthesized by mixing various polysiloxanes with methyl (MK), methyl/phenyl (H44) or without functional groups with sewage sludge in a solvent and pyrolyzed under an inert atmosphere. The adsorbents were characterized using several analytical and functional techniques, and used for adsorption of diclofenac (DCF) and nimesulide (NM) from aqueous solutions. Nitrogen adsorption/desorption measurements showed type I isotherms, which are typically for microporous materials, and the specific surface areas ( $S_{\text{BET}}$ ) were found to be in the range of  $48 \text{ m}^2 \text{ g}^{-1}$  and  $631 \text{ m}^2 \text{ g}^{-1}$ . The sludge content was the major determinant for a decrease in  $S_{\text{BET}}$  and hydrophobicity, as compared with pure polysiloxane samples. Among the composite materials, H67S33-500 (sample with 67% of polysiloxane H44 and 33% of sludge pyrolyzed at  $500^\circ\text{C}$ ) had the highest  $S_{\text{BET}}$

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value of  $487 \text{ m}^2 \text{ g}^{-1}$  while M40T60-600 (sample with 40% of polysiloxane MK and 60% of TEOS and pyrolyzed at  $600^\circ\text{C}$ ) exhibited the highest  $S_{\text{BET}}$  value of  $631 \text{ m}^2 \text{ g}^{-1}$  among the hybrid materials. Experimental variables such as initial pH of the adsorbate solutions was optimized for adsorptive characteristics of the novel adsorbents. The optimum pH for adsorption of DCF and NM onto the adsorbents were 7.0 and 9.0, respectively. The equilibrium of adsorption was investigated using Langmuir, Freundlich and Sips models. Sips isotherm model gave the best fit of the equilibrium data. DCF showed better affinity for adsorbents than NM—suggesting that hydrophobic sites on the surfaces played a key role in the adsorption process.

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## 1. Introduction

Human activities is intrinsically responsible for wastes generation, and the growing demands for environmental cleanliness in the production process force companies to reuse most of their wastes [1]. With the growing needs for resource materials and the environmental protection requirements associated with sustainable development, it has become necessary to study all the possibilities of reusing and recycling industrial and urban wastes and by-products, especially in the fields of chemistry and engineering. This is a way of minimizing management costs in specialized plants [1–3]. In addition, the reuse of wastes represents a sustainable solution to the scarcity of raw materials to be used for production of energy and various end products [4–6].

In this context, due to rapid development of industrial activities in the last couple of years, there have been extensive studies in developing new materials for many applications such as catalysis [7], separation [8,9], membranes [10,11], drug delivery systems [12] and environmental technology [13,14]. Among these materials, adsorbents have played important roles in the fields of separation processes and environmental technology due to its features such as good porosity with high specific surface area, high adsorption capacity, high stability, and ease of synthesis and treatment, among others [2,4,8–10]. Among the known adsorbents, activated carbon (AC) is the most popular. Activated carbons are well-known for their excellent adsorption characteristics because they have enhanced pore structures and high specific surface area ( $S_{\text{BET}}$ ). However, activated carbons do not possess good mechanical strength, fact that precludes its use in system with high flow rate of effluent [15,16].

Based on this context, adsorbents from organosilicas such as polysiloxanes arose within the last few years [17–19]. Polysiloxane-derived hybrid ceramic materials have several advantages, which include better mechanical stability, no or reduced swelling, high temperature stability and the adjustability of higher concentration of chelating groups on the surface, over activated carbons [20,21]. Another advantage of using organosilica materials is that they are easy to modify and functionalize in many ways due to the existence of free hydroxyl groups (O–H) on their surfaces [22,23], which can be used for the binding of functional groups [17,24,25]. However, pure hybrid materials derived from polysiloxanes are expensive adsorbents compared to activated carbons produced from low cost precursors such as industrial wastes and sewage sludge [2,4]. Sewage sludge is an inevitable by-product during wastewater treatment, which is produced in large volumes around the world [26]. These huge amounts of waste materials, consequently, cause major handling and disposal problems, which are associated to high cost. One possibility of overcoming the problem posed above is to combine waste sewage sludge and synthetic polysiloxane material precursors, with the aim of combining their intrinsic properties to produce composite adsorbents. The resulting adsorbents should possess good rigidity like that of the polysiloxanes, associated with

higher hydrophilic behavior of organic matrix materials that could be used as adsorbents for many organic compounds.

To the best of our knowledge, we report for the first time a preparation of new composite adsorbents using sewage sludge and polysiloxanes as precursors in different ratios. The new composite adsorbents were characterized for their specific surface area ( $S_{\text{BET}}$ ) and surface characteristics and tested for the removal of two pharmaceuticals from aqueous solutions.

## 2. Materials and methods

### 2.1. Preparation of adsorbents

Composite adsorbents derived from sludge and/or polysiloxanes were prepared from either a single mixture or binary mixtures of precursors. The precursors, tetraethylorthosilicate (TEOS, Sigma-Aldrich), methylpolysiloxane (Silres<sup>®</sup> MK, Wacker Chemie AG) and methylphenylpolysiloxane (Silres<sup>®</sup> H44, Wacker Chemie AG), were mixed with sewage sludge. The mixture step of all the samples was carried out in ethanol under reflux for three days using the method described by Prentzel et al. [17,18]. The amount of ethanols were calculated according to literature [17,18]. A proportion of 20 ml of ethanol per gram of H44 was used for H44 samples while a proportion of 30 ml of ethanol per gram of MK was used for MK samples. The hydrolysis and polycondensation reactions were catalyzed under basic conditions by adding 0.2 M  $\text{NH}_3$  [18]. Afterwards, the ethanol was removed at reduced pressure. A second step was performed in a furnace at  $200^\circ\text{C}$  in an atmosphere of air for 2 h. Subsequently, the samples were pyrolyzed at  $500$  or  $600^\circ\text{C}$  under inert atmosphere of nitrogen. A heating rate of  $120^\circ\text{C h}^{-1}$  was used up to  $100^\circ\text{C}$ , below the final temperature and then a slower heating rate of  $30^\circ\text{C h}^{-1}$  was applied to reach the maximum temperature ( $500^\circ\text{C}$  or  $600^\circ\text{C}$ ). The samples were pyrolyzed at the maximal temperature for 4 h [18]. Finally, the samples were crushed with a grinder and sieved to a size range  $<250 \mu\text{m}$ . An overview of the reaction for the preparation of the hybrid and composite materials is shown in Fig. 1.

The pyrolyzed materials investigated in this study are listed in Table 1 and denominated by the first letter of the precursor used (for instance “H” stands for H44, “M” for MK, “T” for TEOS and “S” for sewage sludge), the molar percentage of the precursor used (for samples without sludge), the percentage weight of the precursors used for samples with sludge and the pyrolysis temperature in  $^\circ\text{C}$  (500 or 600). For example, H40T60-500 was prepared from H44 and TEOS in a molar ratio of 40:60 (calculated based on the average molar composition per Si atom) and subsequently pyrolyzed at  $500^\circ\text{C}$  under  $\text{N}_2$  atmosphere. H33S67-600 was prepared from sewage sludge and H44 in a weight ratio of 33:67 and pyrolyzed at  $600^\circ\text{C}$ . All samples synthesized are summarized in Table 1.

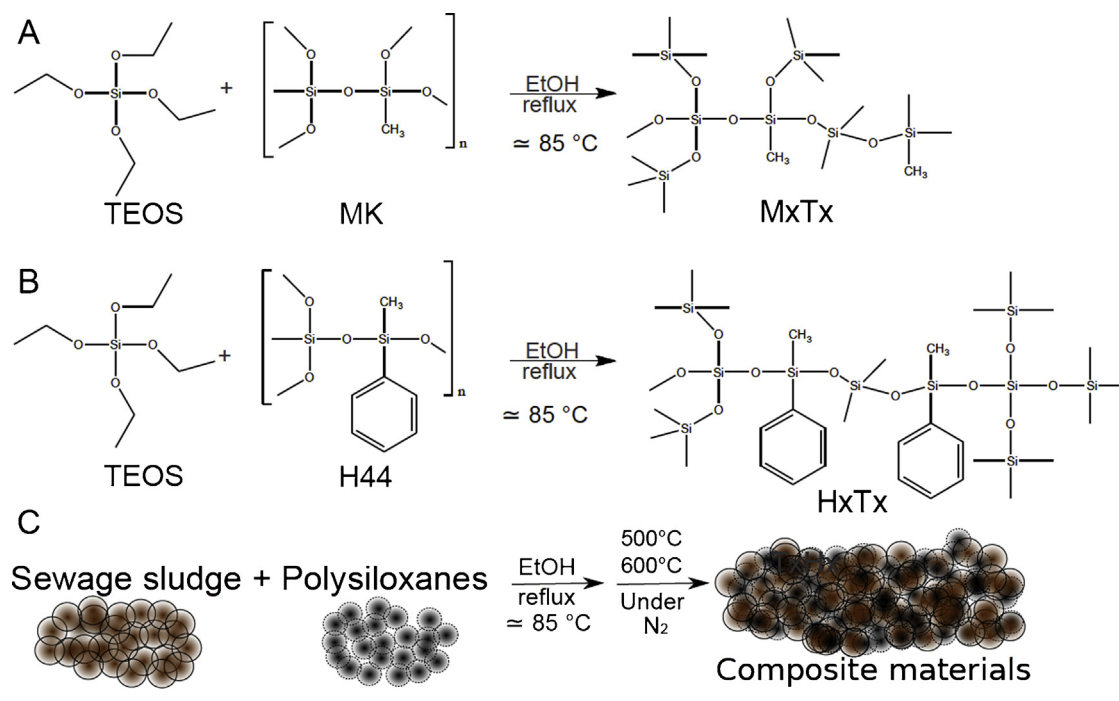


Fig. 1. Scheme of preparation of hybrid and composite materials.

**Table 1**  
Materials prepared according to ratio of each precursor.

Precursor	Samples denotation	M MK <sup>a</sup>	H H44 <sup>a</sup>	T TEOS <sup>a</sup>	S SLUDGE <sup>a</sup>	Temperature
MK	M100-500	100	–	–	–	500
	M100-600	100	–	–	–	600
H44	H100-500	–	100	–	–	500
	H100-600	–	100	–	–	600
TEOS	T100-500	–	–	100	–	500
	T100-600	–	–	100	–	600
Sludge	S100-500	–	–	–	100	500
	S100-600	–	–	–	100	600
MK + TEOS	M40T60-500	40	–	60	–	500
	M40T60-600	40	–	60	–	600
H44 + TEOS	H40T60-500	–	40	60	–	500
	H40T60-600	–	40	60	–	600
H44 + Sludge	H67S33-500	–	67	–	33	500
	H33S67-500	–	33	–	67	500
	H67S33-600	–	67	–	33	600
	H33S67-600	–	33	–	67	600
MK + Sludge	M67S33-500	67	–	–	33	500
	M33S67-500	33	–	–	67	500
	M67S33-600	67	–	–	33	600
	M33S67-600	33	–	–	67	600
TEOS + Sludge	T67S33-500	–	–	67	33	500
	T33S67-500	–	–	33	67	500

<sup>a</sup> Weight percentage.

## 2.2. Solutions and reagents

All solutions were prepared using deionized water. The characteristics of the pharmaceuticals used in this study are presented in Supplementary Figs. 1 and 2. Stock solutions (1.00 g L<sup>-1</sup>) of DCF and NM were prepared by weighing and dissolving calculated amounts of the pharmaceuticals in deionized water. Working solutions were prepared by diluting the stock solution. A 0.10 mol L<sup>-1</sup> NaOH and

a 0.10 mol L<sup>-1</sup> HCl were utilized to adjust the pH of the solutions using a pH meter.

## 2.3. Characterization

Adsorbents in powder form (<250 μm) were used for adsorption experiments. Nitrogen adsorption isotherms were recorded with a commercial system (Belsorp-Mini, Bel Japan Inc.) at –196 °C after drying for 3 h at 120 °C under reduced pressure (<2 mbar).

The morphology of the materials was obtained using scanning electron microscopy (SEM), a JEOL microscope, model JSM 6060, with a voltage of 15 kV.

The functional groups of the materials were determined using Fourier Transform Infra-Red Spectroscopy (FTIR) (Bruker Spectrometer, alpha model) with the ATR (Attenuated Total Reflectance) accessory. The spectrum was recorded with 64 cumulative scans over the range of 4000–400  $\text{cm}^{-1}$  with a resolution of 4  $\text{cm}^{-1}$ .

Thermogravimetric (TGA) analysis of synthesized materials were obtained on a TA Instruments model SDT Q600 (New Castle, USA) with a heating rate of 10  $^{\circ}\text{C min}^{-1}$  at 100  $\text{ml min}^{-1}$  of synthetic air flow. Temperature was varied from 20 to 1000  $^{\circ}\text{C}$  (acquisition time of 1 point per 5 s) using 10.00–15.00 mg of solid.

Elemental (C, H, N) analyses of precursors (sewage sludge, H44 and MK) were performed on a CHNOS Elemental Analyzer (Elementar, Vario EL III, Germany). The elemental analysis of the sewage sludge gave 32.68%, 5.12% and 6.17% as the percentage of carbon, hydrogen and nitrogen, respectively. For the MK, the carbon and hydrogen contents were 19.75% and 4.89%, respectively, while the respective contents for H44 were 44.10 and 4.20.

For vapor adsorption experiments, the samples (in powder form) were dried in 5 ml glasses at 70  $^{\circ}\text{C}$  for 24 h [17,18]. The samples were cooled at room temperature in a desiccator before determining their accurate weights (about 0.5 g). Storage of samples in an atmosphere of saturated solvent vapor was performed in Erlenmeyer flasks plugged with a ground glass joint, using 60 ml of solvent [17,18]. The powder containing glass was placed in such a way that it was not in contact with the wall of the Erlenmeyer. The samples were removed from the Erlenmeyer flask after 24 h and dried carefully from the outside using laboratory tissues. The weight gain during storage was used to calculate the maximal adsorption of vapor [17,18].

#### 2.4. Batch adsorption studies

Aliquots of 20.00 ml (5.00–500.0  $\text{mg L}^{-1}$ ) of DCF and NM were added to different 50-ml flat bottom Falcon Tubes containing 40.0 mg of adsorbents. The flasks were capped, and placed in a shaker model GFL 3015, and the system was agitated between 5 and 360 min. Afterwards, to separate the adsorbent from the aqueous solutions, the mixtures were centrifuged using a centrifuge (Heraeus megafuge 16), and aliquots of 1–5 ml of the supernatant were diluted to 20.0–100.0 ml in calibrated flasks.

The residual solution, after adsorption, was quantified using UV/Visible spectrophotometer (T90+ UV-vis spectrophotometer, PG Instruments, London, United Kingdom) at maximum wavelengths of 285 nm and 392 nm, for DCF and NM, respectively.

The amounts of DCF and NM removed by the novel adsorbents were calculated with the aid of Eq. (1).

$$q = \frac{(C_0 - C_f)}{m} \times V \quad (1)$$

where  $q$  is the amount of DCF or NM adsorbed by the adsorbent ( $\text{mg g}^{-1}$ );  $C_0$  is the initial DCF or NM concentration in contact with the adsorbent ( $\text{mg L}^{-1}$ ),  $C_e$  is the DCF or NM concentration ( $\text{mg L}^{-1}$ ) after the batch adsorption procedure,  $V$  is the volume of DCF or NM solution (L) put in contact with the adsorbent and  $m$  is the mass (g) of adsorbent.

#### 2.5. Equilibrium models

Eqs. (2)–(4) represent respective Langmuir, Freundlich and Sips models [27–29]. These models were used for analysis of equilibrium data.

$$q_e = \frac{Q_{\max} \times K_L \times C_e}{1 + K_L \times C_e} \quad (2)$$

$$q_e = K_F \times C_e^{1/n_F} \quad (3)$$

$$q_e = \frac{Q_{\max} \times K_s \times C_e^{1/n_s}}{1 + K_s \times C_e^{1/n_s}} \quad (4)$$

where  $C_e$  is the supernatant concentration at the equilibrium ( $\text{mg L}^{-1}$ );  $K_L$  is the Langmuir affinity constant ( $\text{L mg}^{-1}$ );  $Q_{\max}$  is the maximum adsorption capacity ( $\text{mg g}^{-1}$ );  $K_F$  is the Freundlich constant related with adsorption capacity [ $\text{mg g}^{-1} (\text{mg L}^{-1})^{-1/n}$ ];  $n$  is the Freundlich exponent (dimensionless);  $K_s$  is the Sips equilibrium constant ( $\text{L mg}^{-1}$ ) and  $n_s$  is dimensionless exponent of the Sips equation.

The kinetic and isotherm parameters were evaluated using statistical and quality assurance [30], and such procedures and equations are described in the supplementary material.

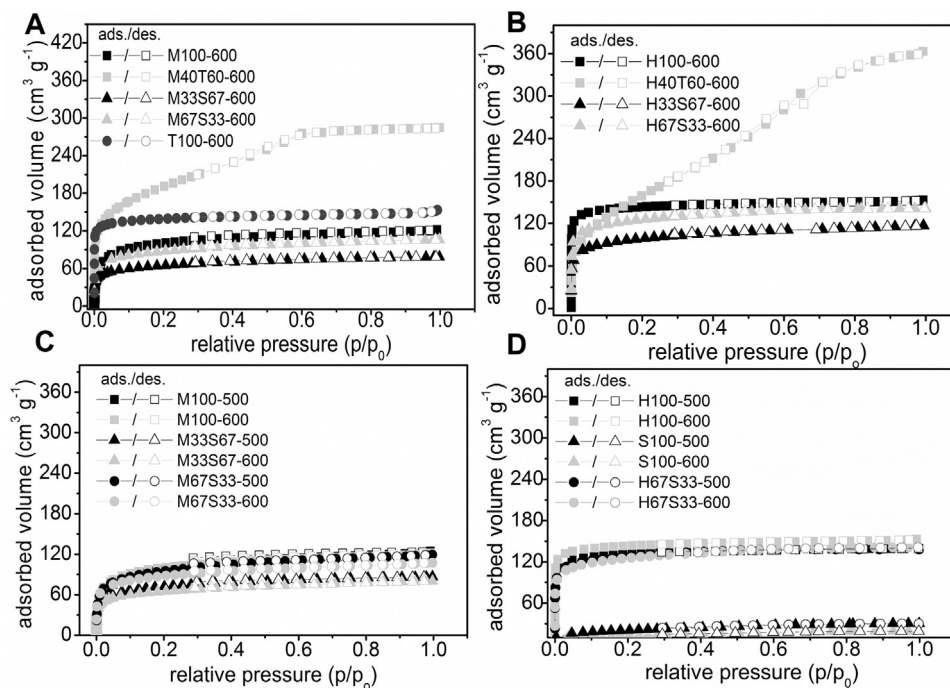
### 3. Results and discussion

#### 3.1. Influence of the experimental conditions on the textural characteristics of the adsorbents

The interpretation of experimental adsorption isotherms is complicated in practice due to uncertainties about the morphology of the adsorbing material. Common adsorbents studied are frequently heterogeneous, having not only an unknown range of pore sizes but also a range of pore shapes, active adsorption sites, blocked and network pores [26]. Fig. 2A and B show the influence of the composition of the samples of the adsorption and desorption of  $\text{N}_2$ . All isotherms can be ascribed to type I isotherm according to International Union of Pure and Applied Chemistry (IUPAC) classification. Type I (the Langmuir isotherm) is for microporous adsorbents (pore diameter < 2 nm) [26]; as relative pressures approaching unity, the curve may reach a limiting value or rise if large pores are present [26]. However, it is seen that the adsorbed  $\text{N}_2$  volumes are different in their dependency on the content of the precursors (see Fig. 2A and B). When relative pressure  $P/P_0$  was about 0.1, the adsorption of  $\text{N}_2$  was saturated, however, when  $P/P_0 > 0.1$ ,  $\text{N}_2$  was adsorbed onto the large pores or on the external surface, even though the amount was very small [31]. The range of adsorbed nitrogen volume was between 84 and 278  $\text{cm}^3 \text{g}^{-1}$  for MK-containing materials and 104 and 357  $\text{cm}^3 \text{g}^{-1}$  for H44-containing materials.

Fig. 2A illustrates that the amount of  $\text{N}_2$  adsorbed gradually decreases from T100-600, M100-600, M67S33-600, M33S67-600 to the combination of TEOS and MK. In M40T60-600, probably, the Si-OH groups of MK condense with the OH groups from TEOS, thus the macromolecular chains are spaced with silica particles. On the other hand, in the samples without TEOS, the condensation occurs through Si-O-Si intermolecular bonds, which limit the size of the pores.

Fig. 2B shows samples with H44 and sludge in different compositions. For these samples, compared to MK samples, a similar trend is observed although the condensation between TEOS and the polysiloxanes is done through the chain ends. The presence of silica particles intercalated between the macromolecular chains in the first stages of the process, probably ensures larger pores after pyrolysis. Similarly, the polysiloxane sample, H40T60-600, exhibits a higher micropore volume due to more effective prevention of pore from collapsing during drying. By analyzing the effect of composition of the samples on the  $\text{N}_2$  isotherms (see Fig. 2A and B), the ratio between MK or H44 and sludge seems to have a slight influence on the maximum uptake of  $\text{N}_2$ . The  $\text{N}_2$  uptake increased when the sludge content was decreased. The highest uptake was found for the sludge free samples (TEOS combination with MK and H44 that is M40T60-600 and H40T60-600). Fig. 2C and D show the influence of the temperature on the generation of micropore volume for single or binary system with MK, H44 and sludge. All isotherms of



**Fig. 2.** Nitrogen adsorption/desorption isotherms of MK, H44, TEOS and Sludge in single and binary systems; (A) and (B) corresponds to the influence of composition; and (C) and (D) corresponds to influence of temperature on the adsorbed volume of  $N_2$ .

the samples are also of type I. Samples pyrolyzed at both temperatures (500 and 600 °C) exhibited almost the same maximum value of  $N_2$  uptake—indicating that temperature in this range is not an important factor that influences the maximum values of  $N_2$  uptake.

Fig. 3 reveals small differences of  $S_{BET}$  values for the samples pyrolyzed under different temperatures. In general, however,  $S_{BET}$  values of samples pyrolyzed at 500 °C were somewhat larger than those pyrolyzed at 600 °C. The highest  $S_{BET}$  values, 500–631  $m^2 g^{-1}$ , are for sludge-free samples (see Fig. 3B). Sludge-containing samples show lower  $S_{BET}$  values of 49–489  $m^2 g^{-1}$ . The highest value is for H67S33-500 (489  $m^2 g^{-1}$ ) and the lowest value (49  $m^2 g^{-1}$ ) is for the pure sludge sample (S100-600)—an evidence that sludge ratio decreases the value of  $S_{BET}$ .

The relationship between specific surface area and sludge content of the samples can be seen in Fig. 3C. Generally, the sludge content decreases the value of  $S_{BET}$ . H44-based materials present larger specific surface areas than MK and TEOS-based samples. When the content of sludge increases in MK-based samples from 0 to 33%, the specific surface area remains almost the same (361 to 347  $m^2 g^{-1}$  and 342–327  $m^2 g^{-1}$  for respective samples pyrolyzed at 500 and 600 °C). However, when the content of the sludge is increased from 33 to 67%, the samples show a sharp decrease in  $S_{BET}$  values from 347 to 230  $m^2 g^{-1}$  (for samples pyrolyzed at 500 °C) and 327–278  $m^2 g^{-1}$  (for samples pyrolyzed at 600 °C). Similar trend is observed for the other materials, however, TEOS-containing samples show remarkable decrease with increasing sludge content from 543  $m^2 g^{-1}$  (T100-500) to 47  $m^2 g^{-1}$  (T33S67-500) and 79  $m^2 g^{-1}$  (T67S33-500).

It can be inferred from the available data that sludge content causes remarkable influence on the evolution of specific surface area. The  $S_{BET}$  values are generally higher for H44-based materials than MK-based materials because the phenyl groups have higher steric demand and decompose at lower temperatures than the methyl groups [17,32].

To determine the surface morphology of selected materials, some adsorbents were comparatively examined with the aid of scanning electron microscopy (SEM), and the results are illustrated

in Fig. 4. SEM images were taken from the surfaces obtained at different temperatures and compositions. As shown in Fig. 4, all selected materials possess rough and heterogeneous surfaces. Samples that were pyrolyzed at 500 °C with a sludge content of 33% are rougher than those pyrolyzed at 600 °C. However, samples pyrolyzed at 500 °C and with a sludge content of 67% possessed high roughness and cracks in the surfaces. Although H44-based samples have higher microporosity (see Fig. 3A and B), these samples show more homogeneous and plane surfaces. A possible explanation could be linked to the precursor characteristics; H44 is more homogeneous than sludge and this gave adsorbents with similar characteristics as the raw material.

### 3.2. Fourier Transformed Infrared Spectroscopy (FT-IR)

Fourier Transform Infra-Red spectroscopy (FTIR) was carried out to identify the functional groups possessed on surface of the materials—it enables better understanding of the surface features. FTIR of S100-600, M100-600, M33S67-600, M67S33-600, H100-600, H33S67-600 and H67S33-600 materials are shown in Fig. 5. Considerable changes were observed among the composite materials and pure polysiloxanes. Five new peaks arose for both set of samples (MK and H44), which are located mainly in the regions around 438, 1410, 1626, 2908, 3431  $cm^{-1}$  (see Fig. 5A and B). These data show that the samples with sludge present much more functional groups on their surface, as expected.

The FTIR spectra of MK mixed with 33 and 67% of sewage sludge (M33S67-600 and M67S33-600) present similar bands; showing smaller differences in the wavenumbers (see Fig. 5B). The same trend was observed for the samples with H44-sludge content. However, it might be inferred that the sludge content causes great influence on the rise of functional groups on the surface of the composite materials.

The high-intensity band at 3384  $cm^{-1}$  is due to the hydroxyl groups stretching vibrations [4]. The inconspicuous band at 2910  $cm^{-1}$  is ascribed to asymmetric and symmetric C–H stretching [4,11]. The band at 1590  $cm^{-1}$  could be assigned to the skeletal

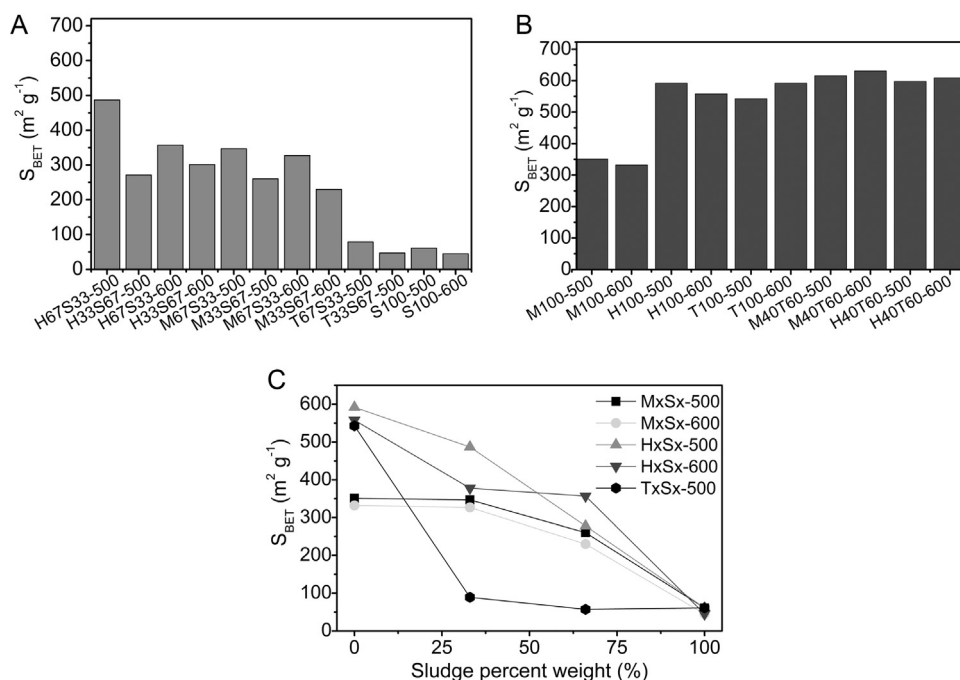


Fig. 3. (A) and (B) Specific surface areas of all adsorbents and (C) influence of sludge content of the samples on the  $S_{\text{BET}}$ .

vibration of benzene [4,11]. The peaks around  $1410\text{ cm}^{-1}$  can be assigned to C=C stretching vibration [4,11]. The small band at  $1380\text{ cm}^{-1}$  could be assigned to C–H bending vibration [4,11]. The strong absorption at  $1035\text{--}1119\text{ cm}^{-1}$  could be assigned to C–O stretching of alcohol and Si–O of silicates. The small FTIR bands at  $778\text{--}797\text{ cm}^{-1}$  are assigned to aromatic out of plane C–H bending; and the bands  $577\text{--}598\text{ cm}^{-1}$  are assigned to aromatic ring bending. The small FTIR bands at  $438\text{--}464\text{ cm}^{-1}$  are attributed to antisymmetric stretching vibrations of Si–O–Si bonds.

The FTIR data indicate that the functional groups on a surface of composite materials (such as oxygenated and hydrogenated groups) might have left their surfaces more hydrophilic compared with pure polysiloxanes.

### 3.3. TGA and DTG analyses

TG and DTG curves of pure polysiloxanes, sewage sludge and composite materials are shown in Supplementary Fig. 3A–D. All the samples synthesized in this work have similar TGA-DTG profiles, therefore, only TGA-DTG profiles of pure polysiloxanes pyrolyzed at  $600^\circ\text{C}$  (M100-600 and H100-600), sewage sludge (S100-600) and composite samples (M67S33-100 and H67S33-600) are presented. Insignificant mass losses were observed for the composite samples (below  $400^\circ\text{C}$ ) and pure polysiloxanes (below  $500^\circ\text{C}$ ). A two-stage weight loss was observed in the curves of the composite materials and pure polysiloxanes (see Supplementary Fig. 3A and B).

The first mass-loss stage, from  $25^\circ\text{C}$  to  $420^\circ\text{C}$ , can be attributed to the evaporation of the adsorbed water and the water molecules that were trapped in the carbonaceous matrix [15,24]. For pure polysiloxanes such as M100-600, the higher mass loss started at  $490^\circ\text{C}$  up to  $680^\circ\text{C}$  but the higher mass loss started at  $520^\circ\text{C}$  up to  $775^\circ\text{C}$  for pure H100-600—the mass loss observed could be attributed to carbon skeleton decomposition through abscission of methyl and phenyl groups [23,24]. Similar explanation might be given for pure sewage sludge, its mass loss is due to loss of the organic, hydrogen and oxygen surface groups [23].

The modified samples (composite materials) showed different trend from pure polysiloxanes and sewage sludge (see Supplemen-

tary Fig. 3A–D). Three smooth peaks were observed for composite samples, but only one peak was observed for pure polysiloxanes (H100-600 and M100-600) and sewage sludge (S100-600). For the composite sample, H67S33-600, the peaks are approximately 467, 512 and  $582^\circ\text{C}$ , however, pure polysiloxane (H100-600) has only one intensive peak at  $656^\circ\text{C}$  (see Supplementary Fig. 3C). Similar trend was observed for the samples containing MK-sludge. The peak of highest weight loss is ca.  $485^\circ\text{C}$  for M100-600, however, for M67S33-600 sample, three smooth peaks appear at about 438, 495 and  $558^\circ\text{C}$  (see Supplementary Fig. 3D).

The appearance of different peaks for the composite materials could be linked to condensation of hydroxyl groups on the sludge surface with Si framework of the polysiloxane [24], which forms surface silanol groups (as seen in Fig. 5). This is supported by O–H broad band centered around  $3400\text{ cm}^{-1}$ ; pure polysiloxanes do not show such band, however, when both H44 and MK were mixed with sewage sludge, such band is created—liberating water and producing siloxane bonds in the process [24].

According to the TG and DTG profiles,  $T_{\text{max}}$  (the temperature when weight loss reaches at maximum) of pure polysiloxanes are ca.  $727^\circ\text{C}$  for H100-600 and ca.  $617^\circ\text{C}$  for M100-600. In contrast,  $T_{\text{max}}$  of the composite materials are higher, which are about  $722^\circ\text{C}$  (12.3% of mass loss) for the M67S33-600 and  $726^\circ\text{C}$  (14.8% of mass loss) for H67S33-600. This fact primarily reveals that the thermal stability of composite materials was strengthened. The data of TGA-DTG further demonstrates that composite materials were successfully modified with sludge content.

### 3.4. Surface characteristics

The surface characteristics of adsorbents are important because surface characteristics give explanation about the existing interactions between adsorbent surface and a selected sorbate. Two solvents with different polarities were chosen, water and *n*-heptane, to characterize the surface of the adsorbents prepared in this study. A higher affinity of a sample for water means a more polar surface and thus more hydrophilic surfaces. More hydrophobic and thus non-polar surfaces will be, in contrast, characterized by

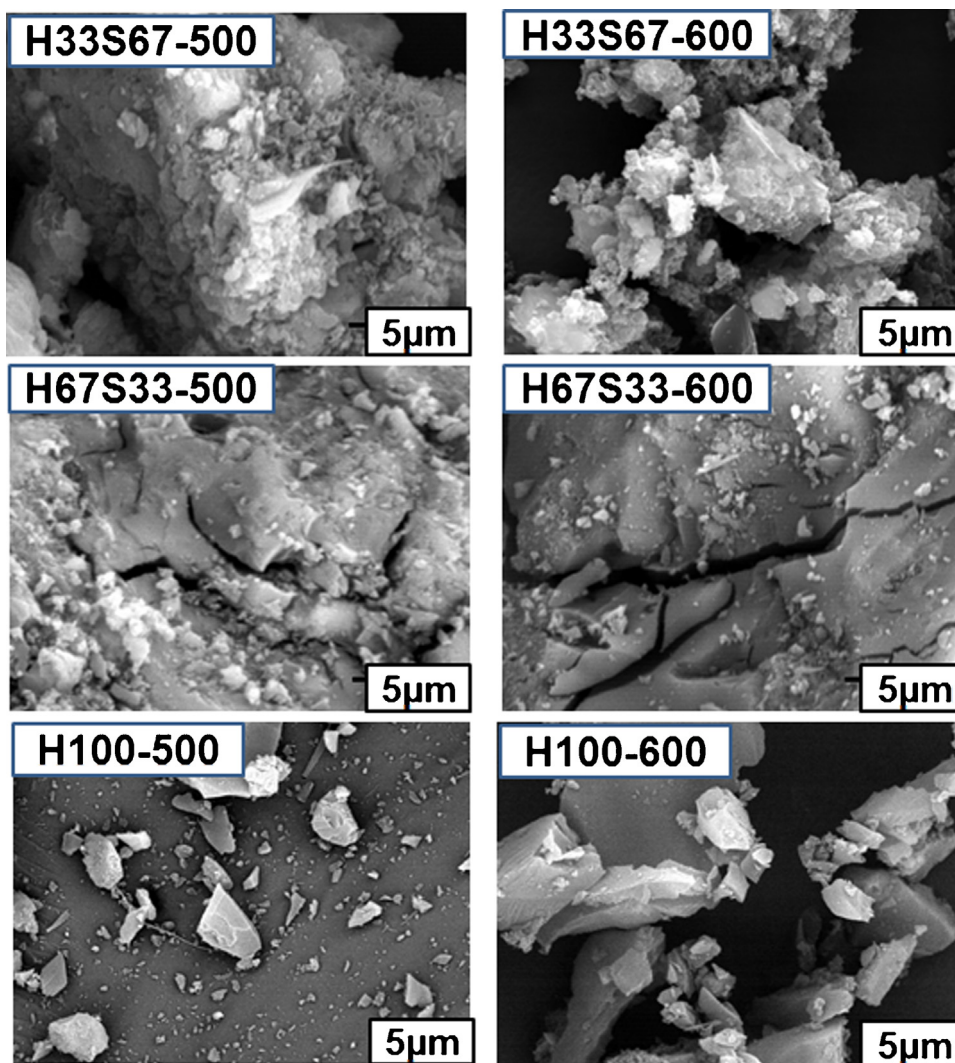


Fig. 4. Scanning electron micrographies of H33S67-500, H67S33-500, H33S67-600, H67S33-600, H100-600 and H100-500 at same magnification.

a higher *n*-heptane uptake. The *n*-heptane was selected because of its pronounced steric factors during adsorption compared to other solvent vapors. Solvents with both polar and non-polar groups adsorb less, and information derived from their adsorption capacity is limited. Fig. 6A and B shows maximum adsorption values of the developed materials [17,18,32].

The values of *n*-heptane to water adsorption ratio are illustrated in Figs. 6A and B. These figures demonstrate that all samples present a ratio higher than 1, which means that the samples have higher affinity for *n*-heptane, and hence are more hydrophobic.

M100-600 and H100-500 possess the highest ratio of *n*-heptane/water adsorption values of 11.61 and 10.48, respectively. The situation is different for samples with sludge content that show lower uptake ratio values of 1.42–5.1 (see Fig. 7A and B).

Regarding the pyrolysis temperature, generally, the samples pyrolyzed at 500 °C are more hydrophobic compared to those pyrolyzed at 600 °C. A possible explanation for this observation could be that at higher temperature, the organic compounds volatilize more easily, and the loss of organic compounds results in loss of hydrophobicity. For the samples with TEOS content, the temperature did not cause a significant influence on values of uptake ratio and almost kept constant despite the inclusion of sludge. Generally, the water sorption capacity increased in the presence of sludge whereas the sorption capacity decreased for *n*-heptane.

Fig. 6C illustrates the effect of sludge content on the surface features of adsorbents. The influence of the surface characteristics of sludge-containing materials shows similar trend for MK and H44-based samples with respect to ratio of *n*-heptane/water adsorption. It was observed that an increase in the sludge content for the H44-based samples caused a remarkable decrease in hydrophobicity as shown in Fig. 6C. This is an indication that sludge allows the adsorbent to be more hydrophilic in relation to the adsorbent without sludge content. The sludge that was pyrolyzed would generate activated carbon materials with more functional groups (as already observed in the FTIR analysis shown above). A possible explanation for this observation might be connected to the fact that H44 has higher carbon content in its structure than the sewage sludge. The elemental analysis of the precursors indicates that H44 has more carbon contents (44.10%) than the sewage sludge (31.68%), therefore, samples with more sludge content show a decrease in the uptake values (ratio of uptake of *n*-heptane/water) (see Fig. 6C).

The behavior of hydrophobicity of the MK-based samples was lower than the H44-based samples, this could be linked to the smaller carbon content of the MK compare to H44. The sludge content of MK-based samples somehow induces a decrease in their hydrophobicities. The sludge with more carbon content than MK is expected to have higher hydrophobicity. In some ways, the carbon content is not the only factor that plays a key role in the



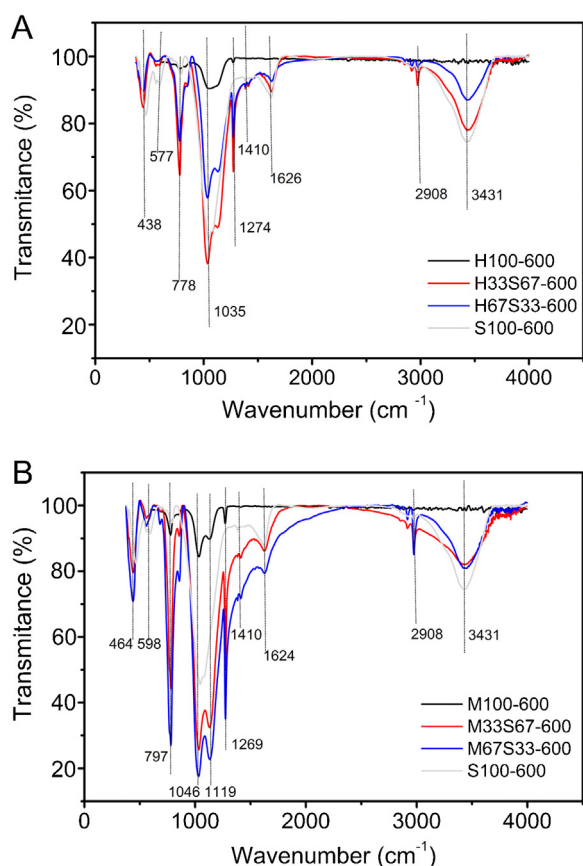


Fig. 5. FTIR spectra of H44-sludge containing sample(A) and MK-sludge containing sample (B).

hydrophobicity of adsorbents. Probably most surface active sites of MK-sludge containing samples were covered by large polar zones (oxygen groups) and on their surface, leading to the loss of hydrophobicity.

### 3.5. Effect of initial pH

It is well known that the pH of the solution is one of the most important factors affecting removal of an adsorbate by an adsorbent because pH can affect the solution chemistry of contaminants and the functional groups on the surface of adsorbents [33,34].

Adsorption experiments were conducted to confirm the removal of the compounds in a wide range of pH values, pH 6–11. A 40 mg of adsorbent materials were added to 20 ml of each pharmaceutical solutions with initial concentration of 200 mg L<sup>-1</sup> to investigate the effect of pH value on the treatment process. The data are shown in Supplementary Fig. 4A and B. For all samples studied, the adsorption capacities show similar trends for the whole pH range. The removal of the DCF was higher under neutral conditions, at pH 7.0, in accordance with results found by Hu and Chen [35] and Saucier et al. [36]. The DCF adsorption capacity slightly decreased after pH 7.0, its adsorption is not favored in alkaline solution. On the other hand, NM removal was higher at pH 9.0 and kept almost constant until pH 11.0.

The favorable adsorption of DCF onto composite materials (especially at pH 6.0–7.0) could be explained on the basis of the electrostatic interactions between the DCF anions and the positive groups on the surface of materials, and also by  $\pi$ - $\pi$  interactions between the benzene rings of the DCF and the organic moieties of the composite materials [2,33–35].

The variance in optimum pH for adsorption of DCF and NM could be related to the differences in the pK<sub>a</sub> values of these pharmaceuticals in water. The DCF has a pK<sub>a</sub> of 4.00 and NM a pK<sub>a</sub> of 6.70; these values were calculated by the Marvin Sketch software (Version 16.1.11.0). Therefore, at pH 7.0 and 9.0 for respective DCF and NM, the pharmaceuticals are deprotonated as anions. The positive groups on the surface of the materials interacted with these anions.

On the basis of the above discussion, the optimum pH values for adsorption of DCF and NM onto hybrid and composite materials are pH 7.0 and 9.0, respectively.

### 3.6. Adsorption of pharmaceuticals

The adsorption capacities of the adsorbents were investigated by using a 50.0 mg L<sup>-1</sup> of DCF and NM pharmaceutical solutions. Fig. 7A shows adsorption capacities ( $q_e$ ), Fig. 7B shows the experimental isotherms for diclofenac (DCF) while Fig. 7C presents the experimental isotherms for nimesulide (NM).

According to Fig. 7A, the TEOS-containing samples (mixed with MK and H44) have the highest adsorption capacities ( $q_e$ ) among all the adsorbents. On the other hand, sludge containing samples show low adsorption capacities for DCF and NM. A possible explanation for this disparity might be connected to the  $S_{BET}$  values, since the samples with sludge content have the lowest  $S_{BET}$  values. On the other hand, samples with pure H44 have high  $S_{BET}$  values but low  $q_e$  values compared to the adsorption of M40T60-600. Another explanation for this observation could be that decreasing in hydrophobicity is associated with increasing sludge content, which has a negative effect on DCF adsorption because DCF has affinity towards hydrophobic surfaces, hence causes lower pharmaceutical uptake.

Comparing adsorption values of DCF and NM, it is seen that DCF has a higher affinity for adsorbent than NM. The polar surface areas of DCF and NM were calculated using Marvin Sketch 16.1.11.0<sup>1</sup> software. These values are 52.16 Å<sup>2</sup> and 104.12 Å<sup>2</sup> for DCF and NM, respectively. The higher the polar surface area of the pharmaceutical, the higher the area of the molecule that interacts with water. On the account that the adsorption of an organic molecule onto active surface of carbon involves dehydration of the organic molecule before being adsorbed on the solid surface, the pharmaceutical that interacts more extensively with the solvent will possess a higher energy barrier to be surpassed so as to release the water to the bulk of the solution, and the adsorption of the adsorbate takes place on the adsorbent surface. Therefore, the difference in polar surface area of the pharmaceuticals explains why the adsorption of DCF was higher than that of NM.

The adsorption isotherms express the specific relationship between the concentration of adsorbate and its degree of accumulation onto adsorbent surface at a constant temperature. Three isotherm models, Langmuir, Freundlich and Sips models were used to fit the experimental data and evaluate the isotherm performance for DCF and NM adsorption.

The isotherms of adsorption of DCF and NM on M67S33-600, M40T60-600, M33S67-600 and S100-600 adsorbents were performed using the following experimental conditions: pH 7.0, contact time of 120 min, mass adsorbent was 40.0 mg, and temperature was fixed at 25 °C for DCF; and pH 9.0, contact time of 120 min, adsorbent dosage of 40.0 mg, and temperature was fixed at 25 °C for NM. The initial concentrations ranged from 5 to 500 mg L<sup>-1</sup> for both pharmaceuticals.

<sup>1</sup> Calculator Plugins of the MarvinSketchVersion 16.1.11.0 software, ChemAxon (<http://www.chemaxon.com>), 2016, were used for structure property prediction and calculation of physical properties of the pharmaceuticals.

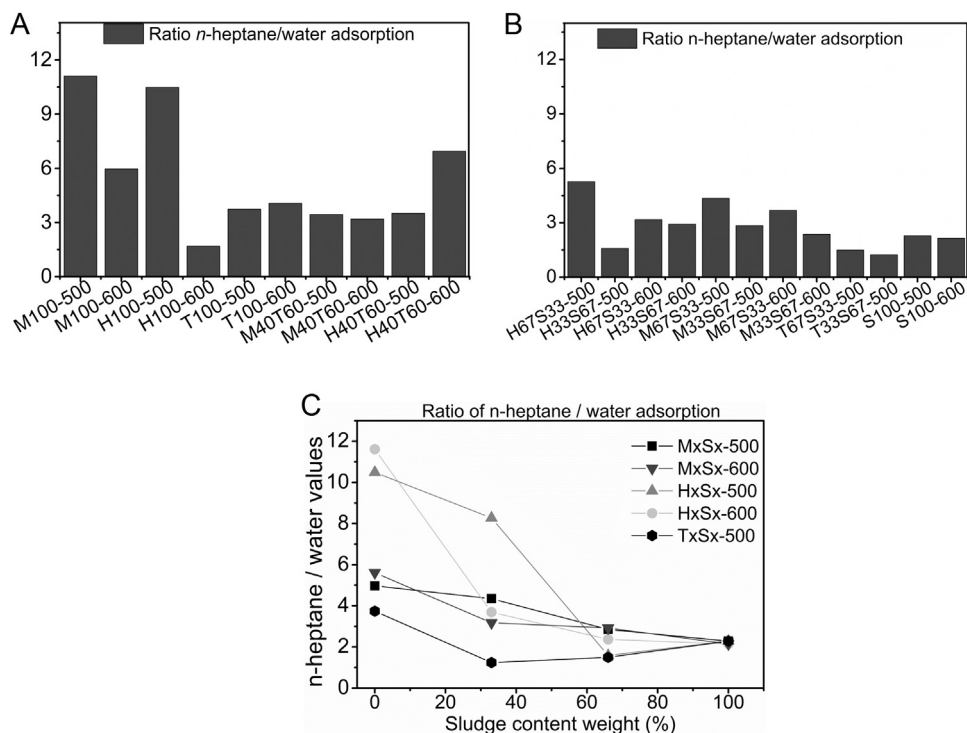


Fig. 6. (A) and (B) Ratio of *n*-heptane and water adsorption values and (C) influence of sludge content of the samples on the *n*-heptane and water adsorption.

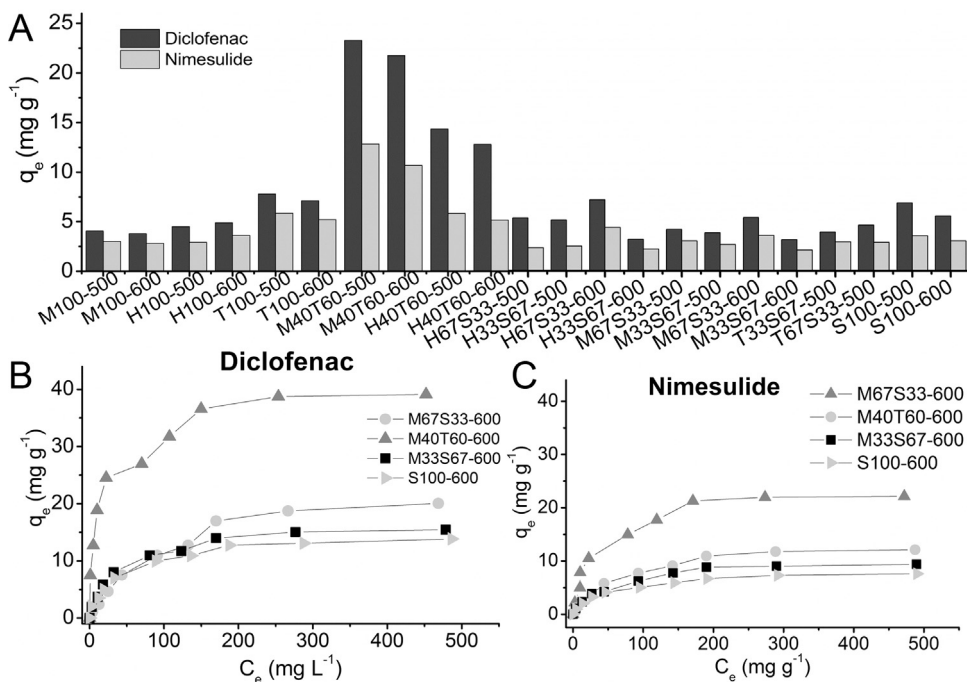


Fig. 7. (A)  $Q_{max}$  of diclofenac and nimesulide adsorptions of the synthesized adsorbents: (Conditions: initial concentration = 50 mg L<sup>-1</sup>; adsorbent mass of 40 mg; contact time of 120 min, and temperature of 25 °C) (B) isotherms of selected materials for diclofenac and (C) isotherms of selected materials for nimesulide: (Conditions: initial concentration ranging from 5 to 500 mg L<sup>-1</sup>; adsorbent mass of 40 mg; contact time of 120 min, and temperature of 25 °C).

M67S33-600, M40T60-600, M33S67-600 and S100-600 were chosen for DCF and NM adsorption isotherms because the samples exhibited best results on the basis of their highest adsorption capacities (at initial concentration of 500 mg L<sup>-1</sup>) for the two pharmaceuticals (see Fig. 7B and C).

The isotherm curves are shown in Supplementary Fig. 5A–H with their parameters in Table 2. On the basis of  $R^2_{adj}$  and SD val-

ues (see Table 2), the Sips model is the best isotherm model for adsorption of DCF and NM on materials. The Sips model presents the highest  $R^2_{ad}$  and lowest values for SD—it means that the values of  $q$  calculated by the isotherm model was closer to the  $q$  measured experimentally [32–35]. The maximum adsorption capacity values ( $Q_{max}$ ) of DCF and NM adsorbed were 41.43 and 26.12 mg g<sup>-1</sup> for M40T60-600 and 27.18 and 14.25 for M67S33-600, respectively.

**Table 2**

Isotherm parameters of DCF and NM adsorption using S100-600, M67S33-600, M33S67-600 and M40T60-600 adsorbents. Conditions: pH 7.0 for DCF and 9.0 for NM; adsorbent mass, 40.0 mg; contact time of 120 min. All values are expressed in four significant digits.

	S100-600	M67S33-600	M33S67-600	M40T60-600
<b>DCF</b>				
Langmuir				
$Q_{\max}$ (mg g <sup>-1</sup> )	14.72	25.57	16.47	37.60
$K_L$ (L mg <sup>-1</sup> )	0.02646	0.009051	0.02772	0.09118
$R^2_{\text{adj}}$	0.9913	0.9887	0.9906	0.9504
SD (mg g <sup>-1</sup> )	0.4321	0.7954	0.5407	3.039
Freundlich				
$K_F$ (mg g <sup>-1</sup> (mg L <sup>-1</sup> ) <sup>-1/nF</sup> )	2.161	1.331	2.455	10.64
$n_F$	3.155	2.177	3.161	4.390
$R^2_{\text{adj}}$	0.9563	0.9486	0.9501	0.9642
SD (mg g <sup>-1</sup> )	1.044	1.958	1.251	2.582
Sips				
$Q_{\max}$ (mg g <sup>-1</sup> )	16.27	27.18	18.01	41.43
$K_g$ (L mg <sup>-1</sup> )	0.2001	0.2155	0.02165	0.02814
$n_i$	1.236	0.5823	1.211	2.010
$R^2_{\text{adj}}$	0.9940	0.9999	0.9928	0.9823
SD (mg g <sup>-1</sup> )	0.3854	0.7887	0.4750	1.815
<b>NM</b>				
Langmuir				
$Q_{\max}$ (mg g <sup>-1</sup> )	8.196	14.21	10.65	23.53
$K_L$ (L mg <sup>-1</sup> )	0.02163	0.01427	0.01828	0.03323
$R^2_{\text{adj}}$	0.9902	0.9927	0.9871	0.9780
SD (mg g <sup>-1</sup> )	0.2645	0.3850	0.3928	1.248
Freundlich				
$K_F$ (mg g <sup>-1</sup> (mg L <sup>-1</sup> ) <sup>-1/nF</sup> )	1.068	1.260	1.222	3.642
$n_F$	3.055	2.595	2.865	13.56
$R^2_{\text{adj}}$	0.9641	0.9497	0.9457	0.9368
SD (mg g <sup>-1</sup> )	0.5081	1.013	0.8063	2.116
Sips				
$Q_{\max}$ (mg g <sup>-1</sup> )	9.438	14.55	11.38	26.12
$K_g$ (L mg <sup>-1</sup> )	0.01465	0.01345	0.01546	0.02409
$n_i$	1.2965	1.045	1.404	1.247
$R^2_{\text{adj}}$	0.9999	0.9928	0.9876	0.9799
SD (mg g <sup>-1</sup> )	0.1855	0.4071	0.3914	1.192

Moreover, Langmuir model presents values closer to those of Sips model. On the other hand, the Freundlich model presents the highest  $SD$ , which indicates that the model is not suitable for the description of removal of DCF and NM onto composite materials in this work. The results indicate that the adsorbents possess relatively higher monolayer capacity for DCF and NM. Moreover, the applicability of Langmuir adsorption isotherm indicates that the surface active sites are distributed evenly onto the solid surface.

According to the data, M40T60-600 has highest adsorption capacities for DCF and NM, followed by M67S33-600, M33S67-600 and S100-600 (see Supplementary Fig. 5 and Table 2). M40T60-600 sample presents the highest  $S_{\text{BET}}$  value among these samples, and it is well-known that the  $S_{\text{BET}}$  values might influence the fast uptake of molecules of DCF and NM because  $S_{\text{BET}}$  value is one of the most important factors that influence the efficiency of adsorption process [14,18,25,36–41].

So far, various adsorbents have been reported for the adsorption of DCF and NM; therefore, it is meaningful to check the competitiveness of the adsorbents used in this work against other adsorbents that have earlier reported. Table 3 shows a comparison between the maximum adsorption capacities various adsorbents. As can be seen in Table 3, our adsorbent materials present very good adsorption capacities compared with other adsorbents reported in the literature. The reason for differences in adsorption capacities of micropollutants might be linked to the different experimental conditions such as the concentration of micropollutants and adsorbent, contact time, pH, and the water source. Therefore, a direct comparison is difficult to make because different adsorbents and experimental conditions were used [34–36,40–48]. However, these

**Table 3**

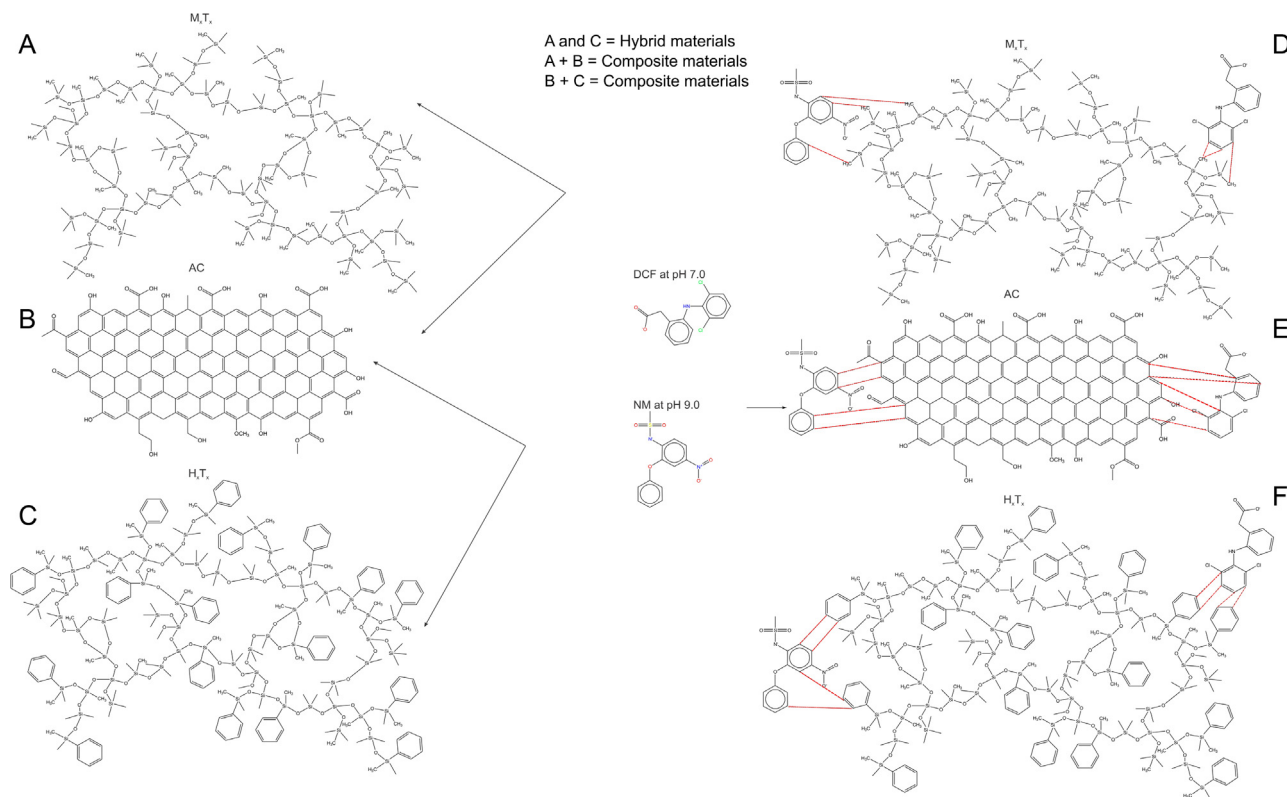
Comparison of adsorption capacities of different adsorbents for DCF and NM.

Adsorbent	Adsorption capacity (mg g <sup>-1</sup> )		
	DCF	NM	Reference
Multi-walled carbon nanotubes	8.640	–	[35]
Activated carbon from cocoa shell	63.47	74.81	[36]
Hybrid adsorbents (sericite + HDTMA)	2.290	–	[42]
Hybrid materials (Bentonite + HDTMA)	17.79	–	[43]
Functionalized silica	35.59	–	[44]
Modified chitosan	9.330	–	[45]
Trimethylsilylated SBA-15	0.8381	–	[46]
Silica aerogel	–	14.18	[47]
Activated carbon from olive-waste cakes	56.2	–	[48]
M40T60-600	41.43	26.12	This work
M67S33-600	27.18	14.55	This work
M33S67-600	18.01	11.38	This work
S100-600	16.27	9.438	This work

results have demonstrated that our hybrid and composite materials exhibit good removal capacities of pharmaceuticals from aqueous solutions.

### 3.7. Adsorption mechanism

Going by the combined data of characterization of materials as well as the equilibrium studies, it is possible to suggest mechanisms for adsorption of DCF and NM onto hybrid and composite adsorbents. The adsorption process involves physical interactions such as van der Waals' interactions, and  $\pi$ - $\pi$  interactions of the aromatic rings of the adsorbent with the aromatic rings of the pharmaceuti-



**Fig. 8.** Proposed adsorption mechanism for adsorption of DCF and NM onto the hybrid and composite materials.

cal [36]. The aromatic rings of pharmaceuticals interact with the phenyl and methyl groups of the pure polysiloxanes through  $\pi$ - $\pi$  interactions, and with functional groups of the composite adsorbents such as OH, C=O, COOH as shown in Fig. 8A–F. Similarly, some electrostatic attractions could occur between the charged pharmaceuticals (DCF at pH 7.0 and NM at pH 9.0) with some defects of silicate structure.

#### 4. Conclusion

In this study, novel adsorbents were synthesized by mixing polysiloxanes with sewage sludge under reflux in ethanol. Single and binary mixtures with different sludge contents and without sludge were investigated. All samples were analyzed and classified as microporous materials, and  $S_{\text{BET}}$  values up to  $641 \text{ m}^2 \text{ g}^{-1}$  were observed. The  $S_{\text{BET}}$  values of sludge-containing samples decreased with increasing sludge content. Water and *n*-heptane, with either mainly polar or dispersive interaction, were used to ascertain the surface characteristics.

The materials were more hydrophobic according to the ratio of *n*-heptane and water adsorption values. However, high sludge content was responsible for a decrease in hydrophobicity of the samples.

The optimum pH values for adsorption of DCF and NM onto hybrid and composite materials were pH 7.0 and 9.0, respectively. Sips isotherm model gave the best fit of equilibrium data. The  $Q_{\text{max}}$  values for respective DCF and NM adsorbed were 41.43 and  $26.12 \text{ mg g}^{-1}$  for M40T60-600 and 27.18 and 14.25 for M67S33-600. The data showed that DCF exhibited uptake values higher than those of NM—signifying the affinity of the adsorbents towards more hydrophobic adsorbate.

Combination of sewage sludge with polysiloxanes to produce new composite adsorbents can bring several benefits to the environment and reduce the production and water treatment costs. The

potential benefits of employing sewage sludge in adsorbents production are apparent because it is an effective solution for a safe environment, beneficial re-use and also add value to this waste.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.colsurfa.2016.03.021>.

#### References

- [1] M.E. Bautista, L. Pérez, M.T. García, S. Cuadros, A. Marsal, Valorization of tannery wastes: lipoamino acid surfactant mixtures from the protein fraction of process wastewater, *Chem. Eng. J.* 262 (2015) 399–408.
- [2] G.S. dos Reis, M. Wilhelm, T.C.A. Silva, K. Rezwan, C.H. Sampaio, E.C. Lima, S.M.A.G.U. Souza, The use of design of experiments for the evaluation of the production of surface-rich activated carbon from sewage sludge via microwave and conventional pyrolysis, *Appl. Therm. Eng.* 93 (2016) 590.
- [3] J.A. Cusidó, L.V. Cremades, C. Soriano, M. Devant, Incorporation of paper sludge in clay brick formulation: ten years of industrial experience, *Appl. Clay Sci.* 5105 (2015) 191–198.
- [4] H. Li, Z. Sun, L. Zhang, Y. Tian, G. Cui, S. Yan, A cost-effective porous carbon derived from pomelo peel for the removal of methyl orange from aqueous solution, *Colloids Surf. A Physicochem. Eng. Asp.* 489 (2016) 191–199.

- [5] U. Morali, S. Sensöz, Pyrolysis of hornbeam shell (*Carpinusbetulus* L.) in a fixed bed reactor: characterization of bio-oil and bio-char, *Fuel* 150 (2015) 672–678.
- [6] D. Vamvuka, S. Sfakiotakis, S. Saxioni, Evaluation of urban wastes as promising co-fuels for energy production—a TG/MS study, *Fuel* 147 (2015) 170–183.
- [7] S. Fedorenko, M. Jilkin, N. Nastapova, V. Yanilkin, O. Bochkova, V. Buriliov, I. Nizameev, G. Nasretudinova, M. Kadirov, A. Mustafina, Y. Budnikova, Surface decoration of silica nanoparticles by Pd(0) deposition for catalytic application in aqueous solutions, *Colloids Surf. A Physicochem. Eng. Asp.* 486 (2015) 185–191.
- [8] M. Wilhelm, C. Soltmann, D. Koch, G. Grathwohl, Ceramers—functional materials for adsorption techniques, *J. Eur. Ceram. Soc.* 25 (2005) 271–276.
- [9] T. Prenzel, M. Wilhelm, K. Rezwan, Tailoring amine functionalized hybrid ceramics to control CO<sub>2</sub> adsorption, *Chem. Eng. J.* 235 (2014) 198–206.
- [10] J. Yin, B. Deng, Polymer-matrix nanocomposite membranes for water treatment, *J. Membr. Sci.* 479 (2015) 256–275.
- [11] T. Li, Z. Zhang, W. Li, C. Liu, J. Wang, L. An, H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub>/polymethylmethacrylate-polyvinyl alcohol sandwich nanofibrous membrane with enhanced photocatalytic activity, *Colloids Surf. A Physicochem. Eng. Asp.* 489 (2016) 289–296.
- [12] V. Lauth, M. Maas, K. Rezwan, Coacervate-directed synthesis of CaCO<sub>3</sub> microcarriers for pH-responsive delivery of biomolecules, *J. Mater. Chem. B* 44 (2014) 7725–7735.
- [13] R. Bryaskova, N. Georgieva, D. Pencheva, Z. Todorova, N. Lazarova, T. Kantardjiev, Synthesis and characterization of hybrid materials with embedded silver nanoparticles and their application as antimicrobial matrices for waste water purification, *Colloids Surf. A Physicochem. Eng. Asp.* 444 (2014) 114–119.
- [14] W. Wei, R. Sun, J. Cui, Z.G. Wei, Removal of nitrobenzene from aqueous solution by adsorption on nanocrystalline hydroxyapatite, *Desalination* 263 (2010) 89–96.
- [15] M. Arshadi, F.S. Vahid, J.W.L. Salvacion, M. Soleymanzadeh, A practical organometallic decorated nano-size SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub>, mixed-oxides for methyl orange removal from aqueous solution, *Appl. Surf. Sci.* 280 (2013) 726–736.
- [16] D.-G.W. Cheng, X. Jin, F. Zhan Chen, Alumina membrane coated activated carbon: a novel strategy to enhance the mechanical properties of a solid catalyst, *RSC Adv.* 6 (2016) 10229–10232.
- [17] T. Prenzel, M. Wilhelm, K. Rezwan, Pyrolyzedpolysiloxane membranes with tailorably hydrophobicity, porosity and high specific surface area, *Microporous Mesoporous Mater.* 169 (2013) 160–167.
- [18] T. Prenzel, T.L.M. Guedes, F. Schlüter, M. Wilhelm, K. Rezwan, Tailoring surfaces of hybrid ceramics for gas adsorption—from alkanes to CO<sub>2</sub>, *Sep. Pur. Technol.* 129 (2014) 80–89.
- [19] C. Racles, M. Mares, L. Sacarescu, A polysiloxane surfactant dissolves a poorly soluble drug (nystatin) in water, *Colloids Surf. A Physicochem. Eng. Asp.* 443 (2014) 223–239.
- [20] M. Arshadi, M. Ghiaci, Highly efficient solvent free oxidation of ethylbenzene using some recyclable catalysts: the role of linker in competency of manganese nanocatalysts, *Appl. Catal. A: Gen.* 399 (2011) 75–86.
- [21] L. Jiang, Y. He, J. Luo, Chemical mechanical polishing of steel substrate using colloidal silica-based slurries, *Appl. Surf. Sci.* 330 (2015) 487–495.
- [22] M.E. Mahmoud, S.S. Haggag, T.M. Abdel-Fattah, Synthesis characterization and metal chelating properties of silica-physisorbed and chemisorbed-2,5-dioxypiperazine, *Polyhedron* 26 (2007) 3956–3962.
- [23] T. Ogawa, J. Watana, K. Eguchi, Y. Oshima, Synthesis of polysiloxane-modified silica hybrid particles by a high temperature water technology, *Polymer* 51 (2010) 2836–2842.
- [24] J.P. Blitz, V.M. Gunko, R. Samala, B.A. Lawrence, Mixed bifunctional surface-modified silicas using tethered aminofunctional silane catalysts, *Colloids Surf. A Physicochem. Eng. Asp.* 462 (2014) 1–8.
- [25] H.Y. Wu, F.K. Shieh, H.M. Kao, Y.W. Chen, J.R. Deka, S.H. Liao, K.C.-W. Wu, Synthesis bifunctionalization, and remarkable adsorption performance of benzene-bridged periodic mesoporous organosilicas functionalized with high loadings of carboxylic acids, *Chem. Eur. J.* 19 (2013) 6358–6367.
- [26] Z. Wu, L. Kong, H. Hu, S. Tian, Y. Xiong, Adsorption performance of hollow spherical sludge carbon prepared from sewage sludge and polystyrene foam wastes, *ACS Sustain. Chem. Eng.* 3 (2015) 552–558.
- [27] I. Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum, *J. Am. Chem. Soc.* 40 (1918) 1361–1403.
- [28] H. Freundlich, Adsorption in solution, *Phys. Chem. Soc.* 40 (1906) 1361–1368.
- [29] R. Sips, Combined form of Langmuir and Freundlich equations, *J. Chem. Phys.* 16 (1948) 490–495.
- [30] M.C. Ribas, M.A. Adebayo, L.D.T. Prola, E.C. Lima, R. Cataluña, L.A. Feris, F.M. Machado, F.A. Pavan, T. Calvete, Comparison of a homemade cocoa shell activated carbon with commercial activated carbon for the removal of reactive violet 5 dye from aqueous solutions, *Chem. Eng. J.* 248 (2014) 315–326.
- [31] E.J. Bottani, J.M.D. Tascón, *Adsorption by carbons, first ed.*, Oxford (2008).
- [32] M. Scheffler, T. Gambaryan-Roisman, T. Takahashi, J. Kaschta, H. Muenstedt, P. Buhler, P. Greil, Pyrolytic decomposition of preceramic organo polysiloxanes, *Ceram. Trans.* 115 (2000) 239–250.
- [33] S. Rovani, M.T. Censi, S.L. Pedrotti Jr., E.C. Lima, R. Cataluña, A.N. Fernandes, Development of a new adsorbent from agro-industrial waste and its potential use in endocrine disruptor compound removal, *J. Hazard. Mater.* 271 (2014) 311–320.
- [34] L. Yang, Z. Wei, W. Zhong, J. Cui, W. Wei, Modifying hydroxyapatite nanoparticles with humic acid for highly efficient removal of Cu(II) from aqueous solution, *Colloids Surf. A Physicochem. Eng. Asp.* 490 (2016) 9–21.
- [35] X. Hu, Z. Cheng, Removal of diclofenac from aqueous solution with multi-walled carbon nanotubes modified by nitric acid, *Chin. J. Chem. Eng.* 23 (2015) 1551–1556.
- [36] C. Saucier, M.A. Adebayo, E.C. Lima, R. Cataluña, P.S. Thue, L.D.T. Prola, M.J. Puchana-Rosero, F.M. Machado, F.A. Pavan, G.L. Dotto, Microwave-assisted activated carbon from cocoa shell as adsorbent for removal of sodium diclofenac and nimesulide from aqueous effluents, *J. Hazard. Mater.* 289 (2015) 18–27.
- [37] J. Liu, W.Y. Li, Y.G. Liu, Q.H. Zeng, S. Hong, Titanium(IV) hydrate based on chitosan template for defluoridation from aqueous solution, *Appl. Surf. Sci.* 293 (2014) 46–54.
- [38] M.A. Adebayo, L.D.T. Prola, E.C. Lima, M.J. Puchana-Rosero, R. Cataluña, C. Saucier, C.S. Umpierrez, J.C.P. Vagheti, L.G. da Silva, L. Ruggiero, Adsorption of Procion Blue MX-R dye from aqueous solutions by lignin chemically modified with aluminium and manganese, *J. Hazard. Mater.* 268 (2014) 43–50.
- [39] L.D.T. Prola, F.M. Machado, C.P. Bergmann, F.E. de Souza, C.R. Gally, E.C. Lima, M.A. Adebayo, S.L.P. Dias, T. Calvete, Adsorption of direct blue 53 dye from aqueous solutions by multi-walled carbon nanotubes and activated carbon, *J. Environ. Manag.* (130) (2013) 166–175.
- [40] L.D.T. Prola, E. Acayanka, E.C. Lima, C.S. Umpierrez, J.C.P. Vagheti, W.O. Santos, S. Lamini, P.T. Djifon, Comparison of *Jatropha curcas* shells in natural form and treated by non-thermal plasma as biosorbents for removal of Reactive Red 120 textile dye from aqueous solution, *Ind. Crop. Prod.* 46 (2013) 328–340.
- [41] T. Calvete, E.C. Lima, N.F. Cardoso, J.C.P. Vagheti, S.L.P. Dias, F.A. Pavan, Application of carbon adsorbents prepared from Brazilian-pine fruit shell for the removal of reactive orange 16 from aqueous solution: kinetic, equilibrium, and thermodynamic studies, *J. Environ. Manag.* 91 (2010) 1695–1706.
- [42] D. Tiwari, C. Lalhriatpuia, S.-M. Lee, Hybrid materials in the removal of diclofenac sodium from aqueous solutions: batch and column studies, *J. Ind. Eng. Chem.* 30 (2015) 167–173.
- [43] D. Tiwari, Efficient use of hybrid materials in the remediation of aquatic environment contaminated with micro-pollutant diclofenac sodium, *Chem. Eng. J.* 263 (2015) 364–373.
- [44] N. Suriyanon, P. Punyapalalul, C. Ngamcharussrivichai, Mechanistic study of diclofenac and carbamazepine adsorption on functionalized silica-based porous materials, *Chem. Eng. J.* 214 (2013) 208–218.
- [45] K.A.A. Pereira, L.R. Osório, M.P. Silva, K.S. Sousa, E.C.S. Filho, Chemical modification of chitosan in the absence of solvent for diclofenac sodium removal: pH and kinetics studies, *Mater. Res.* 17 (2014), 1516–1439.
- [46] T.X. Bui, V.H. Pham, S.T. Le, H. Choi, Adsorption of pharmaceuticals onto trimethylsilylated mesoporous SBA-15, *J. Hazard. Mater.* 254–255 (254) (2013) 345–353.
- [47] G. Caputo, M. Scognamiglio, I. De Marco, Nimesulide adsorbed on silica aerogel using supercritical carbon dioxide, *Chem. Eng. Res. Des.* 90 (2012) 1082–1089.
- [48] R. Baccar, M. Sarrà, M. Bouzid, P. Blázquez, Removal of pharmaceutical compounds by activated carbon prepared from agricultural by-product, *Chem. Eng. J.* 211–212 (2012) 310–317.

## Supplementary Material

### **Preparation of novel adsorbents based on combinations of polysiloxanes and sewage sludge**

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#### *Quality assurance and statistical evaluation of models*

All the experiments were carried out in triplicate to ensure reproducibility, reliability and accuracy of the experimental data. The relative standard deviations of all measurements were below 5% [30]. Blanks were run in parallel and corrected when necessary [30].

The solutions of pharmaceuticals were stored in glass bottles, which were cleaned by immersing in 1.4 mol L<sup>-1</sup> HNO<sub>3</sub> for 24 h [30], rinsing with deionised water, drying and storing them in a suitable cabinet.

Standard pharmaceuticals solutions (between 10.00 and 220.0 mg L<sup>-1</sup>) were used for calibration in parallel with a blank (aqueous solution, a function of pH of the dye solution being measured). The linear analytical calibration curve was performed on the UV-Win software of the T90+ PG Instruments spectrophotometer. All the analytical measurements were carried out in triplicate, and the precisions of the standards were better than 3 % (n=3). The detection limit of DCF and NM was 0.14 mg L<sup>-1</sup> with a signal/noise ratio of 3 [30]. A 80.0 mg L<sup>-1</sup> of standard dye solution was used as a quality control after every five measurements to ensure accuracy of the DCF and NM solutions [30].

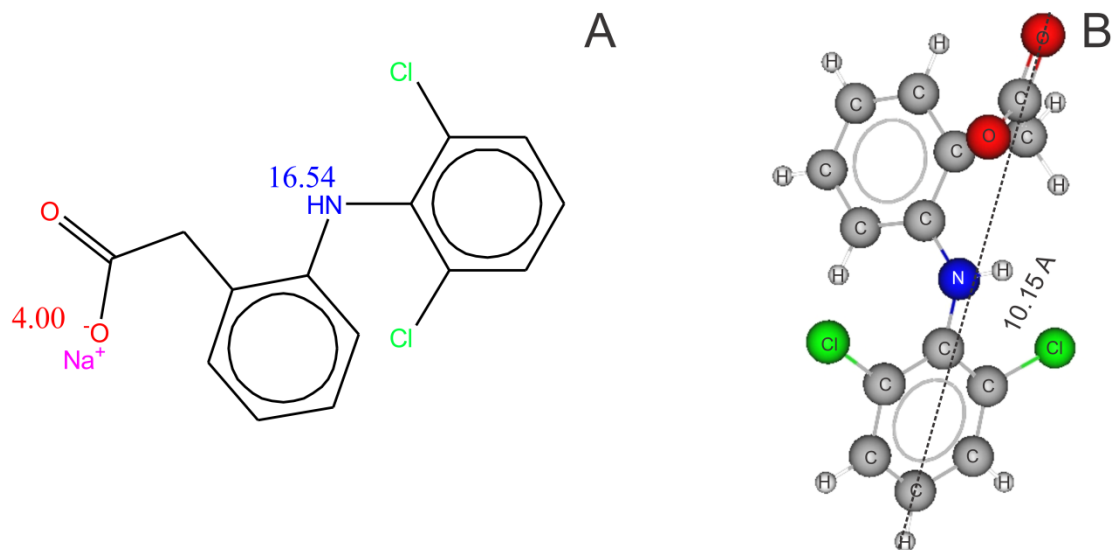
Nonlinear methods with successive interactions calculated by the Levenberg–Marquardt method were used to fit the kinetic and equilibrium data. Interactions were also evaluated using Simplex method, based on the nonlinear fitting facilities of the Microcal Origin 9.0 software. A determination coefficient ( $R^2$ ), an adjusted determination coefficient ( $R^2_{adj}$ ) and the standard deviation (SD) were used to evaluate the suitability of the models [30]. Standard deviation is a measure of the differences between the theoretical and experimental amounts of dye adsorbed. The  $R^2$ ,  $R^2_{adj}$  and  $SD$  are represented in Equations S1, S2 and S3, respectively.

$$R^2 = \left( \frac{\sum_i^n (q_{i,exp} - \bar{q}_{i,exp})^2 - \sum_i^n (q_{i,exp} - q_{i,model})^2}{\sum_i^n (q_{i,exp} - \bar{q}_{i,exp})^2} \right) \quad (S1)$$

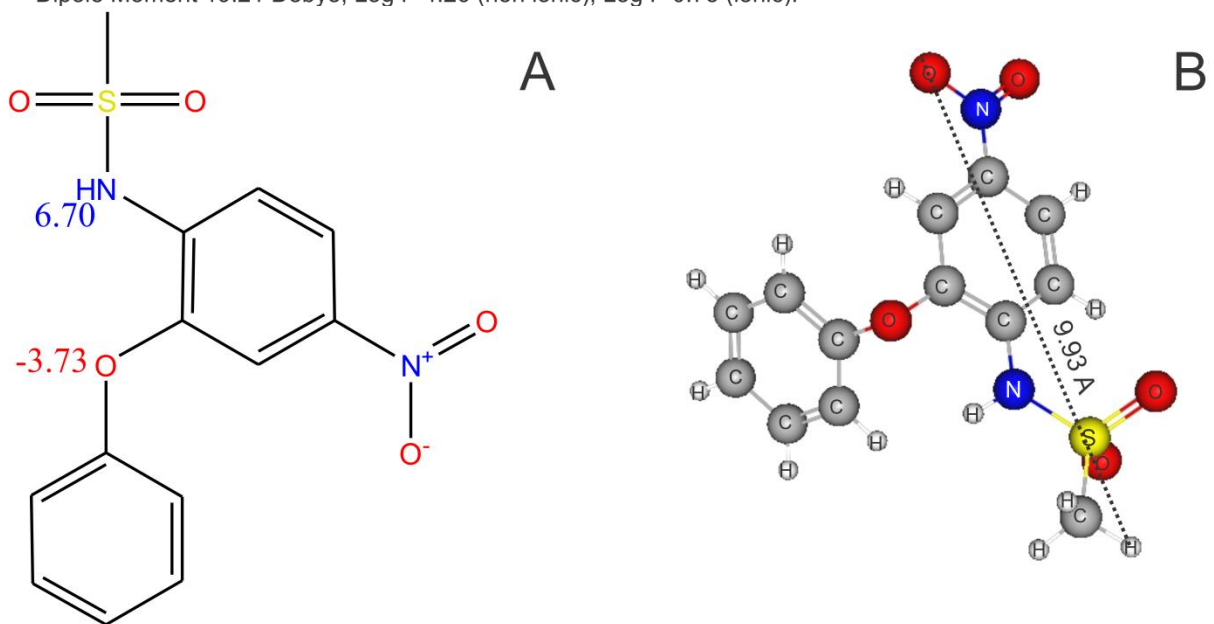
$$R^2_{adj} = 1 - (1 - R^2) \cdot \left( \frac{n-1}{n-p-1} \right) \quad (S2)$$

$$SD = \sqrt{\left( \frac{1}{n-p} \right) \cdot \sum_i^n (q_{i,exp} - q_{i,model})^2} \quad (S3)$$

In these equations,  $q_{i,model}$  represents individual theoretical  $q$  value predicted by the model;  $q_{i,exp}$  represents individual experimental  $q$  value;  $\bar{q}_{i,exp}$  is the average of experimental  $q$  values;  $n$  represents the number of experiments;  $p$  represents the number of parameters in the fitting model [30].

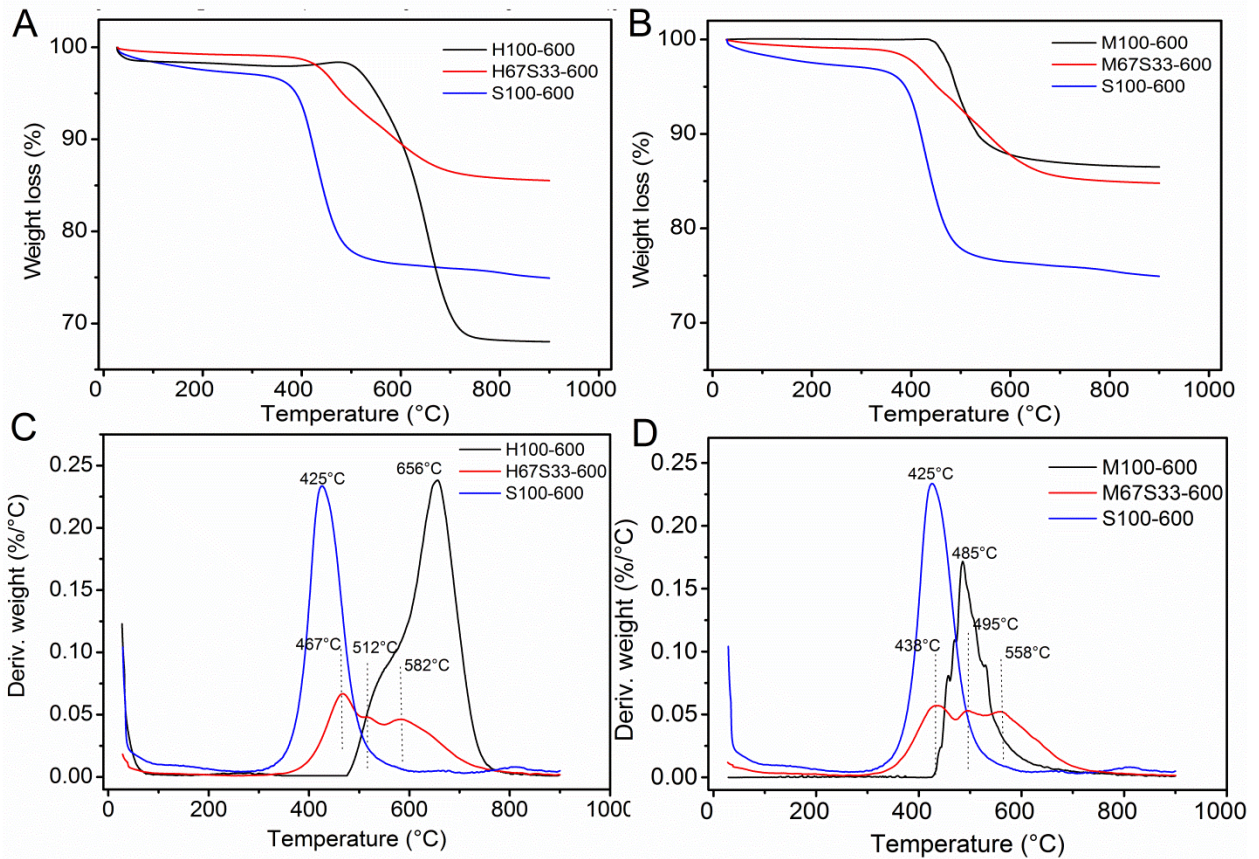


**Supplementary Fig 1: (A) Structural formula of DCF; (B) Optimized three-dimensional structural formula of DCF.** The dimensions and physical-chemical properties of the chemical molecule was calculated using MarvinSketch version 16.1.11.0. Values of  $pK_a$  are given close to the atom. Hydrophilic-lipophilic balance (HLB) 21.92; Van der Waals surface area =  $359.64 \text{ \AA}^2$  (pH 4.0-14.0); Polar surface area  $52.16 \text{ \AA}^2$  (pH 4.0-14.0); Dipole Moment 19.21 Debye, Log P 4.26 (non ionic); Log P 0.73 (ionic).

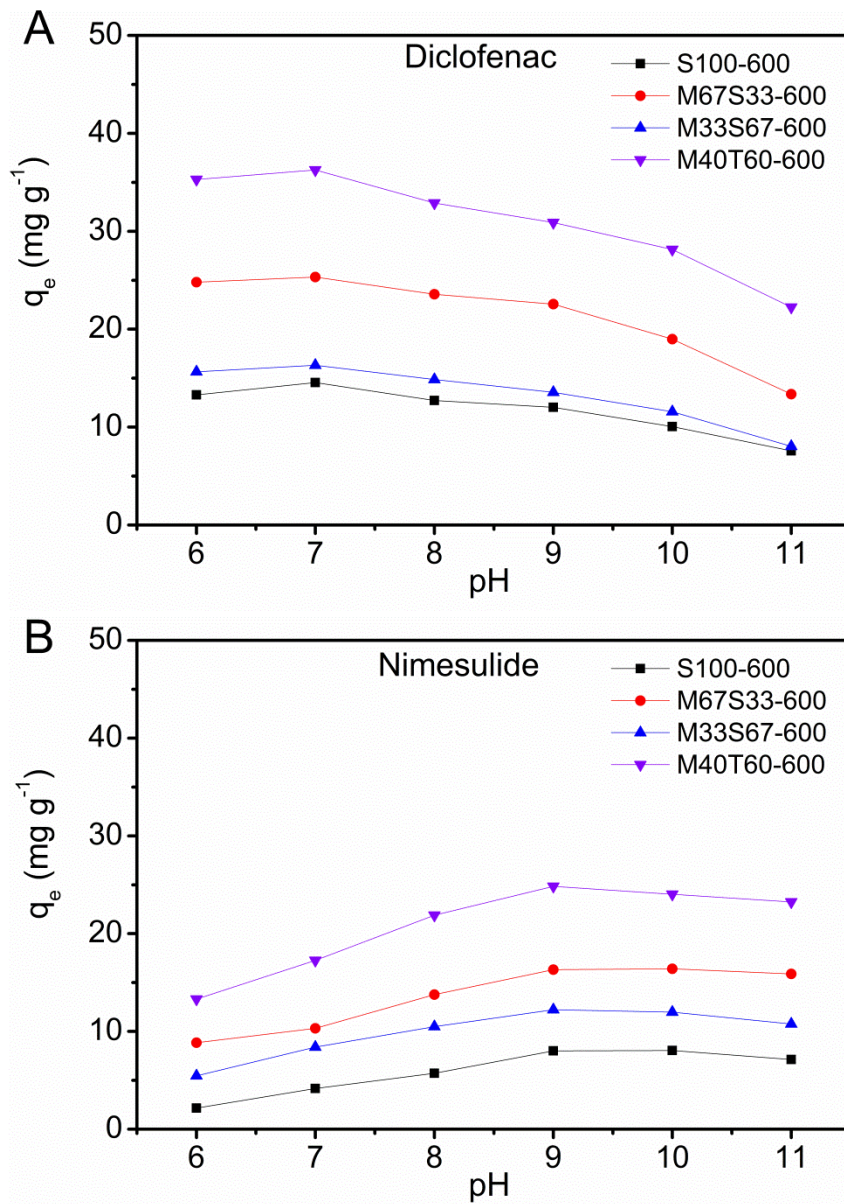


**Supplementary Fig 2: (A) Structural formula of NM; (B) Optimized three-dimensional structural formula of NM.** The dimensions and physical-chemical properties of the chemical molecule was calculated using MarvinSketch version 16.1.11.0. Values of  $pK_a$  are given close to the atom. Hydrophilic-lipophilic balance (HLB) 5.02 Van der Waals surface area =  $406.46 \text{ \AA}^2$  (pH 7.0-14.0); Polar surface area  $104.12 \text{ \AA}^2$  (pH 7.0-14.0); Dipole Moment 11.52 Debye; Log P 1.79.

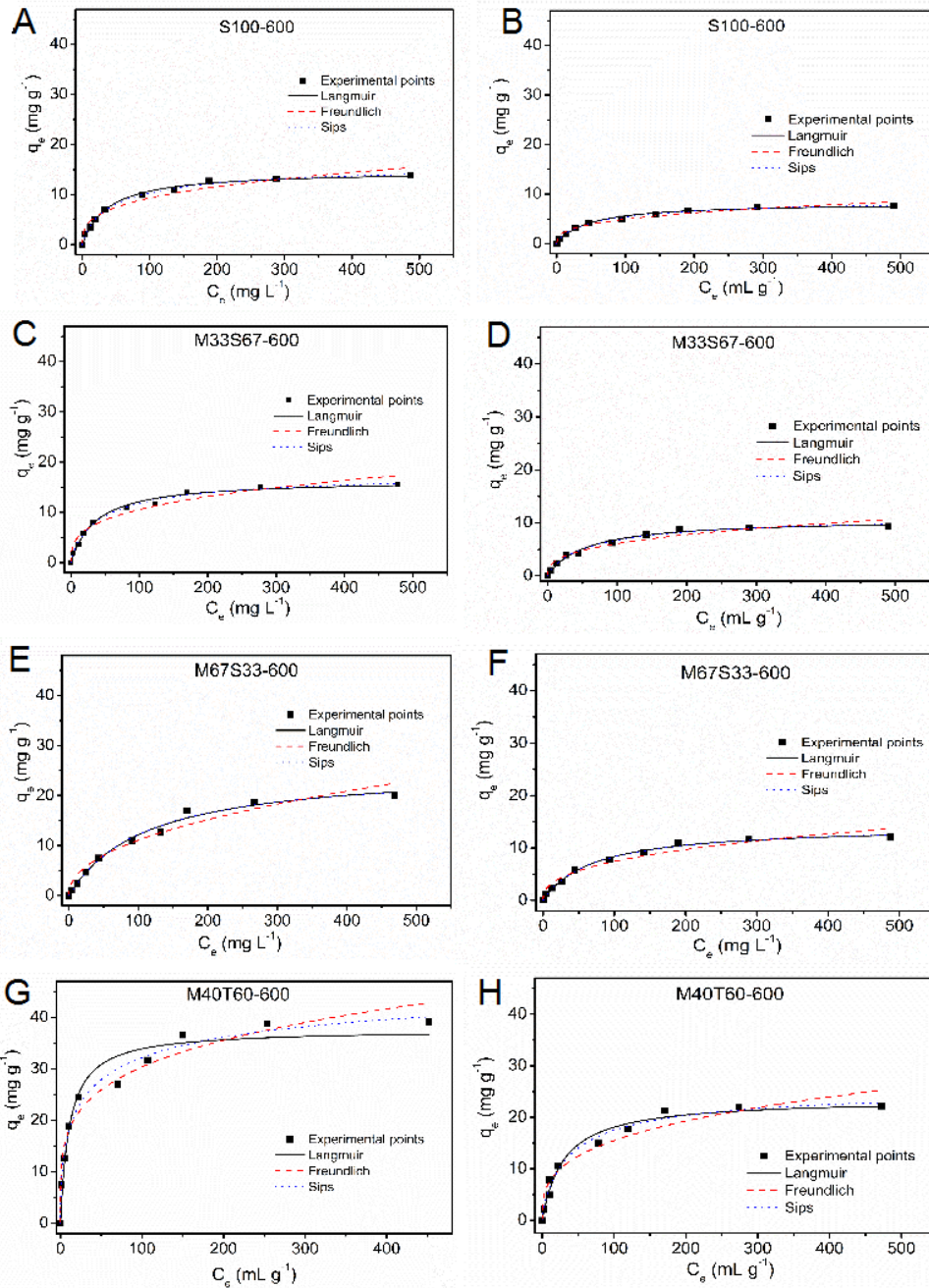




**Supplementary Fig.3.** TGA (A and B) and DTG (C and D) curves of polysiloxanes, sewage sludge and composite materials obtained by pyrolyzing at 600 °C.



Supplementary Fig. 4 - Effect of pH values on the removal of diclofenac and nimesulide onto composite and hybrid materials



**Supplementary Fig. 5** - Adsorption isotherm models fitting in the adsorption of diclofenac and nimesulide by hybrid materials

**Capítulo Sete:** *Activated carbon from sewage sludge for removal of sodium diclofenac and nimesulide from aqueous solutions*

# ***Capítulo Sete***

## Activated carbon from sewage sludge for removal of sodium diclofenac and nimesulide from aqueous solutions

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**Abstract**—Sludge based activated carbons (ACs) were used to remove selected pharmaceuticals such as diclofenac (DCF) and nimesulide (NM) from aqueous solutions. The powered sewage sludge was mixed with different proportions of ZnCl<sub>2</sub>. The mixture was pyrolyzed in a conventional oven using three different temperatures under inert atmosphere. Afterwards, in order to increase the specific surface area and uptake capacity the carbonized materials were acidified with 6 mol L<sup>-1</sup> HCl under reflux at 80 °C for 3 hours. The characterization of ACs was achieved by scanning electron microscopy, FTIR, TGA, hydrophobicity index by water, n-heptane vapor adsorption and nitrogen adsorption/desorption curves. The specific surface area ( $S_{BET}$ ) of adsorbents varied between 21.2 and 679.3 m<sup>2</sup> g<sup>-1</sup>. According to the water and n-heptane analysis data all ACs had hydrophobic surface. Experimental variables such as pH, mass of adsorbent and temperature on the adsorption capacities were studied. The optimum pH, mass of adsorbent and temperature for adsorption of DCF and NM onto ACs were found to be 7.0 (DCF) and 10.0 (NM), 30 mg and 25 °C, respectively. The kinetic adsorption was investigated using general-order, pseudo-first order and pseudo-second order kinetic models, while the general-order model described the adsorption process most suitably. The maximum amounts of DCF and NM adsorbed were 156.7 and 66.4 mg g<sup>-1</sup> for sample 1(500-15-0.5), respectively.

Keywords: Sewage Sludge, Activated Carbons, Adsorption of Pharmaceuticals, Water and n-Heptane Adsorptions, Adsorption Mechanism

### INTRODUCTION

Pharmaceuticals have caused increasing environmental concerns in recent years as they are a group of ubiquitous, persistent and biologically active compounds with recognized toxicities and endocrine disruption functions. Production and consumption of these products results in pharmaceutical-laden wastewaters [1-3] that must be treated before being discharged into the environment [2,4].

However, conventional wastewater and drinking water treatment processes are not designed to be efficient for removing pharmaceuticals at first instance [5-7]. Consequently, a vast number of these compounds have been detected in effluents of wastewater treatment plants (WWTPs), surface water, ground water, and even drinking water samples [7-9].

Recent studies have shown that several pharmaceuticals are suspected to be directly related to the toxicity of aquatic organisms [9,10]. Continual and undetectable effects, with chronic and accumulative potential, may result in irreversible consequences on wildlife and human beings [10,11]. Therefore, the need for development of an effective method of removing pharmaceuticals from water has

become very urgent [12].

Commonly used methods to remove these substances include filtration, ozonization, oxidation, precipitation, coagulation, and adsorption [1,13-17]. However, most of these methods are met with resistance due mainly to the high initial cost involved. In this context, in recent years, many studies have reported the use of the adsorption method for the removal of pharmaceutical substances in wastewater [1,2,16]. Adsorption is a common, and cost-effective, approach for solving many problems concerning the purification of pharmaceutical-laden wastewaters [1,2,18].

Adsorption is a process by which the pollutants are transferred from the effluent to a solid phase, thereby minimizing the bioavailability of the pollutants to the living organisms [19-21]. Another advantage of the adsorption process is that the adsorbents can be regenerated and reused [20-22].

Among the available adsorbents, activated carbons are known for their excellent adsorption characteristics because of their enhanced pore structures and higher specific surface area. This unique property makes activated carbons one of the materials most used for the treatment of industrial wastewaters [23-25]. The major determinants for the ability of activated carbons to adsorb pollutants from aqueous solutions are the nature of the organic material used to prepare the activated carbon and the experimental conditions of the activation processes [23,25].

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Adsorption using activated carbon has been reported as an effective method of eliminating micropollutants. Saucier et al. [2] showed that pharmaceuticals such as diclofenac and nimesulide were effectively removed by 97 and 98%, respectively, from water using cocoa shell activated carbon with a maximum adsorption capacity of 63.47 and 74.81 mg g<sup>-1</sup> to DCF and NM, respectively. In contrast, Sotelo et al. [18] reported high uptake values for the micropollutants such as caffeine (190.9 mg g<sup>-1</sup>) and sodium diclofenac (233.9 mg g<sup>-1</sup>) onto commercially available powdered activated carbon. Jung et al. [16] showed a higher maximum adsorption capacity value for sodium diclofenac, equal to 372 mg g<sup>-1</sup> by applying powdered activated carbon. The reason for various removal values of micropollutants in the previous researches might be the different experimental conditions used such as the concentration of micropollutants and adsorbent, contact time, pH, and the sample used [2,18,23].

This paper reports the preparation of activated carbons (ACs) from powdered sewage sludge by chemical activation with ZnCl<sub>2</sub> using different ZnCl<sub>2</sub>:sludge ratios of 0.5, 1.0 and 1.5. The ACs were pyrolyzed at three different conditions under inert atmosphere. Intending to increase the specific area of the ACs, the carbonized materials were acidified with 1.0 mol L<sup>-1</sup> of HCl to obtain chemi-

cally activated sludge based carbons. As far we know, for the first time, ACs prepared from sewage sludge were tested as adsorbents in the removal of pharmaceuticals such as sodium diclofenac (DCF) and nimesulide (NM) from aqueous solutions.

## MATERIALS AND METHODS

### 1. Solutions and Reagents

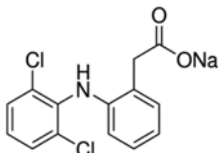
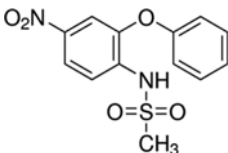
All solutions were prepared using deionized water. The diclofenac (DCF) and nimesulide (NM) (see Table 1) were supplied by Sigma Aldrich and used without purification. The ZnCl<sub>2</sub> was purchased from Vetec and was used for chemical activation of sewage sludge. The characteristics of the pharmaceuticals used on this study are shown in Table 1.

A 1.00 g L<sup>-1</sup> stock solution of DCF and NM was prepared by weighing and dissolving a calculated amount of the pharmaceuticals in deionized water. Different working solutions were prepared by diluting the stock solution.

### 2. Preparation of Sludge Derived Activated Carbons

The raw material used for preparing the activated carbon was the sewage sludge obtained from a municipal wastewater treatment

**Table 1. Chemical structure of used adsorbates in this study**

Sodium diclofenac (DFC)	Nimesulide (NM)
	
CAS 15307-79-6	CAS 21803-78-2
C <sub>12</sub> H <sub>10</sub> Cl <sub>2</sub> NNaO <sub>2</sub>	C <sub>13</sub> H <sub>12</sub> N <sub>2</sub> O <sub>2</sub> S
318.13 g·mol <sup>-1</sup>	308.31 g·mol <sup>-1</sup>
LogK <sub>ow</sub> =3.91	LogK <sub>ow</sub> =2.22
pKa=4.00	pKa=6.70
λ <sub>max</sub> =285 nm	λ <sub>max</sub> =392 nm
Van der Waals surface area=359.64 Å <sup>2</sup>	Van der Waals surface area=406.46 Å <sup>2</sup>
Polar surface area 52.16 Å <sup>2</sup>	Polar surface area 104.12 Å <sup>2</sup>
Dipole Moment 19.21 Debye	Dipole Moment 11.52 Debye
Polarizability 27.74	Polarizability 28.28

**Table 2. Overview of activated carbons prepared by pyrolysis at different conditions and their respective specific surface areas, pore volume and maximum adsorption values**

Samples	Pyrol (°C)	Holding time (min)	Ratio ZnCl <sub>2</sub> /sludge	S <sub>BET</sub> (mg <sup>2</sup> g <sup>-1</sup> )	V (cm <sup>3</sup> g <sup>-1</sup> )	q <sub>DCF</sub> (mg g <sup>-1</sup> )	q <sub>NM</sub> (mg g <sup>-1</sup> )
1- (500-15-0.5)	500	15	0.5	679.3	0.690	162.72	63.01
2- (800-15-0.5)	800	15	0.5	378.7	0.379	126.66	58.62
3- (500-60-0.5)	500	60	0.5	602.5	0.493	155.48	57.31
4- (800-60-0.5)	800	60	0.5	405.4	0.349	142.39	55.21
5- (500-15-1.5)	500	15	1.5	484.2	0.379	148.65	60.54
6- (800-15-1.5)	800	15	1.5	328.0	0.422	92.69	51.35
7- (500-60-1.5)	500	60	1.5	662.2	0.396	151.72	49.34
8- (800-60-1.5)	800	60	1.5	351.6	0.560	124.81	40.32
9- (650-37-1.0)	650	37	1.0	503.7	0.422	140.32	44.35
10- (500-15-0)	500	15	0.0	21.2	0.007	12.33	3.88

plant in Porto Alegre, RS - Brazil. First, the sludge was dried at 105 °C for 24 h until constant weight loss. Finally, it was crushed with a grinder and sieved to a size range below 300 µm. The preparation of the sludge-based ACs followed the three main steps presented by dos Reis et al. [23]:

a. 10.0 g of powdered sewage sludge was mixed with different amounts of ZnCl<sub>2</sub> to adjust different ratios of ZnCl<sub>2</sub>: sludge (see Table 2). Subsequently, 5.0 mL of water was added and thoroughly mixed, by hand, to obtain a homogeneous paste. The resulting paste was placed in a crucible and dried at room temperature for 24 h.

b. The samples were pyrolyzed at temperatures and holding times listed in Table 2. The pyrolysis processes were performed using flow of N<sub>2</sub> gas with flow rate of 100 mL min<sup>-1</sup> and at a constant heating rate of 5 °C min<sup>-1</sup> in a conventional furnace.

c. To complete the chemical activation, a leaching procedure was performed to eliminate the remaining ZnCl<sub>2</sub> of the pyrolyzed carbons, and to increase the specific area of the ACs [2,26]. The following procedure was employed [2,26]: 8.0 g of AC were added to 150 mL of 6 mol L<sup>-1</sup> HCl in a 250 mL reaction flask; the mixture was stirred on a magnetic stirrer under reflux for 3 h at 80 °C. Subsequently, the slurry was cooled and filtered under vacuum using a 0.45 µm membrane in a polycarbonate Sartorius system. After extensive washing with distilled water the solid material was oven dried at 110 °C for 5 h, and finally the carbon sample was milled in a mortar and the activated carbon was sieved to particle sizes ≤90 µm [2,26].

The pyrolyzed materials investigated in this study are listed in Table 2 and are denominated by different numbers. The first number refers to the temperature used in the pyrolysis followed by the holding time and ratio of ZnCl<sub>2</sub>: sludge. To give an example, the sample 1(500-15-0.5) was prepared at 500 °C with 15 minutes of holding time and a weight ratio of 0.5/1.0 of ZnCl<sub>2</sub>: sludge.

### 3. Characterization of the Activated Carbons

Nitrogen adsorption isotherms were recorded with a commercial system (Belsorp-Mini, Bel Japan Inc.) at -196 °C after drying for 3 h at 120 °C under reduced pressure (<2 mbar). The specific surface areas were determined from the Brunauer, Emmett and Teller (BET) method [27]. The pore size distributions were calculated from the desorption branch of the isotherms based on the Barrett-Joyner-Halenda (BJH) model [28].

Surface morphologies of selected samples were observed by using scanning electron microscopy (SEM) (JEOL microscope, model JSM 6060, Tokyo, Japan).

The functional groups of the adsorbents were assessed using Fourier Transform Infra-Red Spectroscopy (FTIR). The spectrum was recorded with 64 cumulative scans over the range of 4,000-400 cm<sup>-1</sup> with a resolution of 4 cm<sup>-1</sup> [29,30].

Thermogravimetric (TGA) analysis of adsorbents were obtained on a TA Instruments model SDT Q600 (New Castle, USA) with a heating rate of 20 °C min<sup>-1</sup> at 100 mL min<sup>-1</sup> of synthetic air flow. Temperature was varied from 20 °C to 1,000 °C (acquisition time of 1 point per 5 s) using 10.00-15.00 mg of solid.

For vapor adsorption experiments about 300.0 mg of powder adsorbent was dried in 10 mL beakers at 105 °C for 24 h. The samples were cooled in a desiccator before determining their accurate

weight (about 300.0 mg). Storage in an atmosphere of saturated solvent vapor was performed in Erlenmeyer flasks capped with glass caps (45/50 ground glass joint), using 60 ml of solvent (water or n-heptane). The dried powder samples inside the beakers were placed in such a way that they were not in contact with the wall of the Erlenmeyer flasks and kept at 25 °C under static conditions. The beakers containing the solid samples were removed from the Erlenmeyer flasks after 24 h, dried carefully from the outside with laboratory tissues. The weight gain during vapor solvent exposition was used to determine the maximal vapor uptake (of water or n-heptane).

### 4. Batch Adsorption Studies

Aliquots of 20.00 mL of 5.00-500.0 mg L<sup>-1</sup> of DCF and NM were added to 50 mL flat Falcon tubes containing varying amount of adsorbents (5.0-200.0 mg). The flasks were capped and placed horizontally in a shaker model TE-240, and the system was agitated for time between 5 and 360 min with temperature varying between 25 and 45 °C. Afterwards, in order to separate the adsorbents from the aqueous solutions, the flasks were centrifuged using a Fanem centrifuge, and aliquots of 1-5 ml of the supernatant were properly diluted to 20.0-100.0 ml in calibrated flasks using water [20, 31].

The residual solution after adsorption was quantified using UV/visible spectrophotometer (T90+ UV-VIS spectrophotometer, PG Instruments, London, United Kingdom), at a maximum wavelength of 275 and 392 nm, for DCF and NM, respectively.

The amount of DCF and NM removed by the activated carbons (q in mg g<sup>-1</sup>) and the percentage of removal (%Removal) were calculated with the aid of Eqs. (1) and (2), respectively:

$$q = \frac{(C_o - C_f)}{m} \cdot V \quad (1)$$

$$\% \text{Removal} = 100 \cdot \frac{(C_o - C_f)}{C_o} \quad (2)$$

where q is the amount of DCF and NM uptaken by the adsorbent (mg g<sup>-1</sup>); C<sub>o</sub> is the initial DCF and NM concentrations put in contact with the adsorbent (mg L<sup>-1</sup>), C<sub>f</sub> is the DCF and NM concentrations (mg L<sup>-1</sup>) after the batch adsorption procedure, V is the volume of DCF and NM solutions (L) put in contact with the adsorbent and m is the mass (g) of adsorbent.

### 5. Quality Assurance and Statistical Evaluation of Models

All the experiments were in triplicate to ensure reproducibility, reliability and accuracy of the experimental data. The relative standard deviations of all measurements were below 5%. Blanks were run in parallel and corrected when necessary [32].

The solutions of DCF and NM were stored in glass bottles, which were cleaned by immersion in 1.4 molL<sup>-1</sup> HNO<sub>3</sub> for 24 h [33], rinsing with deionized water, drying and storing them in a suitable cabinet.

Standard solutions of the pharmaceuticals (between 5.00 and 50.0 mg L<sup>-1</sup>) were used for calibration in parallel with a blank solution. A linear analytical calibration curve was performed on the UV-Win software of the T90+PG Instruments spectrophotometer. All the analytical measurements were in triplicate, and the precision of the standards was better than 3% (n=3) [34]. The detection

limit of pharmaceuticals were 0.14 mg L<sup>-1</sup> with a signal/noise ratio of 3 [35]. A 50.0 mg L<sup>-1</sup> of standard DCF and NM solutions were used for quality control after every five measurements to ensure accuracy of the pharmaceutical solutions [33].

The mathematical fitness of the kinetic and equilibrium data was done using nonlinear methods, which were evaluated using the Simplex method, and the Levenberg-Marquardt algorithm using the fitting facilities of the Microcal Origin 2015 software. A determination coefficient (R<sup>2</sup>), an adjusted determination coefficient (R<sub>adj</sub><sup>2</sup>) and the residual standard deviation (SD) were used to evaluate the suitability of the models [21,36]. Residual standard deviation is a measure of the differences between the theoretical and experimental amounts of DCF and NM adsorbed. The R<sup>2</sup>, R<sub>adj</sub><sup>2</sup> and SD are represented in Eqs. (3), (4) and (5), respectively.

$$R^2 = \left( \frac{\sum_i^n (q_{i, \text{exp}} - \bar{q}_{i, \text{exp}})^2 - \sum_i^n (q_{i, \text{exp}} - q_{i, \text{model}})^2}{\sum_i^n (q_{i, \text{exp}} - \bar{q}_{i, \text{exp}})^2} \right) \quad (3)$$

$$R_{\text{adj}}^2 = 1 - (1 - R^2) \cdot \left( \frac{n-1}{n-p-1} \right) \quad (4)$$

$$SD = \sqrt{\left( \frac{1}{n-p} \right) \cdot \sum_i^n (q_{i, \text{exp}} - q_{i, \text{model}})^2} \quad (5)$$

In these equations,  $q_{i, \text{model}}$  represents individual theoretical  $q$  values predicted by the model;  $q_{i, \text{exp}}$  represents individual experimental  $q$  values;  $\bar{q}_{\text{exp}}$  is the average of experimental  $q$  values;  $n$  represents the number of experiments;  $p$  represents the number of parameters in the fitting model [21,36].

## 6. Kinetic Models

According to the rate law, exponents of chemical reactions are mostly independent of the coefficients of chemical equations, but are sometimes related. This means that the order of a chemical reaction depends on the experimental data. To establish the general rate law equation for adsorption, the adsorption process on the surface of an adsorbent is considered to be the rate determining step [37,38]. Attention is now focused on the change in the effective number of active sites at the surface of adsorbent during adsorption instead of the concentration of adsorbate in bulk solution. Applying the reaction rate law to Eq. (6) gives the adsorption rate expression.

$$\frac{dq}{dt} = k_N (q_e - q_t)^n \quad (6)$$

where  $k_N$  is the rate constant;  $q_e$  is the amount of adsorbate adsorbed by adsorbent at equilibrium;  $q_t$  is the amount of adsorbate adsorbed by adsorbent at a given time,  $t$ ;  $n$  is the order of adsorption with respect to the effective concentration of the adsorption active sites present on the surface of the adsorbent. Application of the universal rate law to the adsorption process has led to Eq. (6), which can be used without assumptions. Theoretically, the exponent  $n$  in Eq. (6) can be an integer or non-integer rational number [37,38].

Eq. (7) describes the number of the active sites ( $\theta_t$ ) available on the surface of adsorbent for adsorption [37,38].

$$\theta_t = 1 - \frac{q_t}{q_e} \quad (7)$$

Eq. (8) describes the relationship between the variable ( $\theta_t$ ) and rates of adsorption.

$$\frac{d\theta_t}{dt} = -k\theta_t^n \quad (8)$$

Where  $k = k_N (q_e)^{n-1}$

For an unadsorbed adsorbent  $\theta_t = 1$ , which decreases during the adsorption process.  $\theta_t$  approaches a fixed value when the adsorption process reaches equilibrium. For a saturated adsorbent,  $\theta_t = 0$  [38].

Eq. (8) gives Eq. (9).

$$\int_1^{\theta_t} \frac{d\theta_t}{\theta_t^n} = -k \int_0^t dt \quad (9)$$

Similarly, Eq. (9) gives Eq. (10).

$$\frac{1}{1-n} \cdot [\theta_t^{1-n} - 1] = -kt \quad (10)$$

Eq. (10) gives Eq. (11) on rearrangement.

$$\theta_t = [1 - k(1-n) \cdot t]^{1/1-n} \quad (11)$$

Substituting Eq. (7) into Eq. (11), and replacing  $k = k_N (q_e)^{n-1}$ , Eq. (12) is obtained.

$$q_t = q_e - \frac{q_e}{[k_N (q_e)^{n-1} \cdot t \cdot (n-1) + 1]^{1/1-n}} \quad (12)$$

Eq. (12) is the general order kinetic equation of adsorption; valid for  $n \neq 1$  [38].

A special case of Eq. (8) is the pseudo-first order kinetic model ( $n=1$ ) [37,38].

$$\frac{d\theta_t}{dt} = -k \cdot \theta_t \quad (13)$$

Eq. (13) on integration gives Eq. (14).

$$q_t = \exp(-k \cdot t) \quad (14)$$

Substitution of Eq. (7) into Eq. (14), and replacing  $k = k_1$  gives the pseudo-first order kinetic model (Eq. (15)).

$$q_t = q_e [1 - \exp(-k_1 \cdot t)] \quad (15)$$

Pseudo-first order kinetic equation is a special case of general kinetic model of adsorption.

When  $n=2$ , the pseudo-second-order kinetic model is a special case of Eq. (12) [38].

$$q_t = q_e - \frac{q_e}{[k_2 (q_e) \cdot t + 1]} \quad (16)$$

Eq. (16) on rearrangement gives Eq. (17).

$$q_t = \frac{q_e^2 k_2 t}{[k_2 (q_e) \cdot t + 1]} \quad (17)$$

Pseudo-first-order (Eq. (15)), pseudo-second-order (Eq. (17)), and



general order equation model (Eq. (12)) were used to evaluate the kinetics of adsorption of the pharmaceuticals on the carbon adsorbents.

### 7. Equilibrium Models

In this work, the Langmuir, Freundlich, and Sips [39-41] isotherm models were tested.

The Langmuir isotherm equation is:

$$q_e = \frac{Q_{max} \cdot K_L \cdot C_e}{1 + K_L \cdot C_e} \quad (18)$$

where,  $C_e$  is the supernatant concentration after the equilibrium of the system ( $\text{mg L}^{-1}$ ),  $K_L$  is the Langmuir equilibrium constant ( $\text{L mg}^{-1}$ ), and  $Q_{max}$  is the maximum adsorption capacity of the material ( $\text{mg g}^{-1}$ ) assuming a monolayer of adsorbate uptaken by the adsorbent.

The Freundlich isotherm model is:

$$q = K_F \cdot C_e^{1/n} \quad (19)$$

where  $K_F$  the Freundlich equilibrium constant [ $\text{mg g}^{-1}(\text{mg L}^{-1})^{-1/n}$ ] and  $n$  is the Freundlich exponent (dimensionless).

The Sips model is an empirical model that consists of the combination of the Langmuir and Freundlich isotherm type models. The Sips [38,41] model takes the following form:

$$q = \frac{Q_{max} \cdot K_S \cdot C_e^{1/n}}{1 + K_S \cdot C_e^{1/n}} \quad (20)$$

where  $K_S$  is the Sips equilibrium constant ( $\text{mg L}^{-1})^{-1/n}$  and  $Q_{max}$  is the Sips maximum adsorption capacity ( $\text{mg g}^{-1}$ ).

At low adsorbate concentrations the Sips model effectively reduces to a Freundlich isotherm, while at high adsorbate concentrations it predicts a monolayer adsorption capacity characteristic of the Langmuir isotherm.

## RESULTS AND DISCUSSION

### 1. Characterization of the Carbon Adsorbents

Activated carbons were prepared by using sewage sludge as an organic precursor. The chemical activation was carried out using  $\text{ZnCl}_2$ . Ten different activated carbons were pyrolyzed at different temperatures ( $500^\circ$ ,  $650^\circ$  and  $800^\circ\text{C}$ ), using different zinc chloride: organic precursor ratios (0:1, 0.5:1, 1:1, and 1.5:1), see Table 2. Afterwards to complete the chemical activation, an acid treatment with  $6 \text{ mol L}^{-1}$  HCl, under reflux for 2 hours, was used to leach out the inorganic compounds of the carbon structure [26,36]. The ACs were characterized by SEM, elemental analysis, solvent vapor (n-heptane and water) adsorption and  $\text{N}_2$  adsorption/desorption isotherms. Likewise, the ACs were tested for their performance in the removal of the DCF and NM in aqueous solutions by batch adsorption method. The characterization of activated carbons prepared will be discussed in the following section.

In Table 2 is shown all the textural characteristics of the carbon adsorbents prepared. It was observed that the samples with higher surface area ( $S_{BET}$ ) presented the highest values for adsorption of the anti-inflammatory DCF and NM (see Supplementary Fig. 1). These results show clearly that improvements in the superficial area of the adsorbent are related to increases in the sorption capacity of

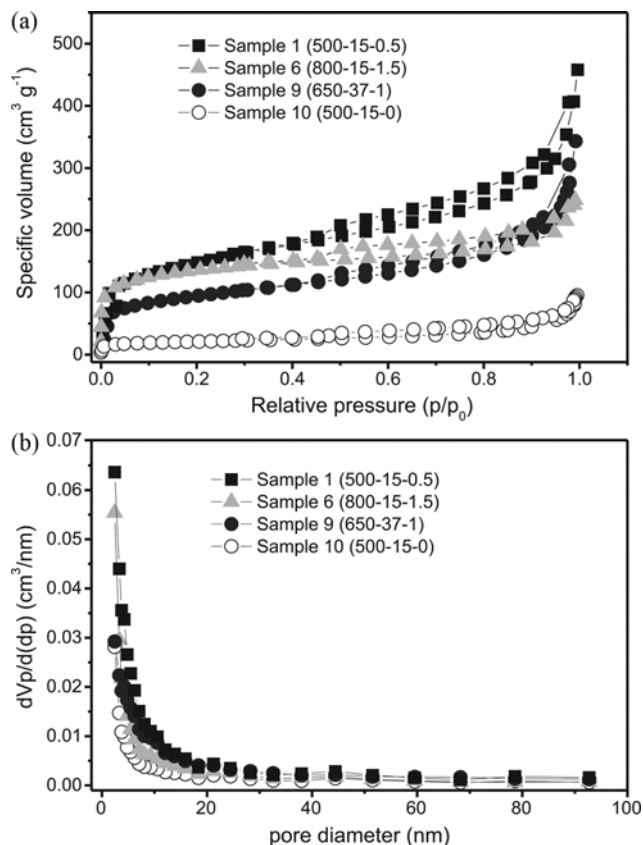


Fig. 1. (a) Nitrogen adsorption/desorption isotherms for activated carbons and their (b) corresponding BJH plots.

the adsorbents for DCF and NM [2,26,36].

Samples 1(500-15-0.5) (high surface area), 6(800-15-1.5) (lower surface area), 9(650-37-1.0) (intermediate surface area), and 10(500-15-0) (no chemical impregnation), were chosen to show the effects of chemical activation with  $\text{ZnCl}_2$  on the evolution of porosity during processing of chemical activation. The isotherms of adsorption and desorption of  $\text{N}_2$  for other samples are not shown in Table 2 in order to facilitate the visualization of Fig. 1.

All samples can be assigned to be of a type IV isotherm according to the International Union of Pure and Applied Chemistry (IUPAC) classification. Type IV isotherms possess a hysteresis loop with capillary condensation phenomenon indicating mesopores [42]. However, the adsorbed  $\text{N}_2$  volumes differ in their dependency on the conditions of pyrolysis (Fig. 1(a) and 1(b)). The range of nitrogen volume adsorbed was between  $227\text{-}458 \text{ cm}^3 \text{ g}^{-1}$ . Based on Fig. 1(a), it is clear that the sample with higher surface area, sample 1(500-15-0.5), presented higher volume of adsorption when compared with sample 6(800-15-1.5). The lower amount adsorbed can be visualized in sample 10(500-15-0) where no chemical activation was carried out. Based on these results, it is clear that the activated carbons which were obtained by the mixture of sludge with  $\text{ZnCl}_2$  presented much higher surface area, implying a higher sorption capacity for removal of anti-inflammatories from aqueous solutions, than the sludge without impregnation with  $\text{ZnCl}_2$ .

According to IUPAC classification, micropores have diameters lower than 2 nm, mesopores between 2-50 nm, and macropores

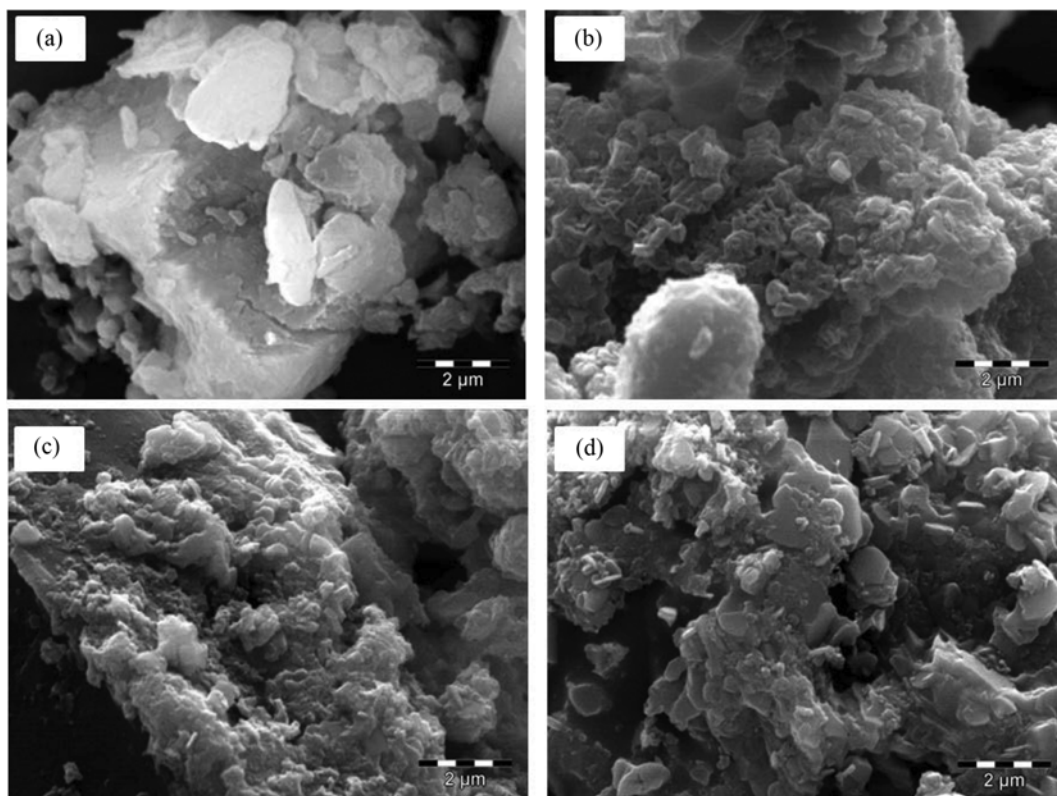


Fig. 2. SEM images of (a) sample 10(500-15-0); (b) sample 1(500-15-1.5); (c) sample 9(650-37-1.0); and (d) sample 6(800-15-1.5). For description of samples see Table 2.

higher than 50 nm [42]. All samples possess micropores and mesopores as illustrated in the BJH plots (see Fig. 1(b)).

Structural heterogeneity and internal solid structure can be represented by characterization of the pore size distribution [42]. The pore size distribution visualized by BJH plots of the samples are shown in Fig. 1. By increasing the temperature of production of activated carbon, the samples illustrated a sharp increase in the range of micropores.

The use of a scanning electron microscope (SEM) is one of the most versatile techniques available for the examination and analysis of microstructure morphology characterization, providing detailed surface information such as shape and size of the particles. The SEM images of samples without chemical treatment, sample 10(500-15-0); sample 1(500-15-0.5); sample 9(650-37-1.0); and sample 6(800-15-1.5) are presented in Fig. 2. The roughness of the carbon materials is visible (see Fig. 2). The main difference in roughness concerns the lesser roughness of the non-washed samples compared to the other chemically treated samples that possess higher roughness. This observation could be attributed to the acidic treatments of sample 1(500-15-0.5), sample 9(650-37-1.0) and sample 6(800-15-1.5) that were leached by HCl solution removing practically all the inorganic contents of the samples, as already described in the literature [2,26,36].

The surface polarity of adsorbents is important for interactions with adsorbates that are solutes dissolved in solvents. *n*-Heptane vapor and water which present different polarities were used to characterize the surface of the adsorbents prepared within this

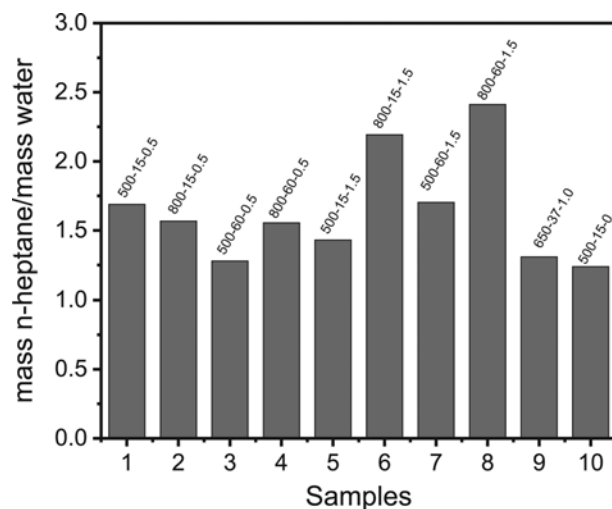


Fig. 3. Ratio of the maximum sorption capacities of water and *n*-heptane onto activated carbons.

study, as shown in Fig. 3 for all materials. Fig. 3 shows the mass ratio of *n*-heptane:water uptake by dried samples of the activated carbons. For all ACs the uptake of *n*-heptane (which shows mainly dispersive interaction) were higher than the uptake of water (which is mainly polar) demonstrating that the more hydrophobic surfaces of the activated carbons were present in the set of samples [43,44].

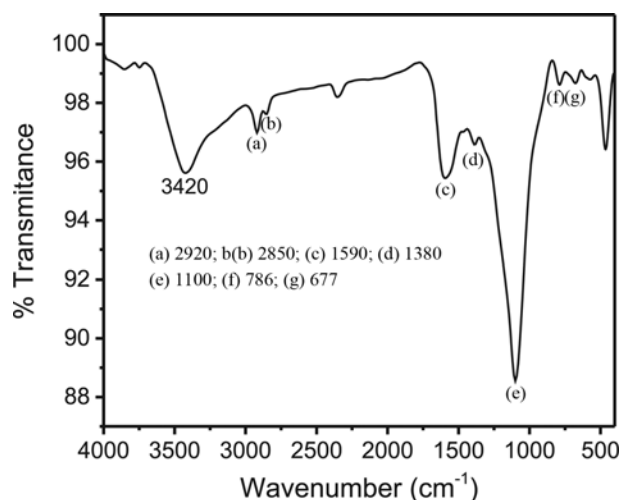


Fig. 4. FTIR spectra of 1(500-15-0.5) sample activated carbon.

Samples 6(800-15-1.5) and 8(800-60-1.5) presented higher *n*-heptane : water ratio for the whole set of preparation conditions of ACs. It may be inferred that higher temperature can influence surface characteristics with regards to hydrophobicity. The polarity of the carbon surface should decrease as activation temperature is increased. The unique exception for this observation occurs for sample 2(800-15-0.5), which has practically the same hydrophobic character of the surface of the activated carbon that was obtained for sample 1(500-15-0.5).

The FTIR spectra of the activated carbons revealed that the functional groups present in the carbon adsorbents were almost identical. From which we may infer that the pyrolysis conditions did not have great influence on the rise of different functional groups on the surface among the carbons. Therefore, only the FTIR spectra of the carbon with the highest  $S_{BET}$  sample 1(500-15-0.5) are shown and can be seen in Fig. 4. A high-intensity band was observed at  $3,420\text{ cm}^{-1}$  which is due to stretching vibrations of the hydroxylic groups [36,37,45,46]. The inconspicuous bands at  $2,920$  and  $2,850\text{ cm}^{-1}$  are ascribed to asymmetric and symmetric C-H stretching [36,37,45,46]. The band at  $1,590\text{ cm}^{-1}$  could be assigned to aromatic ring modes [20,24]. The small band at  $1,380\text{ cm}^{-1}$  could be assigned to C-H bending vibration [19,20]. The strong absorption at  $1,100\text{ cm}^{-1}$  could be assigned to C-O stretching of alcohol and phenol and Si-O of silicates. The small FTIR bands at  $786\text{ cm}^{-1}$  are assigned to aromatic out of plane C-H bending; and the bands at  $677\text{ cm}^{-1}$  are assigned to aromatic ring bending [19,20].

Therefore, the major groups found in the carbons adsorbents include O-H (alcohols, phenols), aromatic rings, CO (phenols, alcohols), Si-O (silicates), and CH (aromatics, aliphatic).

Fig. 5 shows the thermogravimetric (TG) curves of the 1(500-15-0.5) and 6(800-15-1.5) AC samples. According to the TG curves, the total weight loss of sample 1(500-15-0.5) was 45.97%, and of sample 6(800-15-1.5) was 52.90%. Considering that the atmosphere for performing these experiments of TG was synthetic air, the content left after the thermal treatment of  $1,000\text{ }^{\circ}\text{C}$  corresponds to the sample's ash content, as already reported in the literature [2,26,36]. High content of ashes in the samples of adsorbents is directly

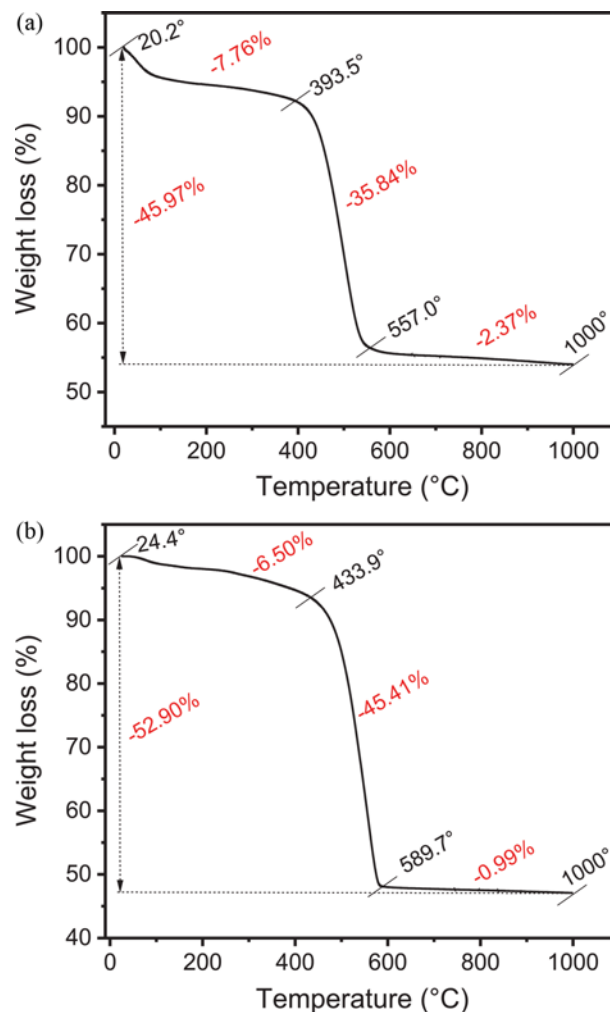


Fig. 5. TGA and DTG curves of (a) sample 1(500-15-0.5) and (b) sample 6(800-15-1.5).

related to the sewage sludge used as organic precursor for the production of activated carbon [47,48].

The TG curves can be grouped into three regions of weight loss. The first region ranged from 6.50 to 7.76% ( $\approx 20$ - $393.50\text{ }^{\circ}\text{C}$ ; for sample 1 from  $24.4^{\circ}$ - $433.9\text{ }^{\circ}\text{C}$  for sample 6, respectively). Such weight loss corresponds to that of adsorbed water, water of crystallization, and water present in the interstitials of the activated carbons [2,26,36]. Major weight losses occur in the second region. These losses range from 35.84% to 45.41% and from 77.93% to 84.85% for activated carbons. The losses in the second region are attributed to the decomposition of the carbonaceous matrix [26,36,48]. The third stage of weight loss was only 2.37% and 0.99% for sample 1 and 6, respectively. The last stage is attributed to the skeleton decomposition of carbon [36,48] producing ashes, since the atmosphere used in the experiments was synthetic air.

## 2. Effects of Initial pH

One of the most important factors that affect the adsorption process is the pH of the solution [20,21]. Therefore, previous pH studies were carried out to determine which pH would enhance the removal of DCF and NM.

Variations of adsorptions of DCF and NM onto 1(500-15-0.5) sample were investigated in the pH range 6-11 using HCl and/or NaOH to control pH. The effect of pH on DCF and NM removals was studied using 30.0 mg of AC in 20 ml of pharmaceutical solutions ( $50 \text{ mg L}^{-1}$ ) at an adsorption time of 240 min to make sure that equilibrium was reached. Plots of pH versus removal (%) of DCF and NM at  $25^\circ\text{C}$  are shown in Supplementary Fig. 2.

For DCF, the influence of the pH on the adsorption capacity on AC caused a decrease of the percentage of removal when the pH of solution was increased. On the other hand, for nimesulide, increase of pH of solution increased the amount adsorbed. For instance, at pH 7.0 the percentage removal of DCF was 91.22%, and at pH 11 it decreased to 58.72%. However for NM the percentage removal at pH 7.0 was 72.32%, and at pH 11.0 it was 81.25%, reaching the highest percentage removal at pH 10.0 with 86.94%.

The difference of optimum pH for adsorption of DCF and NM could be explained by the differences of their  $\text{pK}_a$  values in water. The DCF has a  $\text{pK}_a$  4.00 and NM a  $\text{pK}_a$  6.70; these values were calculated by the software Marvin Sketch 16.3.14.0. Therefore, at pH 7.0 and 10.0 for DCF and NM, respectively, these pharmaceuticals are deprotonated as anions. Positive groups of surface materials could interact with such anions.

Therefore, on the basis of the above discussion, the optimum pH values for adsorption of DCF and NM onto ACs are pH 7.0 and 10.0, respectively.

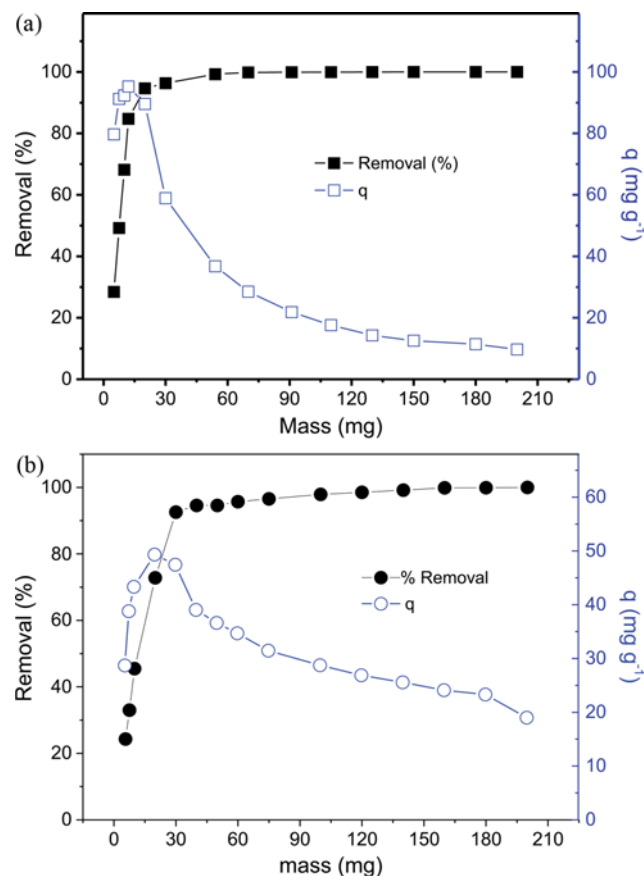


Fig. 6. Effect of the mass of adsorbent on the % removal and sorption capacity ( $q$ ) onto sample 1(500-15-0.5).

### 3. Effect of Adsorbent Mass

The quantity or mass of adsorbent is an important factor in large scale industrial application of adsorbent in the removal of a desired sorbate. The study of adsorbent mass is important in order to avoid waste generation and minimize costs associated with the adsorption process [24,31].

The study of adsorbent dosages for the removal of DCF and NM from aqueous solution was carried out using quantities of 1(500-15-0.5) sludge-activated carbon samples ranging from 5.0 to 150.0 mg with a fixed volume of 20.0 mL of DCF and NM with an initial concentration of  $50 \text{ mg L}^{-1}$ . The optimal adsorption for DCF was attained for a mass of 54.0 mg with 99.24% percentage of removal and  $q$  equal to  $36.56 \text{ mg}\cdot\text{g}^{-1}$  (see Fig. 6(a)). However, for the next experiments a mass of 30.0 mg was chosen because at that amount the percentage of removal was 96.34% and  $q$  equal to  $58.90 \text{ mg}\cdot\text{g}^{-1}$  (see Fig. 6(a)). This choice is justified because the use of 30 mg instead 54 mg leads an amount reduction of AC in the order of 80% while the decrease of uptake ( $q$ ) is just 2.91% (see Fig. 6(a)).

A similar trend was observed for NM adsorption, its optimal adsorption was reached at a mass of 60.0 mg with 95.70% percentage of removal and with  $q$  equal to  $34.68 \text{ mg}\cdot\text{g}^{-1}$  (see Fig. 6(b)), while a mass of 30.0 mg presented a percentage of removal of 92.56% and a sorption capacity of  $47.45 \text{ mg}\cdot\text{g}^{-1}$ . Therefore, an increase of 50% of the mass of the adsorbent led to an increase of only 3.14% of removal and a decrease of 26.91% on the sorption capacity. Therefore, the best mass for adsorption experiments was found to be 30.0 mg for each adsorbent.

### 4. Kinetic Studies

To investigate the mechanism of adsorption and potential rate-controlling steps such as chemical adsorption, diffusion control and mass transport processes, kinetic models have been used to test experimental data. These studies give valuable information for adsorption process design, operation control, and evaluation of the adsorbents [1,2,20,21].

Nonlinear pseudo-first order, pseudo-second order and general-order kinetic models were used to assess the kinetics of adsorption of DCF and NM onto the activated carbon that presented the higher surface area, sample 1(500-15-0.5). All other samples presented the same trend for the kinetic studies and sample 1(500-15-0.5) was chosen to demonstrate the parameters of the kinetic models, because it was considered the best adsorbent in this study as it presented highest  $S_{\text{BET}}$  and performance in uptake of the DCF and NM in aqueous solutions.

Table 3 and Supplementary Fig. 3 show the parameters and curves, respectively, of kinetic experiments performed to determine the equilibrium time required for the uptake of DCF and NM by sample 1(500-15-0.5). The parameters of the curves were obtained by plotting the DCF and NM uptake capacity versus time at  $70 \text{ mg L}^{-1}$  initial concentration. Adsorption studies were carried out for periods of times between 5 min and 10 hours.

Using the SD and the  $R_{\text{adj}}^2$  it can be concluded that the kinetic data were best fitted by the general order kinetic model, as already reported in the literature for several adsorbents and adsorbates [1,2,20,21,26,36,37,44,45].

The general-order kinetic model states that the order of an ad-

**Table 3. Kinetic parameters of DCF and NM adsorption onto sample 1(500-15-05) conditions: Temperature, 25 °C; pH 7.0 and 10.0 for DCF and NM, respectively; and mass of adsorbent 30.0 mg, initial anti-inflammatory concentration 70.0 mg L<sup>-1</sup>. All values of the parameters are expressed with four significant digits**

	DCF	NM
<b>Pseudo first-order</b>		
k <sub>1</sub> (h <sup>-1</sup> )	35.49	10.10
q <sub>e</sub> (mg g <sup>-1</sup> )	112.2	50.14
t <sub>1/2</sub> (h)	0.01953	0.06859
R <sub>adj</sub> <sup>2</sup>	0.9953	0.9246
SD (mg g <sup>-1</sup> )	1.920	3.608
<b>Pseudo second-order</b>		
k <sub>2</sub> (g mg <sup>-1</sup> h <sup>-1</sup> )	1.316	0.3586
q <sub>e</sub> (mg g <sup>-1</sup> )	113.5	52.70
t <sub>1/2</sub> (h)	0.006694	0.05292
R <sub>adj</sub> <sup>2</sup>	0.9989	0.9829
SD (mg g <sup>-1</sup> )	0.9093	1.716
<b>General order</b>		
K <sub>n</sub> [h <sup>-1</sup> ·(g mg <sup>-1</sup> ) <sup>n-1</sup> ]	0.03746	0.02893
q <sub>e</sub> (mg g <sup>-1</sup> )	115.5	54.97
n	3.223	2.734
t <sub>1/2</sub> (h)	0.001144	0.04441
t <sub>0.95</sub> (h)	0.2431	3.249
R <sub>adj</sub> <sup>2</sup>	0.9997	0.9867
SD (mg g <sup>-1</sup> )	0.5056	1.514

sorption process should logically follow the same trend as that of a chemical reaction, where the order of reaction is experimentally measured instead of being restrained by a given model [2,38].

Considering that it is difficult to compare the parameters of the general-order kinetic model, since the exponent *n* is different for DCF and NM, we used *t*<sub>1/2</sub> and *t*<sub>0.95</sub> to compare the kinetics of DCF and NM. The *t*<sub>1/2</sub>, that is defined as the time to achieve half of saturation (*q*<sub>e</sub>) in the kinetic results, *t*<sub>0.95</sub> is the time to achieve 95% of saturation (*q*<sub>e</sub>). The *t*<sub>0.95</sub> was taken mostly for purposes of the general-order kinetic model, because this was the best kinetic model to describe the kinetic experiments. By analyzing these values in Table 3, it could be inferred that the kinetics of adsorption of DCF is faster than that of NM. The *t*<sub>1/2</sub> values of the NM adsorption onto 1(500-15-0.5) are 38.8-fold higher than the values obtained for DCF. With the aid of Marvin Sketch 16.3.14.0 software, the polar surface area of DCF and NM was calculated. These values are 52.16 Å<sup>2</sup> and 104.12 Å<sup>2</sup> for DCF and NM, respectively. The bigger the polar surface area of the pharmaceutical, the higher the area of this molecule that interacts with the water. Since the adsorption of an organic molecule onto an active surface of carbon involves dehydration of the organic molecule before it can be adsorbed on the solid surface, the pharmaceutical which interacts more extensively with the solvent will possess a higher energy barrier to be surpassed so as to release the water to the bulk of the solution, and the adsorption of the adsorbate takes place on the adsorbent surface. Therefore, the difference in polar surface area of the pharmaceuticals explains why the kinetic of adsorption of DCF onto 1-

(500-15-0.5) is faster than that of NM.

Also, the *t*<sub>0.95</sub> was used to calculate the time for the adsorbate to achieve the equilibrium on the adsorbent surface. Based on these values it was observed that the equilibrium for DCF was obtained after 0.2431 h (14.59 min) and for NM the equilibrium was attained after 3.429 h (205.7 min). For the remaining experiments, the time of contact between the adsorbent and adsorbate was fixed at 30 min for DCF and 4 h for NM, in order to guarantee that in these times of contact the equilibrium was attained.

### 5. Equilibrium Studies and Maximum Adsorption Capacity

Adsorption isotherms describe the relationship between the amount of adsorbate adsorbed by the adsorbent (*q*<sub>e</sub>) and the adsorbate concentration remaining in solution after the system attains equilibrium (*C*<sub>e</sub>) at a constant temperature. The adsorption parameters of the equilibrium models provide some insights into the adsorption mechanism, surface properties and affinity of the adsorbent for the adsorbate. In this work the Langmuir, Freundlich and Sips isotherm models were tested. The isotherms of adsorption were measured at 25°, 35° and 45 °C with DCF and NM onto 1(500-15-0.5), 6(650-37-1.0) and 9(800-15-1.5) ACs samples. These samples were chosen because they were pyrolyzed at three different pyrolysis temperatures and, taking out 500-15-0, they presented the lowest *S*<sub>BET</sub> value (9(800-15-1.5); 328.0 m<sup>2</sup> g<sup>-1</sup>), the highest *S*<sub>BET</sub> value (1(500-15-0.5); 679 m<sup>2</sup> g<sup>-1</sup>) and the most intermediate *S*<sub>BET</sub> value (6(650-37-1.0); 503.7 m<sup>2</sup> g<sup>-1</sup>), as well as presented different uptake values for DCF and NM.

Table 4 and Supplementary Fig. 4(a)-(f) show the adsorption isotherm parameters (at 25°, 35° and 45 °C) and their curves (at 25 °C) of DCF and NM adsorbed onto 1(500-15-0.5), 6(650-37-1.0) and 9(800-15-1.5) ACs samples. Considering the SD values, the Sips model best described adsorption equilibrium data of both compounds DCF and NM on the three samples. The values of SD of the Langmuir model ranged from 3.741 to 4.434 for DCF and 3.137 to 8.283 for NM, while the Freundlich model ranges were 7.642 to 29.32 for DCF and 3.592 to 9.114 for NM. For Sips model the SD values ranged between 1.426 to 2.638 for DCF and 1.907 to 2.677 for NM.

Based on the lowest SD values, the best isotherm model fitted was the Sips for all sample adsorbents, (see Table 4), which means that the *q*<sub>e</sub> values fitted by the isotherm model were closest to the *q*<sub>e</sub> values measured experimentally.

The Sips isotherm model [41] is a combination of the Langmuir and Freundlich isotherm models; therefore, the monolayer assumption of Langmuir model is discarded and the infinite adsorption assumption that originates from the Freundlich model is not considered. The Sips model predicts that the active sites of the adsorbent cannot present the same energy. Therefore, the adsorbent may present active sites preferred by the adsorbate molecules for occupation [41]; however, saturation of the active sites should also occur unlike in the Freundlich isotherm model. Taking into account that the adsorbent used in this study has different functional groups as shown by the FTIR spectrum (see Fig. 4), that the adsorbent material presents some micropores and mesopores (see Fig. 1), it is expected that the active sites of the adsorbent will not possess the same energy—this fact is supported by the Sips isotherm model.

**Table 4. Isotherm parameters for DCF and NM adsorption on 1(500-15-1.5), 6(800-15-1.5) and 9(650-37-1.0) samples. Conditions: contact time of 90 min; pH of 7.0 and 10.0, respectively, and adsorbent mass of 30.0 mg for DCF and NM**

	1 (500-15-0.5)			6 (800-15-1.5)			9 (650-37-1.0)		
	25 °C	35 °C	45 °C	25 °C	35 °C	45 °C	25 °C	35 °C	45 °C
<b>DICLOFENAC</b>									
<b>Langmuir</b>									
$Q_{max}$ (mg g <sup>-1</sup> )	155.3	145.8	147.2	90.61	84.14	91.51	146.4	138.6	133.2
$K_L$ (L mg <sup>-1</sup> )	0.3125	0.3014	0.3036	0.2102	0.1867	0.1914	0.3426	0.3621	0.3388
$R_{adj}^2$	0.9891	0.9875	0.9802	0.9843	0.9788	0.8842	0.9914	0.9899	0.9885
SD (mg g <sup>-1</sup> )	3.741	3.322	3.854	2.865	2.722	23.34	4.434	4.812	5.192
<b>Freudlich</b>									
$K_F$ (mg g <sup>-1</sup> (mg L <sup>-1</sup> ) <sup>-1/n<sub>F</sub></sup> )	63.11	61.75	57.98	19.51	18.79	18.12	47.44	46.89	46.16
$n_F$	6.081	6.112	5.845	6.317	6.115	6.004	7.869	7.524	7.301
$R_{adj}^2$	0.9577	0.9502	0.9453	0.9690	0.9704	0.9771	0.9729	0.9701	0.9693
SD (mg g <sup>-1</sup> )	7.642	7.985	8.251	29.32	28.02	27.95	14.53	14.87	15.64
<b>Sips</b>									
$Q_{max}$ (mg g <sup>-1</sup> )	157.4	146.2	150.1	91.42	86.73	90.26	148.0	142.1	146.7
$K_s$ (L mg <sup>-1</sup> )	0.1298	0.1423	0.1298	0.1972	0.2195	0.2014	0.1477	0.1984	0.1865
$n_s$	0.6898	0.5964	0.6898	0.5928	0.5766	0.5687	0.6812	0.6632	0.6539
$R_{adj}^2$	0.9967	0.9911	0.9905	0.9913	0.9875	0.9887	0.9997	0.9991	0.9984
SD (mg g <sup>-1</sup> )	1.868	2.351	2.532	1.426	1.726	1.701	2.638	2.655	2.701
<b>NIMESULIDE</b>									
<b>Langmuir</b>									
$Q_{max}$ (mg g <sup>-1</sup> )	58.33	51.76	56.45	39.73	35.98	38.36	42.44	38.41	40.43
$K_L$ (L mg <sup>-1</sup> )	0.3902	0.3766	0.3863	0.2104	0.2061	0.2133	0.3682	0.3784	0.3555
$R_{adj}^2$	0.8715	0.8725	0.8862	0.9584	0.9665	0.9678	0.9658	0.9698	0.9688
SD (mg g <sup>-1</sup> )	8.283	8.288	8.136	3.183	3.377	3.344	3.137	3.465	3.348
<b>Freudlich</b>									
$K_F$ (mg g <sup>-1</sup> (mg L <sup>-1</sup> ) <sup>-1/n<sub>F</sub></sup> )	24.69	23.22	22.78	13.46	13.02	12.78	21.24	19.84	18.13
$n_F$	5.975	5.862	5.803	4.932	4.545	4.234	5.993	5.745	5.454
$R_{adj}^2$	0.9442	0.9521	0.9455	0.9462	0.9412	0.9302	0.9729	0.9735	0.9701
SD (mg g <sup>-1</sup> )	9.114	9.215	9.199	3.592	3.662	3.971	4.225	4.211	4.228
<b>Sips</b>									
$Q_{max}$ (mg g <sup>-1</sup> )	66.45	64.82	65.88	46.35	42.75	45.95	43.01	40.83	42.24
$K_s$ (L mg <sup>-1</sup> )	0.2624	0.2425	0.2415	0.1931	0.1925	0.2015	0.1475	0.1445	0.1483
$N_s$	1.752	1.525	1.443	0.5631	0.5421	0.5126	0.6815	0.6532	0.5432
$R_{adj}^2$	0.9925	0.9911	0.9986	0.9851	0.9834	0.9821	0.9871	0.9866	0.9805
SD (mg g <sup>-1</sup> )	2.095	2.125	2.221	1.907	1.998	1.882	2.677	2.845	2.994

The effect of temperature on the percentage of removal of DCF and NM by ACs was also evaluated in this work and its results are shown in Table 4. It was observed that  $Q_{max}$  and  $K$  of Langmuir and Sips did not follow a regular pattern, a fact that precludes the determination of the thermodynamic parameters as early reported [2,20,21, 26].

To compare the efficiency of the sludge-activated carbons studied, Table 5 shows a comparison between the maximum adsorption capacities between the ACs studied and various other adsorbents reported in the literature [2,16,18,49,50,52-56]. As can be seen in Table 5, the adsorbent material proposed in this current work presents very good adsorption capacities when compared with other adsorbents reported in the literature. For DCF out of a total of 13 adsorbents the 1(500-15-0.5) sludge activated carbon presented sorp-

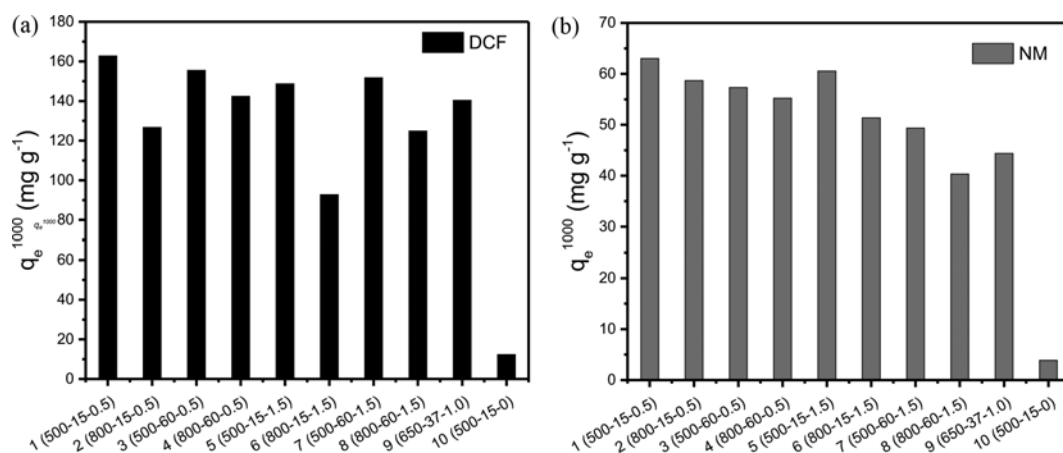
tion capacity higher than 11; and for NM, out of a total of 6 adsorbents, the 1-(500-15-0.5) adsorbent presented sorption capacity higher than 5.

Fig. 7 shows the sorption capacities obtained with an initial concentration of 1,000 mg L<sup>-1</sup> of DCF and NM ( $q_e^{1000}$ ) for all produced activated carbons. From Fig. 7 it is possible to see that the sample not treated chemically 10(500-15-0) showed the lowest  $q_e^{1000}$  for both compounds DCF and NM, while sample 1(500-15-0.5) presented the highest  $q_e^{1000}$  value. This behavior corresponds to the magnitude of  $S_{BET}$  values (Table 2), which may help to explain the  $q_e^{1000}$  variations. As can be seen from Table 2 and Fig. 5, generally the  $q_e^{1000}$  value is higher on AC with higher  $S_{BET}$ . This suggests that  $S_{BET}$  influenced the uptake of both adsorbates significantly.

Fig. 7 demonstrates that  $Q_{max}$  of DCF is much higher than NM.

**Table 5. Comparison of adsorption capacities of different adsorbents for DCF and NM**

Adsorbent	Adsorption capacity ( $\text{mg g}^{-1}$ )		
	DCF	NM	Reference
Activated carbon from cocoa shell	63.47	74.81	[2]
PAC	372.0	-	[16]
PAC	233.9	-	[18]
Modified chitosan	9.33	-	[49]
Functionalized silica	35.59	-	[50]
Composite adsorbent	27.18	14.55	[52]
Hybrid adsorbent	41.43	26.12	[52]
Sludge activated carbon	16.27	9.438	[52]
Multi-walled carbon nanotubes	8.640	-	[53]
Carbon xerogels	80.00	-	[54]
PAC	40.55	-	[55]
Mesoporous silica (SBA-15)	34.18	-	[56]
Silica aerogel	-	14.18	[56]
1 (500-15-0.5) sludge activated carbon	157.4	66.45	This work

**Fig. 7. Adsorption capacity of 1,000 mg L<sup>-1</sup> ( $q_e^{1000}$ ) of DCF and NM onto sludge based activated carbons at 25 °C.**

Also the rate of adsorption of DCF was faster than that of NM according to  $t_{1/2}$  (see Table 3). The higher affinity of sludge activated carbons by DCF rather than NM could be linked to their differences in chemical properties. The van der Waals surface area of DCF and NM was 359.64 A<sup>2</sup> and 406.46 A<sup>2</sup>, respectively (see Table 1), while the polar surface area of DCF and NM was 52.16 A<sup>2</sup> and 104.12 A<sup>2</sup>, respectively (see Table 1). Performing the division of polar surface area by van der Waals surface area and multiplying by 100, the percentage of polar area in relation to the total area of DCF is 14.50% and for NM is 25.62%. Considering that the activated carbons are hydrophobic, as can be seen in Fig. 3, it is expected that DCF would have higher affinity of the hydrophobic surface of the activated carbon when compared with NM.

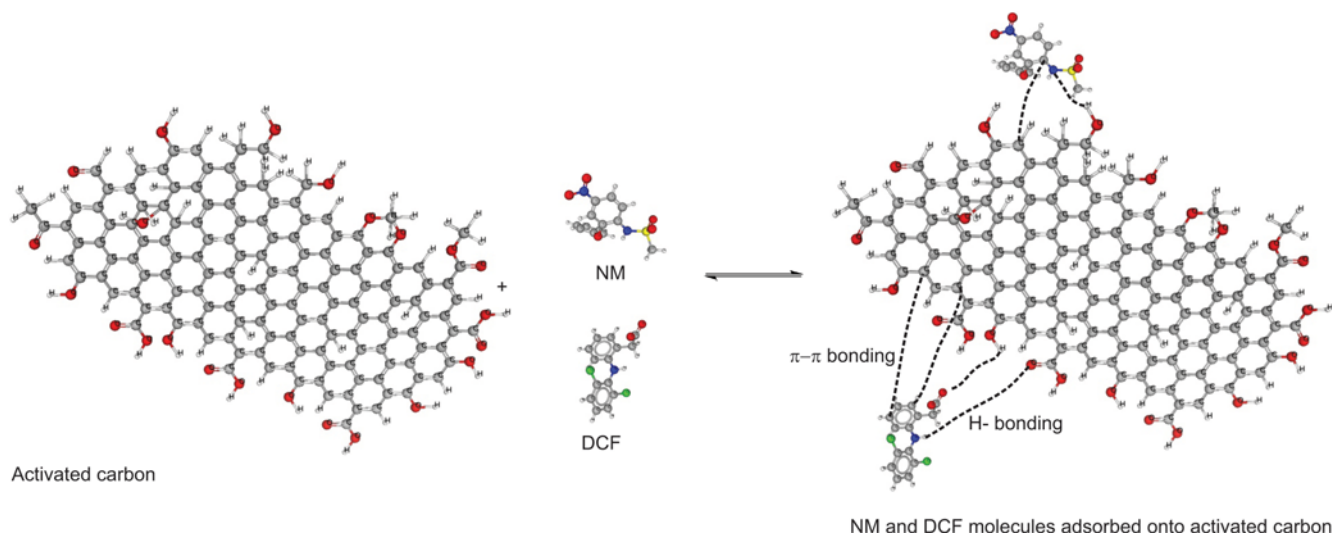
## 6. Adsorption Mechanism

Based on the combined data of characterization of materials as well as the kinetic and equilibrium studies, it is possible to suggest mechanisms for adsorption of DCF and NM onto AC adsorbents. The adsorption process involves physical interactions such as van der Waals interactions, hydrogen bonding and  $\pi$ - $\pi$  interactions of

the aromatic ring of the adsorbent with the aromatic rings of the pharmaceuticals. The aromatic rings of pharmaceuticals interact with the phenyl, OH, C=O and COOH groups of the ACs through  $\pi$ - $\pi$  interactions as shown in Fig. 8.

## CONCLUSION

Activated carbons have been prepared using sewage sludge as starting material and a conventional furnace pyrolysis for heat treatment. The powdered sewage sludge and ZnCl<sub>2</sub> were mixed in different proportions at room temperature. The mixture was heated at three different temperatures, 500°, 650° and 800 °C, under inert conditions. The carbonized materials were treated with a 6 mol L<sup>-1</sup> HCl and refluxed for 3 h to obtain chemically activated ACs. The acidification process leached the inorganics from the carbonaceous matrix, which was confirmed by BET surface area and SEM techniques. According to water and n-heptane adsorption, the samples of ACs were hydrophobic. The sample 1(500-15-0.5) was identified to be the best adsorbent for the removal of DCF and



**Fig. 8. Adsorption mechanism of DCF and NM onto AC.**

NM from aqueous solutions. Adsorption capacity of the ACs produced within this work is among the highest of many works found in literature. At 25 °C, it was observed that the equilibrium for DCF was obtained after 0.2431 h (14.59 min) and for NM the equilibrium was attained after 3.429 h (205.7 min). The general-order kinetic model best described the adsorption process, because the order of adsorption was experimentally measured instead of being restricted by a given model. Sips isotherm model gave the best fit of isothermal data, showing that an adsorption process should occur in multiple sites of the activated carbon. The maximum amounts ( $Q_{max}$ ) of DCF and NM adsorbed were 157.4 and 66.45 mg g<sup>-1</sup> for 1(500-15-0.5), respectively.

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#### SUPPORTING INFORMATION

Additional information as noted in the text. This information is available via the Internet at <http://www.springer.com/chemistry/journal/11814>.

#### REFERENCES

1. S. Rovani, M. T. Censi, S. L. Pedrotti-Jr., E. C. Lima, R. Cataluña and A. N. Fernandes, *J. Hazard. Mater.*, **271**, 311 (2014).
2. C. Saucier, M. A. Adebayo, E. C. Lima, R. Cataluña, P. S. Thuea, P. D. T. Lizie, P.-M. J. Rosero, F. M. Machado, F. A. Pavan and G. L. Dotto, *J. Hazard. Mater.*, **289**, 18 (2015).
3. R. Gothwal and T. Shashidhar, *Clean - Soil Air Water*, **43**, 479 (2015).
4. L. Prieto-Rodríguez, I. Oller, N. Klamerth, A. Agüera, E. M. Rodríguez and S. Malato, *Water Res.*, **47**, 1521 (2013).
5. N. Bolong, A. F. Ismail, M. R. Salim and T. Matsuura, *Desalination*, **239**, 229 (2009).
6. H. J. Lee, E. Lee, S. H. Yoon, H. R. Chang, K. Kim and J. H. Kwon, *Chemosphere*, **87**, 969 (2012).
7. Y. Li, G. Zhu, W. J. Ng and S. K. Tan, *Sci. Total Environ.*, **468-469**, 908 (2014).
8. N. Han, T. Taro, U. Thi and T. Ta, *Clean - Soil Air Water*, **42**, 267 (2014).
9. E. Geiger, R. Hornek-Gausterer and M. T. Saçan, *Ecotoxicol. Environ. Saf.*, **129**, 189 (2016).
10. R. Feito, Y. Valcárcel and M. Catalá, *Ecotoxicology*, **21**, 289 (2012).
11. M. Boonsaner and D. W. Hawker, *Chemosphere*, **122**, 176 (2015).
12. C. Sheng, A. G. A. Nnann, Y. Liu and J. D. Vargo, *Sci. Total Environ.*, **550**, 1075 (2016).
13. J. B. Parsa, T. M. Panah and F. N. Chianeh, *Korean J. Chem. Eng.*, **33**, 893 (2016).
14. W. Gebhardt and H. F. Schroder, *J. Chromatogr. A*, **1160**, 34 (2007).
15. S. Suarez, J. M. Lema and F. Omil, *Bioresour. Technol.*, **100**, 2138 (2009).
16. C. Jung, L. K. Boateng, J. R. V. Flora, J. Oh, M. C. Braswell, A. Son and Y. Yoon, *Chem. Eng. J.*, **264**, 1 (2015).
17. L. R. Rad, M. Irani and R. Barzegar, *Korean J. Chem. Eng.*, **32**, 1606 (2015).
18. J. L. Sotelo, G. Ovejero, A. Rodríguez, S. Álvarez, J. Galán and J. García, *Chem. Eng. J.*, **240**, 443 (2014).
19. G. L. Dotto, E. C. Lima and L. A. A. Pinto, *Bioresour. Technol.*, **103**, 123 (2012).
20. L. D. T. Prola, E. Acayanka, E. C. Lima, C. S. Umpierrez, J. C. P. Vagheti, W. O. Santos, S. Laminsi and P. T. Njifon, *Ind. Crop Prod.*, **46**, 328 (2013).
21. D. C. dos Santos, M. A. Adebayo, S. F. P. Pereira, L. D. T. Prola, R. Cataluña, E. C. Lima, C. Saucier, C. R. Gally and F. M. Machado,



- Korean J. Chem. Eng.*, **31**, 1470 (2014).
22. S. Sadaf and H.N. Bhatti, *Clean Technol. Environ. Policy*, **16**, 527 (2014).
23. G. S. dos Reis, M. Wilhelm, T. C. A. Silva, K. Rezwan, C. H. Sampaio, E. C. Lima and S. M. A. G. U. Souza, *Appl. Therm. Eng.*, **93**, 590 (2016).
24. T. Calvete, E. C. Lima, N. F. Cardoso, J. C. P. Vaghetti, S. L. P. Dias and F. A. Pavan, *J. Environ. Manage.*, **91**, 1695 (2010).
25. H. Marsh and F. R. Reinoso, *Activated Carbon*. Elsevier, Amsterdam (2006).
26. M. C. Ribas, M. A. Adebayo, L. D. T. Prola, E. C. Lima, R. Cataluña, L. A. Feris, M. J. Puchana, F. M. Machado, F. A. Pavan and T. Calvete, *Chem. Eng. J.*, **248**, 315 (2014).
27. S. Brunauer, P. H. Emmett and E. Teller, *J. Am. Chem. Soc.*, **60**, 309 (1938).
28. E. P. Barrett, I. G. Joyner and P. P. Halend, *J. Am. Chem. Soc.*, **73**, 373 (1951).
29. L. Leng, X. Yuana, H. Huang, J. Shao, H. Wang, X. Chen and G. Zeng, *Appl. Surf. Sci.*, **346**, 223 (2015).
30. A. V. Maldhure and J. D. Ekhe, *Chem. Eng. J.*, **168**, 1103 (2011).
31. T. Calvete, E. C. Lima, N. F. Cardoso, S. L. P. Dias and E. S. Ribeiro, *Clean: Air, Soil, Water*, **38**, 521 (2010).
32. E. C. Lima, F. Barbosa-Jr, F. J. Krug and U. Guaita, *J. Anal. Atom. Spectrom.*, **14**, 1601 (1999).
33. E. C. Lima, F. Barbosa-Jr, F. J. Krug and A. Tavares, *Talanta*, **57**, 177 (2002).
34. E. C. Lima, F. J. Krug, J. A. Nóbrega and A. R. A. Nogueira, *Talanta*, **47**, 613 (1998).
35. E. C. Lima, P. G. Fenga, J. R. Romero and W. F. de Giovani, *Polyhedron*, **17**, 313 (1998).
36. C. Saucier, M. A. Adebayo, E. C. Lima, L. D. T. Prola, P. S. Thue, C. S. Umpierres, M. J. Puchana-Rosero and F. M. Machado, *Clean*, **43**, 1389 (2015).
37. W. S. Alencar, E. C. Lima, B. Royer, B. D. dos Santos, T. Calvete, E. A. da Silva and C. N. Alves, *Sep. Sci. Technol.*, **47**, 513 (2012).
38. E. C. Lima, M. A. Adebayo and F. M. Machado, *Chapter 3- Kinetic and Equilibrium Models of Adsorption in Carbon Nanomaterials as Adsorbents for Environmental and Biological Applications*, C. P. Bergmann and F. M. Machado, Eds., Springer (2015).
39. I. Langmuir, *J. Am. Chem. Soc.*, **40**, 1361 (1918).
40. H. Freundlich, *Phys. Chem. Soc.*, **40**, 1361 (1906).
41. R. Sips, *J. Chem. Phys.*, **16**, 490 (1948).
42. P. B. Balbuenat and K. E. Gubbins, *Langmuir*, **9**, 1801 (1993).
43. T. Prenzel, T. L. M. Guedes, F. Schluter, M. Wilhelm and K. Rezwan, *Sep. Purif. Technol.*, **129**, 80 (2014).
44. S. W. Nam, D. J. Choi, S. K. Kim, N. Her and K. D. Zoh, *J. Hazard. Mater.*, **270**, 144 (2014).
45. S. Biniak, G. Szymanski, J. Siedlewski and A. Swiatkowski, *Carbon*, **35**, 1799 (1997).
46. Y. Otake and R. G. Jenkins, *Carbon*, **31**, 109 (1993).
47. K. M. Smith, G. D. Fowler, S. Pullket and N. D. J. Graham, *Water Res.*, **43**, 2569 (2009).
48. G. B. Gasco, C. G. Guerrero, F. Mendez and A. M. Lazaro, *J. Anal. Appl. Pyrol.*, **74**, 413 (2005).
49. K. A. A. Pereira, L. R. Osório, M. P. Silva, K. S. Sousa and E. C. S. Filho, *Mat. Res.*, **17**, 1516 (2014).
50. N. Suriyanon, P. Punyapalakul and C. Ngamcharussrivichai, *Chem. Eng. J.*, **214**, 208 (2013).
51. T. X. Bui and H. Choi, *J. Hazard. Mater.*, **168**, 602 (2009).
52. G. S. dos Reis, C. H. Sampaio, E. C. Lima and M. Wilhelm, *Colloids Surf. A Physicochem. Eng. Asp.*, **497**, 304 (2016).
53. X. Hu and Z. Cheng, *Chin. J. Chem. Eng.*, **23**, 1551 (2015).
54. S. Álvarez, R. S. Ribeiro, H. T. Gomes, J. L. Sotelo and J. García, *Chem. Eng. Res. Des.*, **95**, 229 (2015).
55. C. M. Dai, S. U. Geissen, Y. L. Zhang, Y. J. Zhang and X. F. Zhou, *Environ. Pollut.*, **159**, 1660 (2011).
56. G. Caputo, M. Scognamiglio and I. De Marco, *Chem. Eng. Res. Des.*, **90**, 1082 (2012).

## Supporting Information

### Activated carbon from sewage sludge for removal of sodium diclofenac and nimesulide from aqueous solutions

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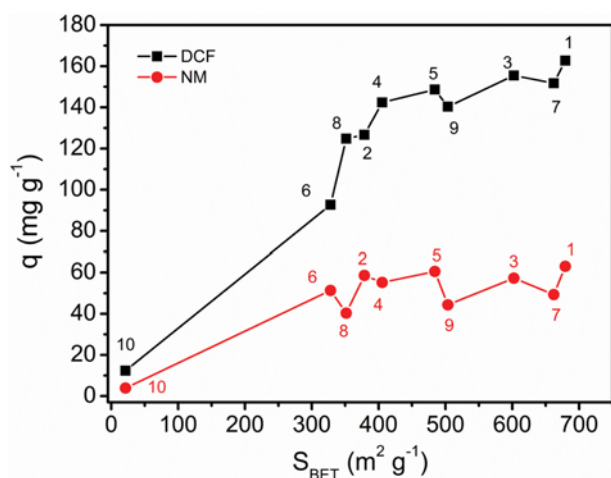


Fig. S1. Adsorption isotherm models fitting in the adsorption of diclofenac and nimesulide by hybrid materials.

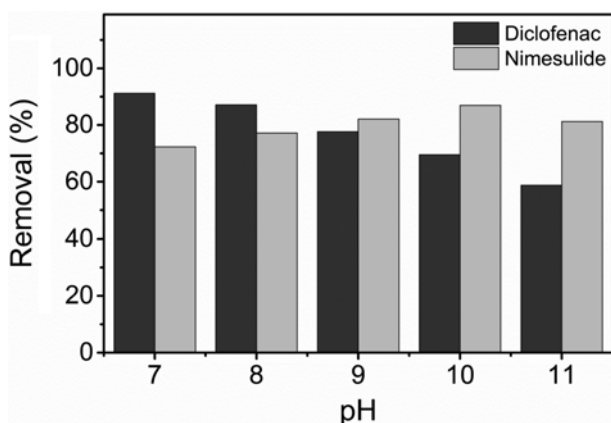


Fig. S2. Dependence of pH on the sorption capacity of DCF and NM pharmaceuticals on 1(500-15-0.5). Conditions: temperature, 25 °C; adsorbent mass, 20.0 mg; adsorbent 25 °C pharmaceutical concentration, 50.0 mg L.

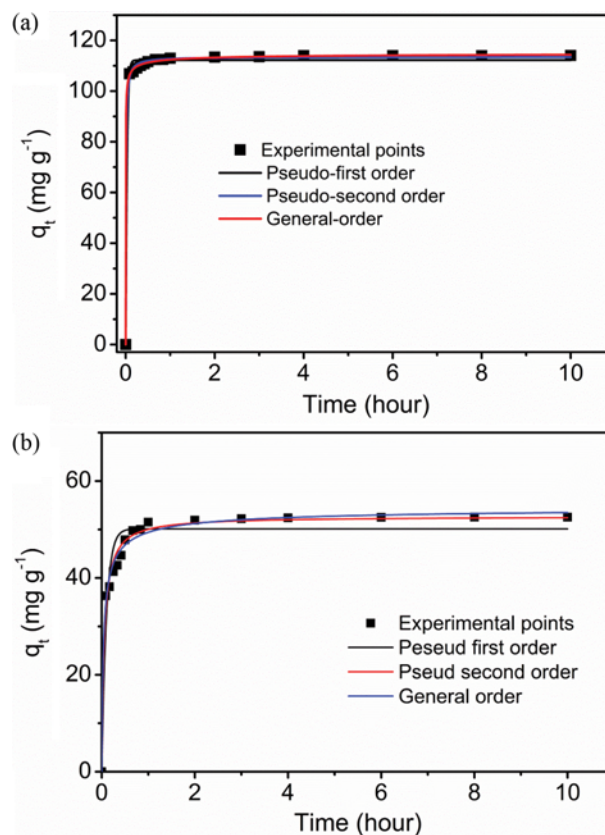


Fig. S3. Adsorption kinetic models fitting in the adsorption of diclofenac and nimesulide onto 1(500-15-0.5) sample.

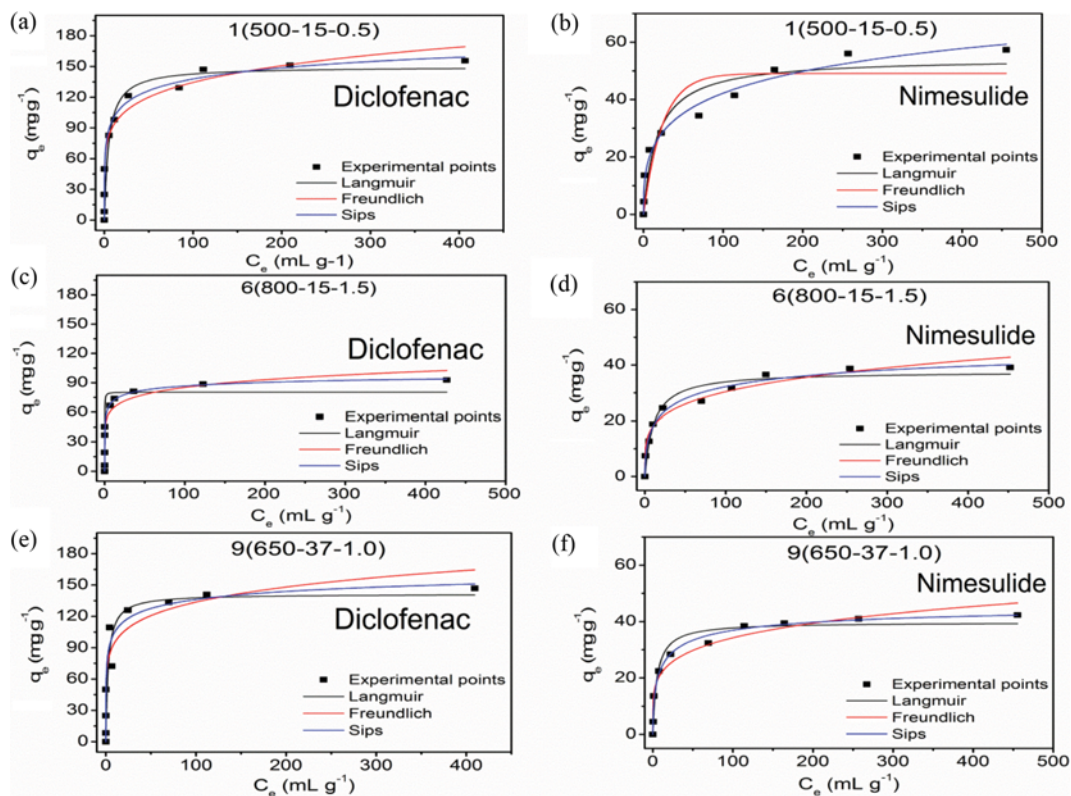


Fig. S4. Adsorption isotherm models fitting in the adsorption of diclofenac and nimesulide by hybrid materials.

# ***Capítulo Oito***

## **9. CONCLUSÕES E PROPOSTAS FUTURAS.**

### **9.1. CONCLUSÃO**

A preparação de carvões ativados através do lodo de esgoto por meio de pirólise convencional e microondas já têm sido investigada há muito tempo. Contudo, até o momento não foi publicado nenhum trabalho no Brasil envolvendo a preparação de CAs a partir de lodo de esgoto doméstico tanto por pirólise convencional ou por microondas. Ademais, também não há publicações envolvendo síntese de novos materiais envolvendo lodo de esgoto e polissiloxanos.

As principais contribuições desta tese referem-se: (i) subsidiar na consolidação do preparo de carvões ativados a partir de lodo de esgoto doméstico pela técnicas de pirólise convencional e por microondas; (ii) fazer um estudo comparativo entre quais dos dois métodos de pirólise produz carvões ativados com melhores  $S_{BET}$  e porosidade, isso porque ainda não há um consenso na literatura no sentido de qual método de pirólise é capaz de produzir carvões ativados com melhores propriedades texturais (iii) subsidiar na proposição de melhores alternativas para o uso de lodo de esgoto no sentido de aplicá-lo como matéria prima para preparação de novos materiais seja no campo da adsorção (como foi o caso desta tese) ou para aplicação em outros campos com por exemplo catálise; (iv) aplicação destes adsorventes na remoção de poluentes orgânicos tais como alguns fármacos (diclofenaco e nimesulida) e alguns compostos fenólicos (m-cresol, fenol, o-cresol, 2-clorofenol, 2-nitrofenol, hidroquinona). Tal aplicação se faz de suma importância para o campo da adsorção de poluentes orgânicos (por meio de carvões a base de lodo) uma vez que, até o presente momento, nenhum trabalho foi publicado quanto à remoção de DCF and NM por carvões de lodo de esgoto. Esses resultados ajudarão a traçar um comparativo no sentido de determinar quais tipos de precursores geram carvões ativados mais eficazes na remoção de fármacos e compostos fenólicos em soluções aquosas.

Portanto, diante do exposto ate aqui, as principais conclusões desta tese são destacadas a seguir:

### **9.2. CONCLUSÕES DOS CAPÍTULOS**

## **Capítulo Oito.** Conclusões e propostas futuras.

**Capítulo quatro:** Conclusões referentes ao artigo intitulado “**The use of design of experiments for the evaluation of the production of surface rich activated carbon from sewage sludge via microwave and conventional pyrolysis**”: De modo a alcançar as melhores condições operacionais do processo de pirólise do lodo de esgoto, por aquecimento convencional e por micro-ondas, para a produção de carvões ativados com elevadas áreas superficiais foi aplicado um planejamento estatístico e metodologia de superfície de resposta.

As condições ótimas para a preparação de carvão ativado pelo método de micro-ondas foram de 980 W de potência, um tempo de permanência de 12 min, e a relação de  $ZnCl_2$ : lodo de 0,5. Sob estas condições foi obtida uma área superficial específica foi de  $501 \text{ m}^2 \text{ g}^{-1}$ . Para a pirólise convencional, as condições ótimas foram uma temperatura de  $500^\circ\text{C}$ , sob um tempo de aquecimento de 15 min, e a relação de  $ZnCl_2$ : lodo de 0,5. Sob estas condições, a  $S_{BET}$  obtida foi de  $679 \text{ m}^2 \text{ g}^{-1}$ .

Os fatores que mais fortemente influenciaram na qualidade dos carvões foram: temperatura que influenciou negativamente para o aquecimento convencional, ou seja o aumento da temperatura causou uma decréscimo no valor da  $S_{BET}$ . Por outro lado, para o processo por microondas, o tempo de permanência foi o fator mais importante, que influenciou de maneira positiva, sendo que ao aumentá-lo a  $S_{BET}$  também foi aumentada.

Concluiu-se então que ambos os processos de pirólise (convencional e micro-ondas) foram capazes de produzir carvões ativados com elevadas áreas superficiais e porosidade, ambos os métodos geraram carvões com perfis similares com uma mistura de micro e mesoporos.

**Capítulo cinco:** Conclusões referentes ao artigo intitulado “**Removal of phenolic compounds from aqueous solutions using sludge-based activated carbons prepared by conventional heating and microwave-assisted pyrolysis**”:

Os estudos demonstraram que ambos os carvões foram altamente eficientes na remoção de compostos fenólicos. Entre os seis compostos fenólicos (m-cresol, fenol, o-cresol, 2-clorofenol, 2-nitrofenol, hidroquinona).

O estudo demonstrou que a adsorção destes compostos fenólicos foi influenciada pelas suas propriedades físico-químicas e que entre estes foi a hidroquinona exibiu maior afinidade com ambos CAs atingindo valores de  $Q_{max}$  de 1218,3 e 1202,1  $\text{mg g}^{-1}$  para CAC-500 e MAC-980, respectivamente. Os carvões foram testados em efluentes

## **Capítulo Oito.** Conclusões e propostas futuras.

sintéticos e ambos as CAs mostraram excelentes resultados no tratamento de efluentes industriais sintéticos removendo eficazmente em torno de 93,82% (CAC-500) e 91,58% (MAC-980).

Um mecanismo de adsorção foi proposto neste trabalho, e foi sugerido que o complexo doador-receptor e interações  $\pi$ - $\pi$  desempenham papéis fundamentais no processo de adsorção.

Com base nos dados deste trabalho, foi possível concluir que os carvões ativados, produzidos pela pirólise por micro-ondas e pelo método convencional, são altamente eficientes na remoção de compostos fenólicos de efluentes aquosos.

**Capítulo seis:** Conclusões referentes ao artigo intitulado “**Preparation of novel adsorbents based on combinations of polysiloxanes and sewage sludge to remove pharmaceuticals from aqueous solutions**”: A partir deste artigo pôde-se concluir que os materiais adsorventes sintetizados a partir de lodo de esgoto e polissiloxanos foram considerados microporosos com valores de  $S_{BET}$  variando de  $641 \text{ m}^2 \text{ g}^{-1}$ .

De acordo com os resultados, para os materiais feitos a partir da mistura de lodo e polissiloxanos, os valores  $S_{BET}$  diminuíram com o aumento no conteúdo de lodo de esgoto. Contudo, o teor de lodo de esgoto nos adsorventes refletiu na maior perda de hidrofobicidade tornando-os menos hidrofóbicos em comparação aos materiais feitos apenas com polissiloxanos.

Em relação aos testes de adsorção envolvendo a remoção dos adsorbatos diclofenaco (DCF) e nimesulida (NM), os dados mostraram que a adsorção de diclofenaco foi quase o dobro do nimesulida evidenciando que as interações hidrofóbicas foram as mais importantes dentro do mecanismo de adsorção uma vez que o DCF é mais hidrofóbico que o NM.

A combinação de lodo de esgoto com polissiloxanos para produzir novos adsorventes compostos podem trazer vários benefícios para o ambiente, diminuição dos custos na preparação de novos materiais adsorventes e também para redução do custo de tratamento da água.

Os potenciais benefícios do emprego de lodo de esgoto na produção de adsorventes são evidentes, pois é uma solução segura e eficaz para o ambiente e também agrega valor a esse resíduo. Sem dúvida, a aplicação de novos adsorventes derivados de lodo de esgoto e de polissiloxanos para tratamento de água apresenta grandes oportunidades para futuras pesquisas.

**Capítulo sete:** Conclusões referentes ao artigo intitulado “**Activated carbon from sewage sludge for removal of sodium diclofenac and nimesulide from aqueous solutions**”:

As  $S_{BET}$  dos CAs variaram de 21,2 à 679,3  $m^2 g^{-1}$  sendo a amostra 1 (500-15-0.5) a que obteve a maior  $S_{BET}$ . De acordo com a adsorção de água e n-heptano, as amostras de carvões ativados (CAs) foram hidrofóbicos. A amostra 1 (500-15-0.5) foi identificado como sendo o melhor adsorvente para a remoção de DCF e NM a partir de soluções aquosas. A 25 ° C, observou-se que o equilíbrio de adsorção para o DCF e NM foram de 0.2431h (14.59min) e 3.429 h (205,7 min), respectivamente. Em relação aos modelos cinéticos de adsorção, o modelo de ordem geral foi o que melhor descreveu o processo de adsorção. Já para os modelos de isotermas foi o de Sips que melhor se ajustou aos dados experimentais. Os valores máximos ( $Q_{max}$ ) de DCF e NM adsorvidas foram 157,4 e 66,45  $mg g^{-1}$  para 1 (500-15-0.5), respectivamente. A capacidade máxima de adsorção dos CAs produzidos neste trabalho está entre os maiores de muitos trabalhos encontrados na literatura.

### 9.3. SUGESTÕES PARA TRABALHOS FUTUROS

- Avaliar a aplicação de outros sais inorgânicos como ativante químico para preparação de carvões ativados;
- Utilizar outros precursores para preparação de novos materiais adsorventes através da combinação com lodo de esgoto, como sílica, óxidos metálicos argilo-minerais como caulim etc.
- Otimizar a combinação de lodo de esgoto e polissiloxanos para preparação de materiais.
- Aplicar esses novos materiais na remoção dos mais diferentes tipos de adsorbatos como metais pesados e poluentes orgânicos como corantes, fenóis etc.
- Aplicar esses novos materiais à base de lodo e polissiloxanos em outros processos químicos como por exemplo catálise.



## REFERÊNCIAS

- [1] W.L. Steffen, A. Sanderson, P.D. Tyson, J. Jager, *Global Change and the earth system: A Planet Under Pressure*. 2005, Springer, Berlin.
- [2] D.I. Stern, M.S. Common, E.B. Barbier, *Economic growth and environmental degradation: the environmental Kuznets curve and sustainable development*. *World Dev.* 24 (1996) 1151–1160.
- [3] Li, C., Kuang, Y., Huang, N., Zhang, C., 2013. The long-term relationship between population growth and vegetation cover: an empirical analysis based on the panel data of 21 Cities in Guangdong Province, China. *Int. J. Engine Res.* 10, 660–677.
- [4] Lu, H., Bai, Y., Ren, H., Campbell, D.E., 2010. Integrated energy, energy and economic evaluation of rice and vegetable production systems in alluvial paddy fields: implications for agricultural policy in China. *J. Environ. Manage.* 91 (12), 2727–2735.
- [5] Diaz, L.F., Savage, G.M., Eggerth, L.L., Golueke, C.G., 1996. *Solid Waste Management for Economically Developing Countries*. International Solid Waste Association, Copenhagen
- [6] S. Fedorenko, M. Jilkin, N. Nastapova, V. Yanilkin, O. Bochkova, V. Buriliov, I. Nizameev, G. Nasretdinova, M. Kadirov, A. Mustafina, Y. Budnikova, Surface decoration of silica nanoparticles by Pd(0) deposition for catalytic application in aqueous solutions, *Colloids Surf. A Physicochem. Eng. Aspects* 486 (2015) 185–191.
- [7] M. Wilhelm, C. Soltmann, D. Koch, G. Grathwohl, *Ceramers - functional materials for adsorption techniques*, *J. Eur. Ceram. Soc.*, 25 (2005) 271-276.
- [8] J. Yin, B. Deng, *Polymer-matrix nanocomposite membranes for water treatment*, *J. Membrane Sci.* 479 (2015) 256–275.
- [9] V. Lauth, M. Maas, K. Rezwan, *Coacervate-directed synthesis of CaCO<sub>3</sub> microcarriers for pH-responsive delivery of biomolecules*, *J. Mater. Chem. B* 44 (2014) 7725-735.
- [10] W. Wei, R. Sun, J. Cui, Z.G. Wei, *Removal of nitrobenzene from aqueous solution by adsorption on nanocrystalline hydroxyapatite*, *Desalination* 263 (2010) 89–96.
- [11] M. Arshadi, F. S. Vahid, J.W.L. Salvacion, M. Soleymanzadeh, *A practical organometallic decorated nano-size SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub>, mixed-oxides for methyl orange removal from aqueous solution*, *Appl. Surf. Sci.* 280 (2013) 726–736.
- [12] T. Prenzel, M. Wilhelm, K. Rezwan, *Tailoring amine functionalized hybrid ceramics to control CO<sub>2</sub> adsorption*, *Chem. Eng. J.* 235 (2014) 198-206.
- [13] T. Prenzel, M. Wilhelm, K. Rezwan, *Pyrolyzed polysiloxane membranes with tailorable hydrophobicity, porosity and high specific surface area*, *Microporous Mesoporous Mater.* 169 (2013) 160–167.
- [14] T. Prenzel, T.L.M. Guedes, F. Schlüter, M. Wilhelm, Kuroschi Rezwan, *Tailoring surfaces of hybrid ceramics for gas adsorption – From alkanes to CO<sub>2</sub>*, *Sep. Pur. Technol.* 129 (2014) 80–89.
- [15] Y. Abe, T. Gunji, *Oligo- and polysiloxanes*, *Prog. Polym. Sci.* 29 (2004) 149–182.
- [16] R. Bischoff, S.E. Cray, *Polysiloxanes in macromolecular architecture*, *Prog. Polym. Sci.* 24 (1999) 185–219.
- [17] K.M. Smith, G.D. Fowler, S. Pullket, N.J.D. Graham, *Sewage sludge-based adsorbents: A review of their production, properties and use in water treatment applications*, *Water Res.* 43 (2009) 2569–2594

- [18] G. Mininni, A. R. Blanch, F. Lucena, S. Berselli, EU policy on sewage sludge utilization and perspectives on new approaches of sludge management, *Environ Sci Pollut Res.* 22 (2015) 7361–7374
- [19] Hartig, C.; Storm, T.; Jekel, M.; Detection and identification of sulphonamide drugs in municipal waste water by liquid chromatography coupled with electrospray ionisation tandem mass spectrometry, *J. Chromatogr. A* 854 (1999) 163-173
- [20] Ternes T.A., Kreckel P., Mueller J. Behaviour and occurrence of estrogens in municipal sewage treatment plants- II. Aerobic batch experiments with activated sludge, *Sci. Total Environ.* 225 (1999) 91-99
- [21] C. Andreoli, M. Von Sperling, and F. Fernandes, *Sludge Treatment and Disposal*. 2005, p. 256.
- [22] Sabesp, “A Questão dos Lodos Produzidos nas ETEs na RMSP . Região Metropolitana de São Paulo,” 2007.
- [23] C. V. Andreoli, M. Von Sperling, F. Fernandes, *Lodo de esgoto: Tratamento e disposição final*. Rio de Janeiro: Editora ABES, 2001. 483 p.
- [24] M. Mendes, P. G. E. G. Vieira, J. F. de Sousa, A. C. Pickler, E. R. M. Leal, C. C. Milhomen, *Produção e tratamento de lodo de esgoto – uma revisão*, revista *Liberato*, 11 (2010) 86-xx.
- [25] J. Beeckmans and P. Ng, Pyrolyzed sewage sludge – its production and possible utility, *Environ. Sci. Technol.* 5 (1971) 1965–1967
- [26] G. Lu, Q. F. Low, J. C, Y. Liu, C, C. Lua, A, Surface area development of sewage sludge during pyrolysis, *Fuel*, 74 (1995) 344–348
- [27] X. Chen, S. Jeyaseelan, N. Graham, Physical and chemical properties study of the activated carbon made from sewage sludge, *Waste Manag.* 22 (2002) 755–760
- [28] M. J. Martin, A. Artola, M. D. Balaguer, M. Rigola, Activated carbons developed from surplus sewage sludge for the removal of dyes from dilute aqueous solutions, *Chem. Eng. J.* 94 (2003) 231–239
- [29] F. Rozada, M. Otero, J. B. Parra, A. Morán, A. I. García, Producing adsorbents from sewage sludge and discarded tyres, *Chem. Eng. J.* 114 (2005) 161–169
- [30] M.A. Ros, E. Lillo-Ródenas, M.A. Fuente, M. J Montes-Morán, A. Martín, High surface area materials prepared from sewage sludge-based precursors, *Chemosphere*, 65 (2006) 132–40
- [31] C. Canals-Batlle, A. Ros, M. A. Lillo-Ródenas, E. Fuente, M. A. Montes-Morán, M. J. Martin, A. Linares-Solano, Carbonaceous adsorbents for NH<sub>3</sub> removal at room temperature, *Carbon* 46 (2008) 176–178
- [32] V. M. Monsalvo, A. F. Mohedano, J. J. Rodriguez, Activated carbons from sewage sludge, *Desalination* 277 (2011) 377–382
- [33] A.C. Lua, T. Yang, Effects of vacuum pyrolysis conditions on the characteristics of activated carbons derived from pistachio nut shells, *J. Colloid Interface Sci.* 290 (2005) 505–513
- [34] K. Nuithitikul, S. Srikhun, S. Hirunpraditkoon, Influences of pyrolysis condition and acid treatment on properties of durian peel-based activated carbon, *Bioresour. Technol.* 101 (2010) 426–429
- [35] Y-F. Huang, P-T Chiueh, W-H. Kuan, S-L Lo, Microwave pyrolysis of lignocellulosic biomass: Heating performance and reaction kinetics, *Energy* 100 (2016) 137-144
- [36] A. M. Sanseverino, *Microondas em síntese orgânica*, *Quim. Nova*, 25 (4) (2002) 660-667

- [37] Y-F. Huang, P-T. Chiueh, W-H. Kuan, S-L. Lo, Microwave pyrolysis of lignocellulosic biomass: Heating performance and reaction kinetics, *Energy* 100 (2016) 137-144
- [38] D. Angim, Effect of pyrolysis temperature and heating rate on biochar obtained from pyrolysis of safflower seed press cake, *Bioresour. Technol.* 128 (2013) 593–597
- [39] T. Kan, V. Strezov, T. J. Evans, Lignocellulosic biomass pyrolysis: A review of product properties and effects of pyrolysis parameters, *Renewable and Sustainable Energy Reviews* 57 (2016) 1126–1140
- [40] G. Gascó, C.G. Blanco, F. Guerrero, A.M. Méndez Lázaro, The influence of organic matter on sewage sludge pyrolysis, *J. Anal. Appl. Pyrolysis* 74 (2005) 413–420
- [41] E. Agrafioti, G. Bouras, D. Kalderis, E. Diamadopoulou, Biochar production by sewage sludge pyrolysis, *J. Anal. Appl. Pyrolysis*, 101 (2013) 72–78.
- [42] V. M. Monsalvo, A. F. Mohedano, J. J. Rodriguez, Activated carbons from sewage sludge, *Desalination*, 277 (2011) 377–382
- [43] C. Liu, Z. Tang, Y. Chen, S. Su, W. Jiang, Characterization of mesoporous activated carbons prepared by pyrolysis of sewage sludge with pyrolusite. *Bioresour. Technol.* 101 (2010) 1097–101
- [44] C. Canals-Batlle, A. Ros, M. A. Lillo-Ródenas, E. Fuente, M. A. Montes-Morán, M. J. Martín, A. Linares-Solano, Carbonaceous adsorbents for NH<sub>3</sub> removal at room temperature, *Carbon*. 46, (2008) 176–178
- [45] M. Seredych and T. J. Bandoz, Removal of copper on composite sewage sludge/industrial sludge-based adsorbents: the role of surface chemistry. *J. Colloid Interface Sci.* 302, (2006) 379–88
- [46] S. Rio, C. Faur-Brasquet, L. Le Coq, P. Le Cloirec, Structure characterization and adsorption properties of pyrolyzed sewage sludge. *Environ. Sci. Technol.* 39 (2005) 4249–4257
- [47] M. Inguanzo, J. Menéndez, E. Fuente, J. Pis, Reactivity of pyrolyzed sewage sludge in air and CO<sub>2</sub>, *J. Anal. Appl. Pyrolysis*, 58–59 (2001) 943–954
- [48] Q.H. Lina, H. Cheng, G.Y. Chen, Preparation and characterization of carbonaceous adsorbents from sewage sludge using a pilot-scale microwave heating equipment, *J. Anal. Appl. Pyrol.* 93 (2012) 113–119
- [49] M.J. Puchana-Rosero, M. A. Adebayo, E. C. Lima, F. M. Machado, P. S. Thue, J. C.P. Vagheti, C. S. Umpierrez, M. Gutterres, Microwave-assisted activated carbon obtained from the sludge of tannery-treatment effluent plant for removal of leather dyes, *Colloids Surf. A: Physicochem. Eng. Aspects* 504 (2016) 105–115
- [50] X. Wang, X. Liang, Y. Wang, X. Wang, M. Liu, D. Yin, S. Xia, J. Zhao, Y. Zhang, Adsorption of Copper (II) onto activated carbons from sewage sludge by microwave-induced phosphoric acid and zinc chloride activation, *Desalination* 278 (2011) 231–237
- [51] A. Bagreev, T. J. Bandoz, D. C. Locke, Pore structure and surface chemistry of adsorbents obtained by pyrolysis of sewage sludge-derived fertilizer, *Carbon*. 39 (2001) 1971–1979.
- [52] L. F. Calvo, M. Otero, A. Morán, A.I. García, Upgrading sewage sludges for adsorbent preparation by different treatments.,” *Bioresour. Technol.* 80 (2001) 143–148.
- [53] D. Slocum, E. McGinnes, F. Beall, Charcoal yield, shrinkage, and density changes During carbonization of oak and Hickory woods, *Wood Sci.* 11 (1978) 42–47
- [54] F. Karacan, U. Ozden, S. Karacan, Optimization of manufacturing conditions for activated carbon from Turkish lignite by chemical activation using response surface methodology, *Appl. Therm. Eng.* 27 (2007) 1212–1218.

- [55] J.A. Muthanna, K.T. Samar, Optimization of microwave preparation conditions for activated carbon from Albizialebeck seed pods for methylene blue dye adsorption, *J. Anal. Appl. Pyrol.* 105 (2014) 199–208.
- [56] P.G. González, T. Hernández-Quiroz, L. García-González, The use of experimental design and response surface methodologies for the synthesis of chemically activated carbons produced from bamboo, *Fuel Process. Technol.* 127 (2014) 133–139.
- [57] X. Duan, J. Peng, C. Srinivasakannan, L. Zhang, H. Xia, K. Yang, et al., Process optimization for the preparation of activated carbon from Jatropha Hull using response surface methodology, *Ener. Source* 33 (2011) 2005–2017.
- [58] L. Zhanyong, K. Wang, J. Song, Q. Xu, N. Kobayashi, Preparation of activated carbons from polycarbonate with chemical activation using response surface methodology, *J. Mat. Cycles Waste Manage.* 16 (2014) 359–366.
- [59] M.K.B. Gratuito, T. Panyathanmaporn, R.A. Chumnanklang, N. Sirinuntawittaya, A. Dutta, Production of activated carbon from coconut shell: optimization using response surface methodology, *Bioresour. Technol.* 99 (2008) 4887–4895.
- [60] D.C. Montgomery, *Design and Analysis of Experiments*, Fifth ed., John Wiley & Sons, New York, 2001.
- [61] G.E.P. Box, W.G. Hunter, J.S. Hunter, *Statistics for Experimenters: An Introduction to Design, Data Analysis and Model Building*, Second ed., John Wiley & Sons, New York, 1978.
- [62] M.A. Bezerra, R. E. Santelli, E.P. Oliveiraa, L.S. Villar, L.A. Escaleira, Response surface methodology (RSM) as a tool for optimization in analytical chemistry, *Talanta* 76 (2008) 965–977
- [63] M. M. Dubinin, Microporous structures of carbonaceous adsorbents, *Carbon*, 20 (1982) 195–200
- [64] H. Marsh, F. Rodriguez-Reinoso, *Activated Carbon*. (Elsevier, London, 2006)
- [65] F.C. Wu, P.H. Wu, R.L. Tseng, R.-S. Juang, Preparation of novel activated carbons from H<sub>2</sub>SO<sub>4</sub>-pretreated corncob hulls with KOH activation for quick adsorption of dye and 4-chlorophenol. *J. Environ. Manage.* 92 (2011) 708–13
- [66] B. Royer, N. F. Cardoso, E. C. Lima, J. C. P. Vagheti, N. M. Simon, T. Calvete, R. C. Veses, Applications of Brazilian pine-fruit shell in natural and carbonized forms as adsorbents to removal of methylene blue from aqueous solutions-kinetic and equilibrium study. *J. Hazard. Mater.* 164 (2009) 1213–1222
- [67] C. Mocelin, Pirólise de lodo de esgoto sanitário: produção de adsorvente e óleos combustíveis. (2007). 112 p. Dissertação (Mestrado em Engenharia Mecânica e de Materiais) Universidade Tecnológica Federal Do Paraná.
- [68] X. Chen, S. Jeyaseelan, N. Graham, Physical and chemical properties study of the activated carbon made from sewage sludge, *Waste Manag.* 22 (2002) 755–60
- [69] F. Rodríguez-Reinoso, M. Molina-Sabio, Textural and chemical characterization of microporous carbons, *Adv. Colloid Interface Sci.* 76–77 (1998) 271–294
- [70] C. Yin, M. Aroua, W. Daud, Review of modifications of activated carbon for enhancing contaminant uptakes from aqueous solutions, *Sep. Purif. Technol.* 52 (2007) 403–415
- [71] X. Wang, N. Zhu, B. Yin, Preparation of sludge-based activated carbon and its application in dye wastewater treatment, *J. Hazard. Mater.* 153 (2008) 22–27
- [72] Á.G. Soares,. (2001). 136p. Adsorção de gases em carvão ativado de celulignina, Tese (doutorado) – Universidade Estadual de Campinas, Campinas.
- [73] C. Yin, M. Aroua, W. Daud, Review of modifications of activated carbon for enhancing contaminant uptakes from aqueous solutions, *Sep. Purif. Technol.* 52 (2007) 403–415

- [74] I. Yilgor, J.E. McGrath, In *Polysiloxane Copolymers/Anionic Polymerization*; Springer-Verlag: New York, 1988; pp 1-86.
- [75] N. M. José, L. A. S. A. Prado, *Materiais híbridos orgânico-inorgânicos: preparação e algumas aplicações*, *Quim. Nova*, 28 (2005) 281-288
- [76] M. Ebelmen, *Recherches sur les combinaisons des acides borique et silicique avec les éthers*. *Annales Chim. Phys.* 16 (1846) 129-166.
- [77] T. Graham, *On the properties of silicic acid and other analogous colloidal substances*, *J. Chem. Soc.* 17 (1864) 318-327.
- [78] D.M. Roy, R. Roy, *An experimental study of the formation and properties of synthetic serpentines and related layer silicate minerals*. *American Mineral.* 39 (1954) 957-975.
- [79] C.J. Brinker, G.W. Scherer, *Sol Gel Science: The Physics and Chemistry of sol-gel processing*. San Diego: Academic Press, 1990.
- [80] C. Sanchez, B. Julian, P. Belleville, M. Popall, *Applications of hybrid organicinorganic nanocomposites*, *J. Mat. Chem.* 35-36 (2005) 3559-3592.
- [81] D.M. Ruthven, *Principles of adsorption and adsorption process*. United States of America: Wiley – Interscience Publication, 1984 p. 1 – 13, 221 – 270.
- [82] E.C. Lima, M.A. Adebayo, F.M Machado, Chapter 3- *Kinetic and Equilibrium Models of Adsorption in Carbon Nanomaterials as Adsorbents for Environmental and Biological Applications*, Bergmann, CP, Machado FM, editors, Springer, pp33-69 (2015).
- [83] Y.S. Ho, G. Mckay, *Pseudo-second order model for sorption process* . *Process Biochemistry*, 34 (1999) 451-465
- [84] Y.S. Ho, G. Mckay, *The kinetics of sorption of divalent metal ions onto sphagnum moss peat*. *Wat. Res.* 34 (2000) 735-742
- [85] S. Lagergren, *Zur theorie der sogenannten adsorption geloster stoffe*, *Kungliga Svenska Vetenskapsakademiens. Handlingar*, 24 (1898) 1-39
- [86] I. Langmuir, *The adsorption of gases on plane surfaces of glass, mica and platinum*. *J. Am. Chem. Soc.* 40 (1918) 1361-1403.
- [87] H. Freundlich, *Über die Adsorption in Lösungen*. *Z. Phys. Chem.* 57 (1906) 385-470
- [88] Y. Liu, H. Xu, S.F. Yang, J.H. Tay, *A general model for biosorption of Cd<sup>2+</sup>, Cu<sup>2+</sup> and Zn<sup>2+</sup> by aerobic granules*, *J. Biotechnol.* 102 (2003) 233-239
- [89] R.J. Sips, *On the Structure of a Catalyst Surface*, *Chem. Phys.* 1948, 16, 490
- [90] O. Redlich, D.L. Peterson, *A useful adsorption isotherm*. *J. Chem. Phys.* 63 (1959) 1024–1027
- [91] A. Mulroy, *When the cure is the problem*. *Water Environ. Technol.* 13 (2001) 32–36
- [92] C. Hartig, T. Storm, M. Jekel, *Detection and identification of sulphonamide drugs in municipal waste water by liquid chromatography coupled with electrospray ionisation tandem mass spectrometry*. *J. Chromatogr., A* 1999, 854, 163-173
- [93] T.A. Ternes, M. Stumpf, J. Mueller, K. Haberer, R.D. Wilken, M. Servos, *Behavior and occurrence of estrogens in municipal sewage treatment plants—I. Investigations in Germany, Canada and Brazil*. *Sci. Total Environ.* 225 (1999) 81–90
- [94] M. Winkler, J.R. Lawrence, T.R. Neu, *Selective degradation of ibuprofen and clofibric acid in two model river biofilm systems*. *Water Res.* 35 (2001) 3197-3205.
- [95] A.C. Jonhson, A. Belfroid, A. Di Corcia, *Estimating steroid oestrogen inputs into activated sludge treatment works and observations on their removal from the effluent*. *Sci. Total Environ.* 256 (2000) 163-173.
- [96] E. Zuccato, S. Castioglioni, R. Fanelli, *Identification of the pharmaceuticals for human use contaminating the Italian aquatic environment*. *J. Hazard Mat.* 122 (2005) 2005.

- [97] D.W. Kolpin, E.T. Furlog, M.T. Meyer, E.M. Thurman, S.D. Zaugg, L.B. Barber, H.T. Buxton, Pharmaceuticals, hormones and other organic wastewater contaminants in US streams, 1999–2000: A national reconnaissance. *Environ. Sci. Technol.* 36 (2002) 1202.
- [98] D. Calamari, E. Zuccato, S. Castiglioni, R. Bagnotti, R. Fanelli, Strategic survey of therapeutic drugs in the rivers Po e Lombo in northern Italy, *Environ. Sci. Technol.* 37 (2003) 1241-1248.
- [99] M. Stumpf T.A. Ternes R.D. Wilken S.V. Rodrigues W. Baumann, Polar drug residues in sewage and natural waters in the state of Rio de Janeiro, Brazil. *Sci. Total Environ.* 225 (1999) 135-41.
- [100] F. Rozada, M. Otero, a Morán, A.I. García, Activated carbons from sewage sludge and discarded tyres: production and optimization, *J. Hazard. Mater.* 124 (2005) 181–91
- [101] F. Kirschhöfer, O. Sahin, G.C. Becker, F. Meffert, M. Nusser, G. Anderer, S. Kusche, T. Kläusli, A. Kruse, G. Brenner-Weiss, Wastewater treatment--adsorption of organic micropollutants on activated HTC-carbon derived from sewage sludge, *Water Sci Technol.* 73 (2016) 607-616
- [102] R. Baccar, M. Sarrà, J. Bouzid, M. Feki, P. Blánquez, Removal of pharmaceutical compounds by activated carbon prepared from agricultural by-product, *Chem. Eng. J.* 211–212 (2012)310–317
- [103] C. Saucier, M.A. Adebayo, E.C. Lima, R. Cataluna, P.S. Thue, L.D.T. Prola, M.J. Puchana-Rosero, F.M. Machado, F.A. Pavan, G.L. Dotto, Microwave-assisted activated carbon from cocoa shell as adsorbent for removal of sodium diclofenac and nimesulide from aqueous effluents, *J. Hazard. Mater.* 289 (2015) 18–27
- [104] R.N. Coimbra, V. Calisto, C.I.A. Ferreira, V.I. Esteves, M. Otero, Removal of pharmaceuticals from municipal wastewater by adsorption onto pyrolyzed pulp mill sludge, *Arab. J. Chem.* <http://dx.doi.org/10.1016/j.arabjc.2015.12.001>
- [105] D. Tiwari, C. Lalhriatpui, S-M Lee, Hybrid materials in the removal of diclofenac sodium from aqueous solutions: Batch and column studies, *J. Ind. Eng. Chem.* 30 (2015) 167–173
- [106] Z. Hasan, N.A. Khan, S. H. Jung, Adsorptive removal of diclofenac sodium from water with Zr-based metal–organic frameworks, *Chem. Eng. J.* 284 (2016) 1406–1413
- [107] A. M. M. Vargas, A. L. Cazetta, M. H. Kunita, T. L. Silva, V. C. Almeida, Adsorption of methylene blue on activated carbon produced from flamboyant pods (*Delonix regia*): Study of adsorption isotherms and kinetic models, *Chem. Eng. J.* 168 (2011) 722–730