Federal University of Rio Grande do Sul

Institute of Chemistry

Preparation and characterization of microwave–assisted activated carbons from biomass and application for the removal of Emerging Organic Contaminants (EOCs) in aqueous media.

Doctorate candidate: *Pascal Silas Thue*

August 2017

Porto Alegre, RS

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This thesis is submitted in fulfilment of the requirements of the degree of Doctor in Chemistry.

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August 2017

Porto Alegre, RS

Preface

This work was carried out in the Department of Inorganic Chemistry, Universidade Federal do Rio Grande do Sul, from April 2014 to August 2017, and is submitted in fulfilment of the requirements of the degree of Doctor in Chemistry. This thesis is the result of my own work and includes nothing that is the outcome of work done in collaboration except where specifically indicated in the text. None of the work contained in this dissertation, or any part thereof, has been submitted for any other degree at the Universidade Federal do Rio Grande do Sul or any other institution. This thesis does not exceed 65,000 words, and contains fewer than 75 figures.

Pascal Silas Thue

Examination Jury

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Examiner:

"*Quem tem o Filho tem a vida; quem não tem o Filho de Deus não tem a vida. Estas coisas vos escrevo, a vós que credes no nome do Filho de Deus, para que saibais que tendes a vida eterna. E esta é a confiança que temos nele, que se pedirmos alguma coisa segundo a sua vontade, ele nos ouve. E, se sabemos que nos ouve em tudo o que pedimos, sabemos que já alcançamos as coisas que lhe temos pedido.*"

1 João 5: 12-15.

"O homem não pode receber coisa alguma se do céu não lhe for dada."

João 3:27.

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List of Publication composing the thesis

The work contained in this thesis has led to the following publications:

1- Thue P.S., Adebayo M A., Lima E.C., Sieliechi J.M., Machado F M., Dotto G. L., Vaghetti J.C.P., Dias S.L. P. Preparation, characterization and application of microwave-assisted activated carbons from wood chips for removal of phenol from aqueous solution. Journal of Molecular Liquids 223 (2016) 1067–1080.

2- P.S. Thue, G.S. dos Reis, E.C. Lima, J.M. Sieliechi, G. L. Dotto, A.G. N. Wamba, S.L. P. Dias, F.A. Pavan, Activated carbon obtained from Sapelli wood sawdust by microwave heating for *o*-cresol adsorption, Res. Chem. Intermed. 2016. doi:10.1007/s11164-016-2683-8.

3- Thue P.S., Lima E.C., Sieliechi J.M., Saucier C., Dias S.L.P., Vaghetti J.C.P., Rodembusch F.S., Pavan F.A. Effects of first–row transition metals and impregnation ratios on the physicochemical Chemical properties of microwave-assisted activated carbons from wood biomass; Journal of Colloid and Interface Science, 486 (2017) 163–175.

Additional Publications and presentations

1. Saucier, Caroline; Adebayo, Matthew A.; Lima, Eder C.; Cataluña, Renato; **Thue, Pascal S.**; Prola, Lizie D.T.; Puchana-Rosero, M.J.; Machado, Fernando M.; Pavan, Flavio A.; Dotto, G.L. Microwave-assisted activated carbon from cocoa shell as adsorbent for removal of sodium diclofenac and nimesulide from aqueous effluents. Journal of Hazardous Materials (Print). , v.289, p.18 - 27, 2015.

2. Dos Reis, Glaydson S.; Adebayo, Matthew A.; Sampaio, Carlos H.; Lima, Eder C.; **Thue, Pascal S.**; De Brum, Irineu A. S.; Dias, Silvio L. P.; Pavan, Flavio A. 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 (Print) , (2017) 228: 33.

3. Puchana-Rosero, M.J.; Adebayo, Matthew A.; Lima, Eder C.; Fernando M. Machado; **Thue, P.S.**; Umpierres, Cibele S. Microwave-assisted activated carbon obtained from the sludge of tannery-treatment effluent plant for removal of leather dyes. Colloids and Surfaces. A, Physicochemical and Engineering Aspects (Print). , v.504, p.105-115 - 115, 2016.

4. Saucier, Caroline; Adebayo, Matthew A.; Lima, Eder C.; Prola, Lizie D. T.; **Thue, Pascal S.**; Umpierres, Cibele S.; Puchana-Rosero, Mayerly J.; Machado, Fernando M. Comparison of a Homemade Bacuri Shell Activated Carbon With Carbon Nanotubes for Food Dye Removal. Clean (Weinheim. Print). , (2015) v.43, p.1389 - 1400.

5. Leite, A. J.; Sophia A, C.; **Thue, Pascal S.**; Dos Reis, Glaydson S.; Dias, Silvio L. P.; Eder C. Lima; Vaghetti, Julio C.P.; Pavan, Flávio A.; Alencar, W. S. Activated carbon from avocado seeds for the removal of phenolic compounds from aqueous solutions. Desalination and Water Treatment, (2017) 71, p.168 - 181.

6. Umpierres, Cibele S.; **Thue, P. S.**; Lima, Eder C.; Dos Reis, Glaydson S.; De Brum, Irineu A. S.; Alencar, W. S.; Dias, Silvio L. P.; Dotto, G. L. Microwave activated carbons from Tucumã (Astrocaryum aculeatum) seed for efficient removal of 2-nitrophenol from aqueoussolutions. Environmental Technology. , 2017.

7. Dotta Filho; Pavan, Flavio A.; Mazzocato, A. C.; **Thue, Pascal S.**; Dotto, G. L. Eragrostis plana Nees a novel eco-friendly adsorbent for removal of crystal violet from aqueous solutions. ENVIRONMENTAL SCIENCE AND POLLUTION RESEARCH , 2017 DOI 10.1007/s11356-017-9365-y.

Presentations:

1. **Pascal S. Thue**, Lima, Eder C; Prola, Lizie D. T; Saucier, Caroline: Produção de carvão ativo de resíduos lignocelulósicos por irradiação de micro-ondas. Regional Conference Les Doctoriales Rio Grande Do Sul, Bento Gonçalves-RS, on 8-12 November, 2015. *Poster presentation*.

2. C. Saucier, E.C. Lima, L. D. T. Prola, **P. S. Thue**, R Cataluña, M.J. Puchana-Rosero, M.A.Adebayo, F.Machado: 2º SIMPOSIO; IBEROAMERICANO DE ADSORCIÓN, Cartagena de Indias Colombia 26-30 de Abril de 2015; Microwave-assisted activated carbon from cocoa shell as adsorbent for removal of sodium diclofenac and nimesulide from aqueous effluents. *Oral Presentation*.

3. Prola, L. D. T.; Lima, E. C.; Saucier, C.; **Thue, P. S**.; Rosero, M. J. P.; Umpierres, C. S: 38ª Reunião Annual da Sociedade Bresileira de Química, Águas de Lindóia, on 25-28 May, 2015: Poster title: Microwave-assisted activated carbon from cocoa shell as adsorbent for removal of sodium diclofenac and nimesulide from aqueous effluents. *Poster presentation*.

4. Caline Rorigues Gally, Liziê Daniela Tentler Prola, Éder Cláudio Lima, Mayerli Johana Puchana-Rosero, Caroline Saucier, **Pascal Silas Thue** and Cibele Santanna Umpierres: XIII Encontro da SBP Mat João Pessoa 2014, from Setember 28th to October 2nd. Adsorption of direct blue 53 dye from aqueous solutions by multiwalled carbon nanotubes; International Conference. *Poster presentation*.

Patents:

1. **Thue, P.S.**; Lima, Eder C.; Dias, Silvio L.P.; Vaghetti, Julio C.P. CARVÃO ATIVADO MAGNÉTICO,PROCESSO DE OBTENÇÃO E APLICAÇÃO DO MESMO, 2016. Categoria: Processo. Instituição onde foi depositada: INPI - Instituto Nacional da Propriedade Industrial. País: Brasil. Natureza: Patente de Invenção. Número do registro: BR10201603035. Número do depósito PCT: 870160078447.

2. Eder C. Lima; WAMBA, ALFRED G. N.; **THUE, P. S**.; DIAS, SILVIO L.P.; Julio.CP Vaghetti. MATERIAL POZOLANA MODIFICADO COM AMINOSILANO, PROCESSO DE OBTENÇÃO E USOS DO MESMO, 2017. Categoria: Processo. Instituição onde foi depositada: INPI - Instituto Nacional da Propriedade Industrial. País: Brasil. Natureza: Patente de Invenção. Número do registro: BR1020170142. Número do depósito PCT: 870170045431.

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Abbreviations

SEM: Scanning Electron Microscopy

FTIR : Fourier transform infrared spectroscopy

NIR : Near-Infrared

DRS : Diffuse Reflectance Spectroscopy

DRUV: Diffuse reflectance ultraviolet-visible

TGA: Thermogravimetric analysis

DTG: Derivative Thermogravimetric

BET: Brunauer, Emmett and Teller

BJH : Barret, Joyner and Halenda

XRD: X-ray Diffraction

XRF: X-ray Fluorescence

pH_{pzc} : Point of zero charge

MWAC: Microwaves Activated Carbons

EA: Elemental analysis

S_{BET}: Surface area

V_{tot}: Total pore volume

V_{mes}: Mesopore volume

V_{mic}: Micropore volume

AC: Activated Carbon

Abstract

In this thesis activated carbons from lignocellulosic biomass were prepared *via* microwave–assisted pyrolysis, characterized and applied into the removal of Emerging Organic Contaminants (EOCs) in aqueous media. A scientific understanding of the three-step preparation of activated carbons (AC) using first-row transition metals as activating agents by microwaves heating is also provided. The mixtures obtained after preparation step were pyrolysed in a microwave system in less than 11 min. Afterwards a 6 mol L^{-1} HCl was used to treat the pyrolysed materials, under reflux, to eliminate the inorganic components—producing activated carbons. This technology allows producing activated carbons with high porosity. Elemental analysis, FTIR, UV-Vis DRS, SEM, N_2 adsorption/desorption curves, TGA, XRD X-ray fluorescence, pH_{zpc}, hydrophobic properties, total acidity and basicity groups were used to characterise biomass, intermediary materials and activated carbons. Results showed that the metals were bound successfully in different amounts with surface functional groups of the wood biomass through ion exchange and surface complexation interaction during the impregnation step. However, MWAC prepared with Zn^{2+} showed higher pore volumes and surface areas, which was related to their high adsorption capacity (q_e). The samples prepared with the mixtures biomass: inorganic components (20% lime + 80% $ZnCl_2$ or 20% lime + 40% $ZnCl_2$ + 40% $FeCl_3$) at different ratios were used for the complete adsorption study of phenol (PhOH) and *o*-cresol from aqueous solution. Results indicated that adsorption kinetic was very fast and equilibrium contact time was attained in the first 10 min for both molecules. Pseudo first-order, pseudo-second order and Avrami fractional-order kinetic models were used to probe the kinetic of adsorption. Among the three models; Avrami fractional-order kinetic model best described the adsorption kinetics of PhOH and *o*-cresol onto the activated carbons. The main interaction of PhOH or *o*-cresol with the activated carbons should be governed by hydrophobic interactions, hydrogen bonds, polar interactions and electron donor-acceptor interaction. While desorption experiment showed that activated carbons can be regenerated easily using a mixture of EtOH (10 or 50%) + NaOH (5 M). Additionally, MWAC prepared with $CuCl_2$, $CoCl_2$ and $NiCl_2$ also exhibited high adsorption capacity. The adsorption order of the molecules is as shown: 2-nitro phenol > Bisphenol A > hydroquinone > 4-nitro phenol > 2-naphtol > paracetamol > caffeine > resorcinol. However, $ZnCl_2$ demonstrate to be the best activating agent, which allows for the development of materials of high porosity as well as good adsorptive properties, and this trend is followed subsequently by $CuCl_2$, $CoCl_2$, and $NiCl_2$.

Resumo

Nesta tese, carvões ativos (AC) oriundos de biomassa lignocelulósica foram preparados por pirólise assistida por microondas, caracterizados e aplicados na remoção de contaminantes orgânicos emergentes (EOCs) em meio aquoso. Foram estudadas as três etapas da preparação dos carvões ativos utilizando metais de transição como agentes de ativação. As misturas obtidas após a etapa de preparação foram pirolisadas num sistema de microondas em menos de 11 min. Em seguida, utilizou-se uma solução de HCl 6 mol L^{-1} para tratar os materiais pirolisados, sob refluxo, lixiviando os componentes inorgânicos e produzindo os carvões ativos. Esta tecnologia permitiu a produção de carvões ativos com alta porosidade. Análise elementar, FTIR, DR-UV, microscopia eletrônica de varredura, adsorção-dessorção de nitrogênio, TGA, DRX, FRX, pH$_{pzc}$, propriedades hidrofóbicas e acidez e basicidade totais foram utilizados para a caracterização da biomassa, do material pirolisado e dos carvões ativos. Os resultados indicaram que os metais foram ligados em diferentes quantidades na superfície da biomassa através de interação iônica e interação de complexação superficial, durante a etapa de impregnação. Os carvões ativos (MWAC) obtidos a partir da impregnação com Zn^{2+} apresentaram maior volume de poros e maior área superficial específica. Esses dados foram relacionados com a capacidade de adsorção. Amostras preparadas com as misturas de biomassa : componentes inorgânicos em diferentes proporções (20% de cal+ 80% de ZnCl$_2$ ou 20% de cal+ 40% de ZnCl$_2$ + 40% de FeCl$_3$) foram utilizadas para o estudo completo de adsorção de fenol (PhOH) e o-cresol. Os resultados indicaram que a cinética de adsorção para ambas as moléculas foi rápida e o tempo de contato em equilíbrio foi alcançado nos primeiros 10 minutos. Os modelos cinéticos de pseudo-primeira ordem, pseudo-segunda ordem e de ordem fracionária de Avrami foram utilizados para investigar a cinética de adsorção. Destes três modelos, o de ordem fracionária de Avrami descreveu melhor a cinética de adsorção de PhOH e *o*-cresol na superficie dos cavões ativos. As principais interações de PhOH ou o-cresol com os materias devem ser regida por interações hidrófóbicas, ligações de hidrogênio, interações polares e interação doadores e aceitadores de elétrons. Os estudos de dessorção mostraram que os carvões ativos podem ser regenerados facilmente utilizando-se uma mistura de EtOH (10 ou 50%) + NaOH (5 M). Além disso, o MWAC preparado com CuCl$_2$, CoCl$_2$ e NiCl$_2$ também apresentou alta capacidade de adsorção. As capacidades de adsorção (qe) das moléculas seguiram esta ordem: 2-nitrofenol > bisfenol A > hidroquinona > 4-nitrofenol > 2-naftol > paracetamol > cafeína > resorcinol. Todavia, ZnCl$_2$ parece ser o melhor agente ativador, permitindo o desenvolvimento de materiais de alta porosidade, bem como boas propriedades de adsorção, e essa tendência é seguida posteriormente por CuCl$_2$, CoCl$_2$ e NiCl$_2$.

1. Introduction

The current estimated global demand for activated carbons is 1.1 million tons per annum, increasing at a rate of 9 %/year, and expected to further increase to more than 10 %/year over the next 5 years[1,2]. This fact has inflated the price of activated carbon on the market. The performance of activated carbon is influenced by surface area, pore volume, pore size distribution and surface chemistry, including oxygen-containing functional groups, degree of polarity and active surface area[2]. These properties are directly related to the physical and chemical properties of the precursor material, the type of the production method and conditions[3].

Finding an economical way of producing activated carbon, as well as understanding the key mechanisms involved in the process (impregnation and pyrolysis step), and production of highly porous materials are still outstanding challenges. Many studies have been performed on the development of low-cost activated carbons from various agricultural by-products or wastes, such as: sunflower seed hull and sugar cane bagasse[4], wood chips[5], cocoa shells[6], pistachio shells[7], cotton stalks[8], corn shells[9], pine corns[10], corn cobs[11], *Elaeagnus angustifolia* seeds[12], barley husks[13], wood sawdust[14], orange peels[15], etc. However, studies continuing to seek novel biomasses for the production of low-cost adsorbents and with high porosity.

Conventionally, activated carbons are usually prepared through physical or chemical activation using a muffle furnace[4,5,16,17]. In these methods, heat is transferred to the samples by conduction and convection mechanisms. This thermal gradient leads to an inhomogeneous microstructure with a high heating rate[18]. As an alternative heating method, microwave irradiation has attracted considerable attention in recent years[6,19-23]. By using microwave heating, it is possible to produce activated carbon in a fast and easy way[6,19-23]. Due to the remarkable reduction in pyrolysis time, microwave-assisted pyrolysis has become an attractive alternative for the preparation of activated carbon. In this approach, microwaves supply energy to the carbon particles, which is converted into heat within the particles themselves by dipole rotation and ionic conduction. The microwave heating method has the advantages of rapid temperature rise, uniform temperature distribution and energy savings over conventional heating methods[23].

The common activating agents used during the carbonization process are $FeCl_3$[16], H_3PO_4 [17], KOH [19] and K_2CO_3 [14,15]. Generally, $ZnCl_2$ and $FeCl_3$ have proven to be excellent activating agents due their ability to develop narrow pore sizes and high surface areas of activated carbon[24]. As an activating agent, $FeCl_3$ provides similar characteristics to $ZnCl_2$, including the promotion of the dehydration process of biomass materials, the restriction of the formation of tars and the improvement of the carbon yield[25]. However, up to the best of our

knowledge, no study has been performed on the incorporation of $CoCl_2$, $NiCl_2$ and $CuCl_2$, first-row transition metal salts into a wooden biomass (*Entandrophragma cylindricum* or Sapelli) structure and their effects on the physicochemical properties of the activated carbons produced *via* microwave-assisted pyrolysis. First-row transition metals have been successfully used in the catalysis industry for upgrading during the thermo-chemical conversion of biomass to bio-oil[26-29]. Likewise, only $ZnCl_2$ and $FeCl_3$ have been used extensively in the development of porous activated carbons[4,9,10]. However, $CoCl_2$, $NiCl_2$ and $CuCl_2$ have not yet been reported in the literature as potential activating agents for the development of porous activated carbons.

On the other hand, emerging organic contaminants (EOCs), detected in groundwater have drawn a lot of preoccupation. In fact, emerging contaminants such as pharmaceuticals, personal care products (PCPs), pesticides (including some phenols), synthetically and naturally occurring hormones, flame retardants and some disinfection by-products, most of them considered as potential endocrine disrupting compounds (EDCs), usually end up into the wastewater cycle after their industrial and domestic uses. Therefore, they can be detected in wastewater treatment plants effluents, since the conventional treatment technologies are not effective for the removal of these contaminants[30]. Phenol and its derivatives are usually used in the synthesis of pesticides and some time can be used directly for agricultural purposes. Because of high toxicity to living organisms[31], these compounds must be removed from industrial effluents before their wastes are disposed.

Several techniques for treatment of wastewaters contaminated with such pollutants have been proposed. These generally include membrane filtration[32], oxidative degradation[33], biodegradation[34], photocatalytic degradation[35], photo-Fenton[36], and adsorption[37-41]. Amount them, adsorption process is generally accepted because of simplicity, easy operation and low-cost. Adsorption process involves transference of toxic substances from the aqueous phase to a solid phase thereby ameliorates exposure of living organisms to pollutants. After decontamination of effluents using adsorption technology, the treated effluents are safe to be released into the environment or the water could be reutilised for some industrial processes, which require water of low purity. Another advantage of adsorption method is that the spent adsorbents can be regenerated and reused[42].

1.1-Objectives

The main goal of this work is to valorize lignocellulosic residue in the preparation and characterization of microwave–assisted activated carbons and application for the removal of Emerging Organic Contaminants (EOCs) in aqueous media. A part of this general objective was achieved by realizing several key objectives.

1. Firstly, the mechanism preparation of activated carbons using $FeCl_3$, $ZnCl_2$, $CoCl_2$, $NiCl_2$ and $CuCl_2$ as activating agents at different impregnation ratios was studied.

2. Secondly, several techniques were used to characterize the materials such as N_2-adsorption/desorption analyses, SEM, FTIR, XDR, XF, UV-Vis DRS, elemental analysis, TGA/DTG, pH_{zpc}, total acidity and basicity groups, and hydrophobic/hydrophilic ratio.

3. Finally, the activated carbons produced were used for the removal of bisphenol A, paracetamol, caffeine, 2-naphtol, 2-nitro phenol, 4-nitro phenol, resorcinol and hydroquinone from aqueous solution. A complete adsorption experimental study was carried out for phenol and o-cresol in aqueous solution. This includes equilibrium isotherms, kinetics, thermodynamic, adsorption mechanism, simulated of effluents and desorption study. The influence of some main adsorption parameters such as pH, initial concentration, and mass adsorbent were further considered.

1.2-Structure of the thesis

This thesis was structured in the form of scientific *Scopus* articles, according to the Resolution N˚ 093/2007, of 12/06/2007 of the Post-graduation assembly of the Federal University of Rio Grande do Sul (UFRGS), which establishes guidelines for the publication and writing of Ph.D Thesis, Master dissertations and completion of Specialization Courses. In this view, the thesis was structured as follows:

1. General Introduction: briefly present the background, the scope and the objectives of this work.

2. Literature reviews: reviews the literature relating to activated carbon preparation technology, the environmental concerns about emerging organic contaminants (EOCs), the accent was put to phenols and it derivatives and caffeine. Additionally, some technologies commonly used to tackle those pollutants in aqueous solution were listed. However adsorption process, which was the process used in this thesis is presented in detail.

3. Materials and methods: describes the methods used in this study for the preparation of microwave-activated carbons using $FeCl_3$, $CoCl_2$, $NiCl_3$ and $CuCl_2$, and $ZnCl_2$ as activating

agents. Advanced methods for characterization of the produced materials are described as well as the analytical method for the phenols and caffeine´s determination in aqueous solution after adsorption process. Furthermore, the experimental conditions and batch test adsorption procedures are also described in detail.

4. Conclusion and future studies: Summarizes the main results obtained in this thesis. The proposals for future work are also offered.

5. **Annexes 1** and **2** present the preparation, characterization and application of microwave-assisted activated carbons from wood chips for removal of phenol and O-cresol from aqueous solution. $FeCl_3$ and $ZnCl_2$ were used as activating agents during the preparation of activated carbons, and was combined with lime ($CaCO_3$ + $Ca(OH)_2$ + CaO) to prevent permeation of aqueous solution in the carbonaceous material. Several characterizations was done to the four activated carbons produced and batch adsorption experiments were carried out with phenol and O-cresol molecules in aqueous solution. This includes, equilibrium isotherms, kinetics, thermodynamic, adsorption mechanism, simulated of effluents and desorption study. The influence of some main adsorption parameters such as pH, initial concentration, and mass adsorbent were further considered.

6. **Annex 3** presents the study related to the effect of first–row transition metals and impregnation ratios on the physicochemical properties of microwave-assisted activated carbons from wood biomass. The effect of four activating agents $CoCl_2$, $NiCl_2$, $CuCl_2$, and $ZnCl_2$ at different impregnation ratios on the development of pore characteristics of surface functional groups of activated carbons produced *via* assisted microwaves irradiation was studied. Several techniques were used to characterize the 16-activated carbons produced. Additionally, the adsorption capacity of the aforementioned material was evaluated in the removal of bisphenol A, paracetamol, caffeine, 2-naphtol, 2-nitro phenol, 4-nitro phenol, resorcinol and hydroquinone from aqueous solution.

2. Literature Review

2.1-Activated Carbons (ACs)

AC [Chemical Abstract Service (CAS) registry number: 7440-44-0 and atomic weight (A.W.): 12.00 g][43] is a carbon-based material which has a high surface area and relatively high porosity. Its structure[44] is shown in **Figure 1** and it is primarily composed of sp^2 graphite crystallites which comprise 3 to 4 parallel hexagonal carbon ring layers separated by 3.44 - 3.65 Å interlayer spacing which is slightly greater than that (3.35 Å) in graphite and are approximately 10 nm in length. However, the major structure in AC is composed of microcrystalline and amorphous graphitic-like sheets, called "basal planes" which are randomly cross-linked, unevenly stacked, and surrounded by a number of unpaired electrons. In fact, sp^2 orbitals which are the basis of graphitic and aromatic structures, are directed in a plane at 120^0 to each other and the fourth electron in a p-orbital is free to form π-bond with neighbouring atoms. These particular architectural features make AC enormously porous and useful for applications in catalysis and adsorption with a wide range of molecules. Moreover, AC contains various heteroatoms such as oxygen, hydrogen, nitrogen, phosphorous, and sulphur. However, the covalently bound atomic or adsorbed molecular oxygen is the major heteroatom, which can strongly alter the chemical properties of AC.
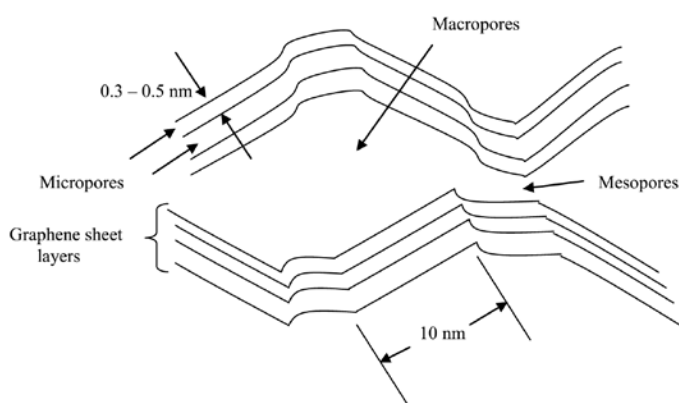
Figure 1. *Diagram of AC morphology. Straight line segments refer to graphene sheets. (adapted from Ref.* *44).*

2.2- Preparation of Activated Carbons from Biomass

In the last decades, many studies have been performed on the development of low-cost activated carbons from various agricultural by-products or wastes, as an alternative for expensive coal-based activated carbon. Biomass mainly derived from industrial and agricultural solid waste is a preferable option for activated carbon precursors, such as: sunflower seed hull and sugar cane bagasse[4], wood chips[5], cocoa shells[6], pistachio shells[7], cotton stalks[8], acorn shells[9], pine corns[10], corn cobs[11], *Elaeagnus angustifolia* seeds[12], barley husks[13], wood sawdust[14], orange peels[15], etc. Biomass materials are cheaper, renewable and abundantly available.

Sapelli (*Entandrophragma cylindricum*) is a wood with a red colour and it is highly demanded for their durability. It is very strong and therefore widely used for various purposes and in particular in the manufacture of small bridges. This wood contains plant constituents such as cellulose, hemicellulose, lignin, and pectin at a very high rate of about 98%. Chips and sawdust are waste biomass from wood processing. A study in 28 sawmills in the city of Ngaoundere, Cameroon revealed very high use of lignocellulosic wood species (3.120 tons per year) such as Ayous, Sapelli and Iroko. The transformation of these species generates tons of waste per year[5]. Therefore, any attempt to reuse this waste will be useful for the country.

Figure 2. *Chips (A) and sawdust (B) waste biomass from wood processing*

2.3- Production processes of Activated Carbons.

There are mainly two processes by which activated carbons are produced: Conventional processes and most recently, microwaves assisted pyrolysis. The former is known as a

traditional heating system, with an external heat source such as an oil bath or heating mantle where heat is transferred from the surface towards the center of the material by conduction, convection, and radiation. However the latter is known as internal heating where dielectric heating transfers electromagnetic energy to thermal energy; it is a kind of energy conversion rather than heating. The both techniques are usually performed in the inert atmosphere.

2.3.1- Conventional processes

Conventionally, activated carbons are usually prepared through physical or chemical activation using a muffle furnace[4,5,16,17]. In these methods, heat is transferred to the samples by conduction and convection mechanisms in inert atmosphere (N_2 or Ar). This thermal gradient leads to an inhomogeneous microstructure with a high heating rate[18].

2.3.1.1- Physical activation

Activated carbon (AC) is produced by carbonizing and subsequent activation of the precursor. In physical activation, char is produced, at the first step, by carbonization (pyrolysis) of precursor. This step removes non-carbon species and produces char with a high percentage of carbon. Because of blockage of the pores by tars[45], the internal surface area of char is too low and it does not have a developed porous structure. Second step of physical activation is high temperature gasification (activation) using oxidizing agents such as steam or carbon dioxide (CO_2), which produces activated carbon with high porosity. Porosity development is due to the penetration of oxidizing agent into the internal structure of char and removal of carbon atoms by reaction which results in opening and widening of inaccessible pores[45, 46].

Both reactions between steam-carbon (heterogeneous water-gas reaction) and CO_2-carbon are endothermic[47]. This oxidation process is described in equations (1) and (2) as follows:

$$C_{(s)} + H_2O_{(g)} \longrightarrow CO_{(g)} + H_{2(g)} \qquad (29 \text{ kcal mol}^{-1}) \qquad (1)$$
$$C_{(s)} + CO_{2(g)} \longrightarrow 2CO_{(g)} \qquad (39 \text{ kcal mol}^{-1}) \qquad (2)$$

Macropores arising from randomly cross-linked and unevenly stacked basal planes are found on the surface of AC, however meso and micropores are found within the structure of AC because those pores are the result of oxidation. A schematic[48] of the porous structure of AC is shown in **Figure 3**. Furthermore, heteroatoms are covalently bonded into the structure of AC during carbonization (e.g., nitrogen from the inert atmosphere) and activation (e.g., oxygen, hydrogen, sulphur, and phosphorous from chemical oxidizing agents).
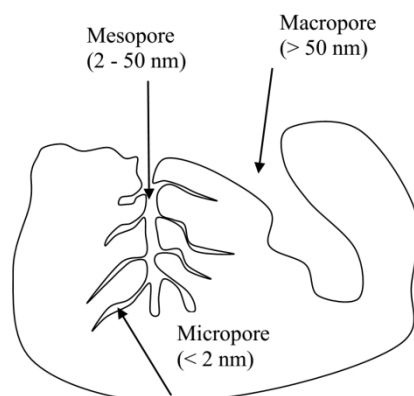
Figure 3. *Schematic of the pore structure observed in AC (adapted from Ref. 48).*

2.3.1.2- Chemical activation

Chemical activation of the precursor with a chemical (dehydrating) agent is another important industrial process for producing activated carbons. It is shown that some operating conditions such as temperature and heating rate affect the micropores distribution size to some extent[49]. The chemical activation is considered as a suitable method for producing highly microporous or mesoporous activated carbons; and is a combined process of carbonization and activation at relatively low reaction temperatures (500°C - 700°C).

The common activating agents used during the carbonization process are $FeCl_3$[16], H_3PO_4 [17], KOH [19] and K_2CO_3 [14,15].

In comparison with the physical activation, the chemical activation mechanism is not well understood[50], but it seems that the chemical agent dehydrates the sample, inhibits the tar formation and volatile compounds evolution, and therefore enhances the yield of the carbonization process[51]. After impregnating the organic precursor by chemical agent, the carbon material is pyrolyzed under inert atmosphere (500-700°C) for a suitable time (30 min- 2 h). After the carbonization, the inorganic contents present in the carbonized material should be eliminated by an efficient extraction with acid/base and water[5,23]. This extraction step makes the pore structure available, by removing the impregnating agent and its salts. In some cases, the precursor is in the form of fiber, cloth, or felt and the final activated carbon is in the same form.

Generally, $FeCl_3$ and $ZnCl_2$ have proven to be excellent activating agents due to their ability to develop narrow pore size distributions and high surface areas of activated carbon[24]. As an activating agent, $FeCl_3$ provides similar characteristics to $ZnCl_2$, including the promotion of the dehydration process of biomass materials, the restriction of the formation of tars and the

improvement of the carbon yield[25]. Depending on the nature of biomass, $FeCl_3$ and $ZnCl_2$ can be mix with other inorganics such as Lime ($CaCO_3$ + $Ca(OH)_2$ + CaO) in the preparation of activated carbons in other to form homogenous paste and prevent permeation of aqueous solution in the carbonaceous material as reported for preparation of cocoa shell activated carbon[6,52] and composite adsorbents from coffee waste[53]. However, up to the best of our knowledge, no study has been performed on the incorporation of $CoCl_2$, $NiCl_2$ and $CuCl_2$, first-row transition metal salts into a wooden biomass structure and their effects on the physicochemical properties of the activated carbons. First-row transition metals have been successfully used in the catalysis industry for upgrading during the thermo-chemical conversion of biomass to bio-oil[26-29]. Likewise, only $FeCl_2$ and $ZnCl_2$ have been used extensively in the development of porous activated carbons[4,9,10]. However, $CoCl_2$, $NiCl_2$ and $CuCl_2$ have not yet been reported in the literature as potential activating agents for the development of porous activated carbons. The mechanism reaction of the biomass with transition metals during the pyrolysis process could be quite different to others activating agents. Therefore, setting the information mechanisms involved in the process (impregnation and pyrolysis step), and production of highly porous materials are some of the most important and fundamental issues in the field. Moreover the application in the water contaminated by emerging organic contaminants (EOCs) in aqueous solution can be very interesting to solve important environmental issue.

2.3.2- Microwaves heating process

2.3.2.1- Theoretical aspects of microwave

Microwave energy is a form of electromagnetic energy with the frequency range of 300 MHz to 300 GHz and the corresponding wavelengths are between 1 mm and 1 m. In this process, the materials couple with microwaves, absorb the electromagnetic energy volumetrically, and transform into heat.

The frequency and wavelength range of microwaves are shown in **Figure 4**. Microwaves have longer wavelengths and lower available energy quanta than other forms of electromagnetic energy such as visible, ultraviolet or infrared light. The first microwaves application came to the extensive use in communication such as radar, television and satellite applications. The second application is microwave heating of different materials. The most commonly used frequencies for heating purposes are 915 MHz and 2.45 GHz, which are derived from electrical energy with the transformation efficiency of about 85% and 50%, respectively[18].
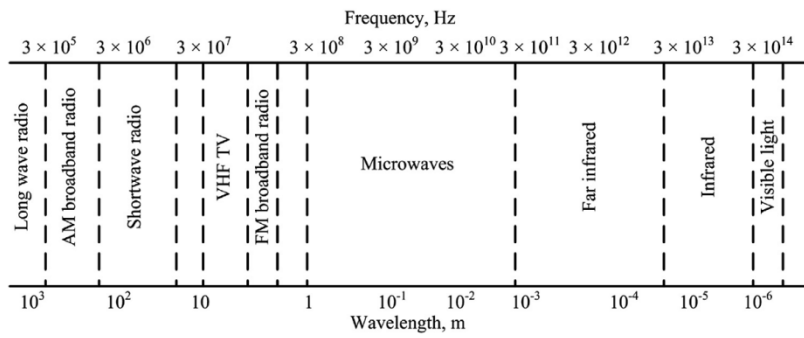
Figure 4. *Frequency and wavelength range of microwaves (adapted from Ref. 54)*

The dielectric interaction of materials with microwaves can be described by two important parameters: absorbed power (*P*) and depth of microwave penetration (*D*). They will determine the uniformity of heating throughout the material. The average absorbed power, *P*, which is volumetric absorption of microwave energy (W/m³) in material, is expressed[55] as:

$$P = 2\pi f \varepsilon'' E^2 \tag{3}$$

$$d = (c\varepsilon^0)/2\pi\varepsilon'' \tag{4}$$

f: electromagnetic wave frequency (Hz); ε'': dielectric loss (F/m); ε^0: permittivity of free space (8.85×10^{-12} F/m); E: electric field strength (v/m) and c the speed of light (3×10^8 m/s).

2.3.2.2- Advantages of microwaves assisted-pyrolysis

As an alternative heating method, microwave irradiation has attracted considerable attention in recent years[6,19-23]. By using microwave heating, it is possible to produce activated carbon in a fast and easy way[6,19-23]. Due to the remarkable reduction in pyrolysis time, microwave-assisted pyrolysis has become an attractive alternative for the preparation of activated carbon. In this approach, microwaves supply energy to the carbon particles, which is converted into heat within the particles themselves by dipole rotation and ionic conduction. The microwave heating method has the advantages of rapid temperature rise, uniform temperature distribution and energy savings over conventional heating methods[23].

Microwave synthesis is a non-contact technique where the heat is transferred to the product via electromagnetic waves, and large amounts of heat can be transferred to the interior of the material, minimizing the effects of differential synthesis[56, 57]. On the other hand, microwave radiation method is both internal and volumetric, where the huge thermal gradient from the interior of the sample to the cool surface allows the microwave-induced reaction to

proceed more quickly and effectively at a lower bulk temperature (**Figure 5**), providing shorter processing time and saving energy[58].
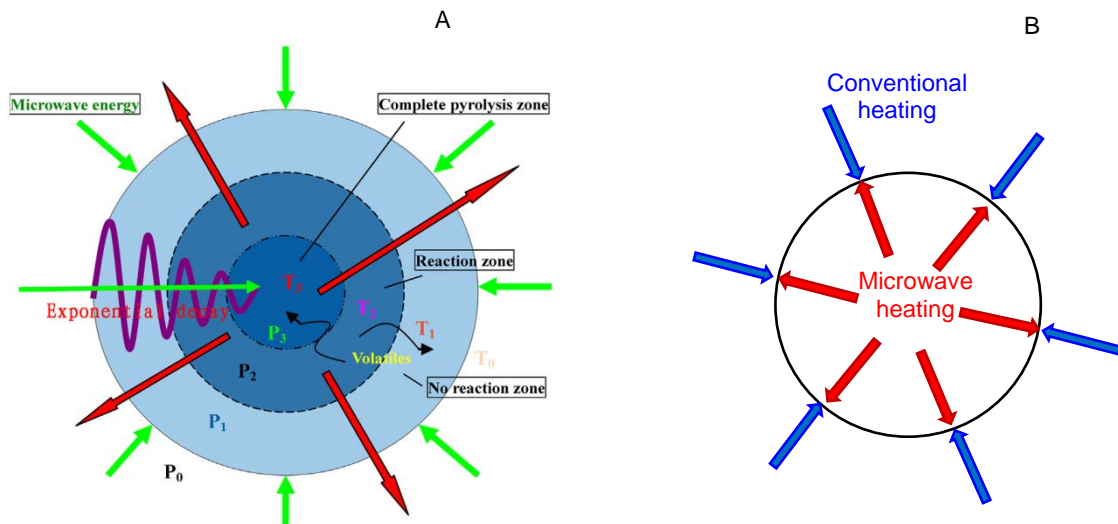

Figure 5. *Schematic diagram of energy conversion and heat and mass transfer process during microwave heating **(A)** (T – Temperature, $T_3>T_2>T_1>T_0$; P–Pressure, $P_3>P_2>P_1>P_0$); **(B)** microwave and conventional heating mechanism (adapted and modified from Ref. 59)*

Activation agents are the main absorbers of microwave radiation at the initial stage of activation. Without using a chemical agent, the carbonaceous raw materials are hardly heated[60].

After the development of pore structure at the initial stages, the AC itself could receive the energy from microwave radiation during the activation process. Besides being used to develop high porous materials, transition metals usually offer good heat conduction proprieties into the microwaves system. Depending on the metal ions or others inorganics present in the impregnated organic precursor, the speed will be quite different. This may have a breathing effect to the porosity of the activated carbon.

2.3.2.3. Disadvantages of microwaves assisted-pyrolysis

Although microwave heating offer several advantages that were previously pointed out, it is important to underline that this technology suffers from some drawbacks in comparison with conventional heating methods:

• Microwave radiation presents an additional hazard over traditional heating methods, although this is easily contained within an appropriate Faraday cage. The nonionizing nature of the radiation also limits risk in the event of exposure, with the radiation having insufficient energy per quantum to create biologically damaging ionised atoms or molecules.

11

- Control of temperature is general difficult and need further study.

- While the property of microwave heating only to target microwave-receptive materials can be an advantage in some cases, in the event that microwave transparent materials (such as plastics) require heating, an intermediate microwave receptor must be used.

- Using microwave heating places limits on the materials that can be used in the construction of a reactor. While metal is essential in an electromagnetic containment role, its use should be minimised within the reactor itself to avoid causing arcing, with sharp metallic corners and small physical gaps between metal surfaces presenting the highest risk of potential arc formation[61].

2.4- Organic contaminants and Environmental Impacts

As a result of rapid development of chemical and petrochemical industries due to the increase of the world population, surface and ground waters are polluted by various organic and inorganic chemicals such as phenolic compounds, dyes, pesticides and heavy metals.

2.4.1- Phenolic compounds

Phenol and its derivatives are organic compounds with one or more *OH* groups attached to an aromatic ring; acting as intermediates in the production of synthetic resins, flavours, pesticides and disinfectors[62].

Ranked as second class of pollutants in the environment, phenol and its derivatives are considered noxious, because they are toxic and harmful to living organisms even at low concentrations[31,63]. Phenols are being discharged into the waters from various industrial processes such as oil refineries, petrochemical plants, paper mill, pharmaceutical factory, ceramic plants, dyes, coal conversion processes and phenolic resin industries[64]. The utilization of phenol-contaminated waters, foodstuff or any consumed products containing phenol could causes protein degeneration, tissue erosion, paralysis of the central nervous system, also damages the kidney, liver and pancreas in human body[65]. According to the recommendation of World Health Organization (WHO), the maximum admissible amount for phenolic contents in drinking waters[66] is 1 $\mu g.L^{-1}$; and the regulations by the U.S. Environmental Protection Agency (USEPA)[67], call for lowering phenol content in wastewaters less than 1 $mg.L^{-1}$. Therefore, removal of phenols from waters and wastewaters is an important issue in order to protect public health and environment.

Cresols are organic compounds which are methylphenols. The worldwide production only of *O*-cresol is approximately 37000-38000 tones/annum. Cresols are a widely occurring

natural and manufactured group of aromatic organic compounds which are categorized as phenols. These pollutants are widely found in the effluent from many chemical and allied industries, namely petrochemical, oil refinery, metal refining, chemical and glass fiber manufacturing, ceramic plants, steel plants and phenolic resin manufacturing. As they are slowly oxidized by length exhibition in the air, these pollutants are known to possess high toxicity and low biodegradability, for which their occurrence in wastewater has become an important environmental issue[68]. In order to decrease the potential risk of these pesticides and reduce their appearance in the water, the Europe an Community Directive has determined a tolerance level of 0.5μg/L in water intended for human consumption. In this sense, *O*-cresol was chosen as a pollutant because it is one of most abundant phenolic compound frequently found in industrial wastewater. In recognition of its toxicity and high mobility in the environment, the Environmental Protect ion Agency (EPA) and the European Environmental Agency (EEA) have included this compound in the lists of priority pollutants to be monitored in industrial effluents[69, 70].

Because they can be used directly as pesticides, cresols are considered as Emerging Organic Contaminants (EOCs), concept which is revised in the next section.

2.4.2- Emerging Organic Contaminants (EOCs)

Synthetic organic substances are widely used in industry to manufacture food preservatives and pharmaceutical products. The release of these 'micro-organic pollutants' into environment, especially groundwater, has elicited interest among scientists due to their potential toxicity[71]. Although the concentrations of these substances, in aquatic systems, are relatively low, long term exposure may harm terrestrial and aquatic organisms. Hence, they are classified as emerging contaminants. 'Emerging Organic Contaminants' (EOCs), which include compounds newly discover or developed, and substances that are recently listed as pollutants, contain a wide range of compounds, such as pesticides, personal care products (PCPs), food additives, healthcare products and tailor-made nano-sized materials[71]. These compounds are released into environment *via* several pathways including the effluents of hospital[72] and industrial sites, agricultural land and household waste[73].

2.3.2.3. Caffeine (CAF)

Caffeine ($C_8H_{10}N_4O_2$) is one of the drugs which is an alkaloid belonging to methylxanthine family. In humans, caffeine acts as a central nervous system (CNS) stimulant. It is present in cola drinks, coffee, tea and energy drinks. The global average consumption of caffeine is about 70 mg person^{-1} day^{-1} but varies in different countries[74]. In Brazil, the average consumption is 171 mg person^{-1}day^{-1}, being coffee the main source of caffeine in the Brazilian diet[75]. Despite the fact that caffeine is extensively metabolized by

humans with only approximately 3% excreted unchanged in the urine[76], it is broadly found in the environment due to its continual introduction into the sewage system by the disposal of unconsumed coffee, tea or soft drinks down drains, and the rinsing of coffee pots and cups. Caffeine (CAF) is one of the most commonly used anthropogenic markers in surface and groundwater. It has been used as a therapy for diuretic, but an excessive consume of caffeine may cause various adverse effects, such as sleep deprivation, risk of cardiovascular diseases, reduction of fertility rates and an increasing of miscarriages. CAF presents high water solubility (Ks values is more than 10 g L^{-1}), low accumulation (log K_{ow} is less than 0.5) and high removal in conventional wastewater treatment plants (about 80%). However, many part of ingested caffeine is metabolized in humans, mainly to theophylline, theobromine and 1,7- dimethylxanthine (paraxanthine), which are frequently detected in the influent and effluent of wastewater treatment plants. Such releasing metabolites or degradation products can be more harmful than the original compounds[77].

In addition, caffeine is used as an adjuvant in many prescription and over-the-counter drugs, e.g. in combination with nonsteroidal anti-inflammatory drugs in analgesic formulations and with ergotamine in drugs for treating migraine[78].

Table 1. EOCs detected in groundwater via different pathways (Source: Adapted from 75)

Sources	Compounds
Pharmaceuticals	Paracetamol, Carbamazepine, Ibuprofen, Primidone, Clofibric acid, Ketoprofen, Triclosan, Lopamidol, Diclofenac, Phenazone, Sulphamethoxazole, Lincomycin, Propyphenazone, Sulphamethazine
Hormones	Estrone, 17b-estradiol
Industry	Nonylphenol, Galoxalide, Bisphenol A
Life-style	Caffeine, Cotinine

2.5- Water remediation Technologies

Considering the negative effects of Caffeine, phenol and its derivatives on the environment, many studies have been carried out aimed at their elimination from wastewaters and water intended for human consumption. Conventional water treatment processes have proven ineffective for the removal of these compounds. Thus several methods such as chemical oxidation, precipitation, distillation, solvent extraction, ion exchange, membrane processes, and reverse osmosis, etc. have been widely used for removal of phenols from aqueous solutions[67]. These methods have been found to be restricted, since they are very expensive which involve high initial capital and operational

costs. On the other hand adsorption is more attractive among the others because the pollutant can be removed from the aqueous effluent and the adsorbent can be reused several times, making the process of wastewater treatment economically feasible. Therefore, the produced activated carbons were used for the removal of bisphenol A, paracetamol, caffeine, 2-naphtol, 2-nitro phenol, 4-nitro phenol, resorcinol and hydroquinone from aqueous solution. A complete adsorption experiments were carried out with phenol and *O*-cresol molecules.

2.5.1- Adsorption process

Adsorption is a mass transfer process which involves the accumulation of substances at the interface of two phases, such as, liquid–liquid, gas–liquid, gas–solid, or liquid–solid interface (**Figure 6**). The substance being adsorbed is the *adsorbate* and the adsorbing material is termed the *adsorbent*. The properties of adsorbates and adsorbents are quite specific and depend upon their constituents. The constituents of adsorbents are mainly responsible for the removal of any particular pollutants from wastewater when applying for that purpose[79]. Generally, the interaction can occurred by two ways: Physical Interaction (physisorption) or/and Chemical interaction (chemisorption).

Physisorption occurs when the interaction between the solid surface and the adsorbed molecules has a physical nature. In this case, the attraction interactions are Van Der Waals forces and, as they are weak the process results are reversible (<40kJ mol^{-1}). Additionally, it occurs lower or close to the critical temperature of the adsorbed substance.

On the other hand, if the attraction forces between adsorbed molecules and the solid surface are due to chemical bonding, the adsorption process is called *chemisorption*. Contrary to physisorption, chemisorption occurs only as a monolayer and, furthermore, substances chemisorbed on solid surface are hardly removed because of stronger forces at stake (>200kJ mol^{-1}). In this case the interactions are covalent or ionic bonds because of higher temperature (involves higher activation energies compared to physisorption) that may favoured the chemical interaction with the molecules at the surface of adsorbent[80]. Chemisorption is a slow and irreversible process, involving electron sharing or electron transfer, causing the formation of chemical bond; limited to the formation of a monolayer, adsorbate molecules adsorb only at specific sites on the surface. Under favourable conditions, both processes can occur simultaneously or alternatively. Physical adsorption is accompanied by a decrease in free energy and entropy of the adsorption system and, thereby, this process is exothermic.

Adsorption process has been widely used in the removal of EOC in aqueous solution. This technology offers several advantages over others methods such as high adsorption

capacity, regenerability of the adsorbent, simplicity and inexpensive. In addition, after decontamination of effluents using adsorption technology, the treated effluents are safe to be released into the environment or the water could be reutilised for some industrial processes, which require water of low purity[42]. There are several factors affecting adsorption, hereafter, some of them are described.
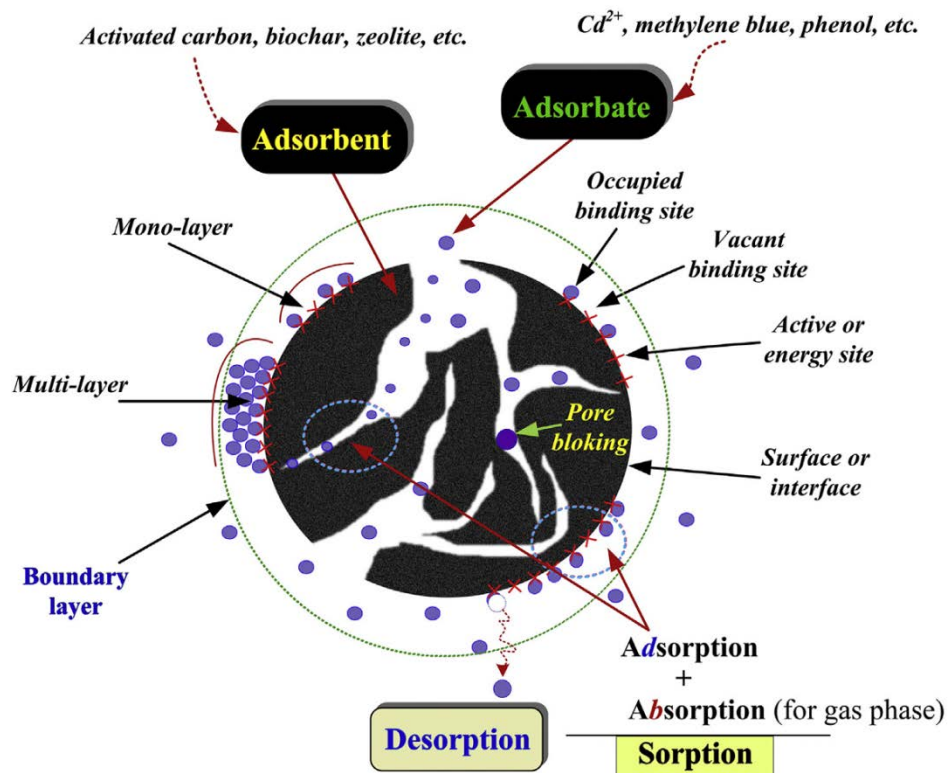

Figure 6. *Some basic terms used in adsorption science and technology. (adapted and modified from Ref.81)*

2.5.2- Factors affecting adsorption process in aqueous media

The main factors affecting the adsorption process are: (i) surface area, (ii) nature and initial concentration of adsorbate, (iii) solution pH, (iv) temperature, (v) interfering substances and (vi) nature and dose of adsorbent.

Since adsorption is a surface phenomenon, the extent of adsorption can be proportional to the specific surface area which is defined as that portion of the total surface area that is available for adsorption[82]. Thus more finely divided and more porous is the solid greater is the amount of adsorption accomplished per unit weight of a solid adsorbent[83]. The major contribution to surface area is located in the pores of molecular dimensions.

The physicochemical nature of the adsorbent drastically affects both rate and adsorption capacity. The solubility of the solute greatly influences the adsorption equilibrium. In general, an inverse relationship can be expected between the extent of adsorption of a solute and its solubility in the solvent where the adsorption takes place. Molecular size is also relevant as it relates to the rate of uptake of organic solutes through the porous of the adsorbent material if the rate is controlled by intraparticle transport. In this case the reaction will generally proceed more rapidly with decrease of adsorbate molecule[84].

The pH of the solution affects the extent of adsorption because the distribution of surface charge of the adsorbent can change (because of the composition of raw materials and the technique of activation) thus varying the extent of adsorption according to the adsorbate functional groups[85].

Another important parameter is the temperature. Adsorption reactions are normally exothermic; thus the extent of adsorption generally increases with decreasing temperature[82]. Finally, the adsorption can be affected by the concentration of organic and inorganic compounds. The adsorption process is strongly influenced by a mixture of many compounds which are typically present in water and wastewater. The compounds can mutually enhance adsorption, may act relatively independently, or may interfere with one other. In most cases, natural organic matter (NOM) negatively affects the adsorption of emerging compounds in surface waters and wastewaters[85].

2.5.3- Adsorption Isotherms

In other to successfully represent the dynamic adsorptive behaviour of any substance from the fluid (liquid or gas) to the solid interface, it is crucial to have a satisfactory description of the equilibrium state between the two phases composing the adsorption system. Generally, an adsorption isotherm describes the relationship between the amount of adsorbate adsorbed by the adsorbent (q_e) and the adsorbate concentration remaining in solution after equilibrium is reached, at a constant temperature (C_e). The parameters from the adsorption equilibrium models provide useful pieces of information on the surface properties, adsorption mechanism and interaction between the adsorbent and adsorbate[86]. There are numerous equations for describing the adsorption equilibrium of an adsorbate on an adsorbent. The most employed and discussed in the literature is the Langmuir equation[87]. Other isotherm models such as Freundlich isotherm[88], Sips isotherm[89], Liu isotherm[90], Redlich–Peterson isotherm[91] are also well discussed in the literature and described hereafter.

2.5.3.1. Langmuir Isotherm model

The Langmuir isotherm[87] is based on the following assumptions:

- adsorbates are chemically adsorbed at a fixed number of well-defined sites;
- a monolayer of the adsorbate is formed over the surface of the adsorbent when it gets saturated;
- each site can hold only one adsorbate species;
- all sites are energetically equivalent;
- interactions between the adsorbate species do not exist.

The Langmuir isotherm equation is depicted by **Equation. 5**:

$$q_e = \frac{Q_{\max} \cdot K_L \cdot C_e}{1 + K_L \cdot C_e} \tag{5}$$

where q_e is the adsorbate amount adsorbed at equilibrium (mg g^{-1}); C_e is the adsorbate concentration at equilibrium (mg L^{-1}); Q_{max} is the maximum sorption capacity of the adsorbent (mg g^{-1}) assuming a monolayer of adsorbate uptake by the adsorbent; K_L is the Langmuir equilibrium constant (L mg^{-1}).

2.5.3.2. Freundlich Isotherm model

Freundlich isotherm[88] model is an exponential equation, and assumes that the concentration of adsorbate on the adsorbent surface increases as the adsorbate concentration increases. Theoretically, using this expression, an infinite amount of adsorption will occur. Similarly, the model assumes that the adsorption could occur *via* multiple layers instead of a single layer as Langmuir model assumes. The equation has a wide application in heterogeneous systems. **Equation 6** shows the Freundlich isotherm model:

$$q_e = K_F \cdot C_e^{1/n_F} \tag{6}$$

where q_e is the adsorbate amount adsorbed at equilibrium (mg g^{-1}); C_e is the adsorbate concentration at equilibrium (mg L^{-1}); K_F is the Freundlich equilibrium constant [mg.g^{-1}.(mg.L^{-1})$^{-1/nF}$]; n_F is the exponent of Freundlich model (n_F is dimensionless).

2.5.3.3. Liu Isotherm model

The Liu isotherm[90] model is a combination of the Langmuir and Freundlich isotherm models, but the monolayer assumption of Langmuir model and the infinite adsorption assumption that originates from the Freundlich model are discarded. The Liu model predicts that the active sites of the adsorbent cannot possess the same energy. Therefore, the adsorbent may present active sites preferred by the adsorbate molecules for occupation, however,

saturation of the active sites should occur unlike in the Freundlich isotherm model. **Equation 7** defines the Liu isotherm model:

$$q_e = \frac{Q_{\max} \cdot (K_g \cdot C_e)^{n_L}}{1 + (K_g \cdot C_e)^{n_L}}$$

(7)

where q_e is the adsorbate amount adsorbed at equilibrium (mg g^{-1}); C_e is the adsorbate concentration at equilibrium (mg L^{-1}); Q_{max} is the maximum sorption capacity of the adsorbent (mg g^{-1}); K_g is the Liu equilibrium constant (L mg^{-1}); n_L (dimensionless) is the exponents of Liu model. Contrary to the Sips isotherm (show hereafter), n_L could assume any positive value.

2.5.3.4. Sips Isotherm model

Sips model, an empirical model, consists of the combination of the Langmuir and Freundlich isotherm models. The Sips model[89] takes the following form:

$$q_e = \frac{Q_{\max} \cdot K_s \cdot C_e^{1/n_s}}{1 + K_s \cdot C_e^{1/n_s}} \qquad \text{where } 0 < 1/n_s \leq 1$$

(8)

where q_e is the adsorbate amount adsorbed at equilibrium (mg g^{-1}); K_S is the Sips equilibrium constant (mg.L^{-1})$^{-1/ns}$; Q_{max} is the Sips maximum adsorption capacity (mg.g^{-1}); n_s (dimensionless) is the exponent, related to the heterogeneity surface of the adsorbent. It is assumed that the *$1/n_S$* should be ≤1 for integration purpose[89].

2.5.4- Adsorption Kinetics

Adsorption kinetic studies are important in treatment of aqueous effluents because they provide valuable pieces of information on the reaction pathways and the mechanism of adsorption reactions. Many kinetic models were developed in order to find intrinsic kinetic adsorption constants. Herein, we present only the most commonly employed and the same that were discussed in this thesis.

2.5.4.1. Pseudo-first-order model

Traditionally, the kinetics of adsorption of an adsorbate is described using the expressions originally given by Lagergren[92]. A simple kinetic analysis of adsorption is the pseudo-first-order equation in the form of **Equation. 9**

$$\frac{dq}{dt} = K_f \cdot (q_e - q_t) \tag{9}$$

where q_t is the amount of adsorbate adsorbed at time t (mg g^{-1}), q_e is the equilibrium adsorption capacity (mg g^{-1}), k_f is the pseudo-first-order rate constant (min^{-1}), and t is the contact time (min). The integration of Equation.9 with initial conditions, $q_t = 0$ at $t = 0$, and $q_t = q_t$ at $t = t$ leads to **Equation. 10**:

$$q_t = q_e \cdot \left[1 - exp(-k_1 \cdot t) \right] \tag{10}$$

2.5.4.2. Pseudo-second-order model

According to this model, the adsorption kinetic is proportionally to the number of active sites of the adsorbent, rather than the concentration of the solution. This model was first discussed by Blanchard[93] *et al.*, 1984. The well-known pseudo-second-order equation of kinetic adsorption model is given by:

$$q_t = \frac{q_e^2 k_2 t}{\left[k_2 (q_e) \cdot t + 1 \right]} \tag{11}$$

where, k_s is the pseudo-second-order rate constant (g mg^{-1}min^{-1}); and others terms the same as previously defined.

2.5.4.3. Avrami fractional-order model

This model is an empirical equation, which was proposed as an alternative Avrami kinetic equation to find a correlation between good experimental and calculated data[94]. The model is an adaptation of kinetic thermal decomposition modelling. The Avrami kinetic equation could be written as:

$$q_t = q_e \cdot \left\{ 1 - exp \left[-(k_{AV} \cdot t) \right]^{nAV} \right\} \tag{12}$$

where k_{AV} is the Avrami kinetic constant (min^{-1}), and n_{AV} is a fractional adsorption order, which is related to the adsorption mechanism[94].

3. Experimental

3.1. Chemicals, reagents and solutions

Deionised water was used for the preparation of all solutions. Bisphenol A, paracetamol, caffeine, 2-naphtol, 2-nitro phenol, 4-nitro phenol, resorcinol, hydroquinone, phenol and *O*-cresol (**Figure 7**), were purchased from Sigma-Aldrich (São Paulo, SP Brazil) and used without further treatment for the preparation of all solutions. Bisphenol A and paracetamol were prepared with a buffer solution (0.05 M boric acid and 0.05 M sodium borate) because of their pharmaceutical properties. Whereas the others solutions were prepared as described elsewhere[95]. The transition metal salts $FeCl_3$, $CoCl_2$, $NiCl_2$, $CuCl_2$ and $ZnCl_2$ were purchased from Neon (São Paulo, Brazil). These reagents were used as activating agents. In aqueous solution (pH close to 6), Co, Ni, Cu and Zn have an oxidation state of +2.
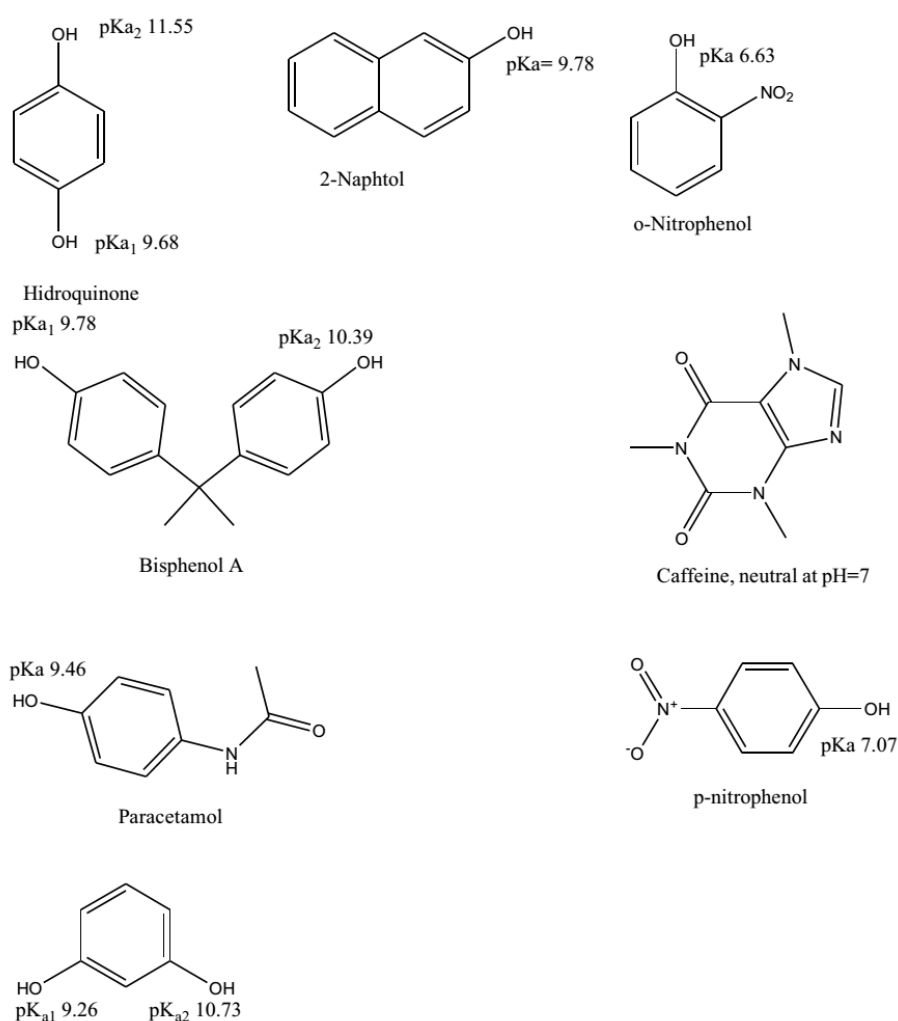

Figure 7. *Structural formula of phenols and caffeine. The pKa of the chemical molecule was calculated using MarvinSketch 16.8.22.0*

3.2. Biomass

Sapelli sawdust was used as a precursor for the preparation of the microwave-assisted activated carbons. It contains *ca* 98% of cellulose, hemicellulose, lignin and pectin[5]. In this study, Sapelli sawdust (*Entandrophragma cylindricum*) was obtained from sawmills of Ngaoundere city, Cameroon (7.3276500°, 13.5847200°, 1128 m) as previously reported[5,96]. The ash and moisture contents of the Sapelli wood chips were 10.42% and 16.48%, respectively[5,96], whilst its elemental analysis (C, H, N, O) was 46.16%C, 6.17% H, 0.22% N and 37.03% O (**Table. 2**).

Table 2. Elemental and Inorganic chemical composition of Sapelli wood chips[5,96]

Sample	% C	%H	%N	%O[*]	%Ash
Sapelli wood	46.16	6.17	0.22	37.03	10.42
Inorganic Composition	**% Element**				
Ca	0.3738				
Si	0.1650				
Mg	0.0675				
Al	0.1064				
S	0.0013				
Fe	0.0169				
K	0.0132				
Sr	0.0112				
Ni	0.0354				

[*]obtained by difference (**%O =**100**% - % C - %H - %N - %Ash)**

3.3. Preparation of the activated carbons (MWAC)

In this thesis, two processes were adopted in the preparation of the activated carbons. In the first process, lime ($CaCO_3$ + $Ca(OH)_2$ + CaO) was added in the preparation of activated carbons as an inorganic component to prevent permeation of aqueous solution in the carbonaceous material as described in **Annexes 1** and **2** (see experimental part). Briefly biomass and inorganic components (20% lime + 80% $ZnCl_2$ or 20% lime + 40% $ZnCl_2$ + 40% $FeCl_3$) were mixed to form pastes with inorganic : organic ratios of 1.0 and 1.5 . The mixtures were pyrolysed in a microwave in less than 11 min. Afterwards a 6 mol L^{-1} HCl was used to treat the carbonised materials, under reflux, to eliminate the inorganic components—producing the activated carbons.

However, in the second process, only the transition metals were mixed with the biomass (no lime was added) to form pastes, as described as follows and reported in **Annex**

3 (see experimental part):

A known amount of the transition metal salt was dissolved in 100.0 mL of deionised water, after which 100.0 g of dried Sapelli sawdust (milled to diameter < 300 µm) was added to the solution and mixed continuously at approximately 80°C for 120 min to overcome the natural recalcitrance of the lignocellulosic biomass structure, as well as to ensure a high interaction between the transition metal ions and the lignocellulosic material. The impregnation ratios in mass of the metal salt : biomass were 0.5:1, 1:1, 1.5:1 and 2:1 (w/w).

After mixing, the paste was oven-dried at 90°C for 720 min. Pyrolysis of the dried sawdust impregnated with different solutions of Co, Ni, Cu, and Zn was carried out in a quartz reactor as described elsewhere[23,96], under a nitrogen atmosphere (150 mL min^{-1}). The quartz reactor was inserted in a microwave oven and heated for 5.3 minutes at 1200 W. The system was then cooled after pyrolysis for 5 minutes under 60 mL min^{-1} of nitrogen. The total time for one cycle of pyrolysis was less than 11 min including 5 min of cooling down. Subsequently, other cycles of pyrolysis were carried out.

Following the activation, the metals were thoroughly leached out with HCl 6 mol L^{-1} to complete the chemical activation process, then filtered and rinsed with deionised water several times until the pH value was approximately 6–7, as described elsewhere[97]. Finally, they were dried at 105°C for 24 h and milled (Ø< 53 µm)—producing sixteen activated carbons.
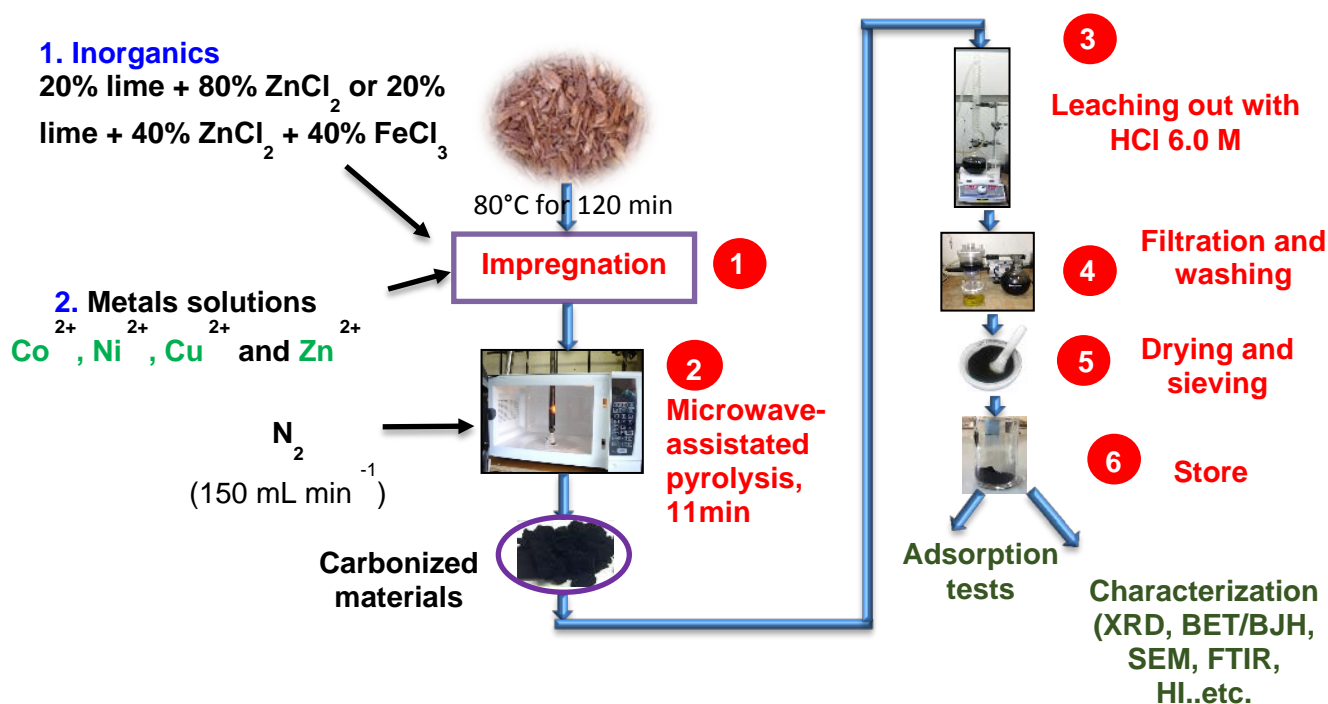

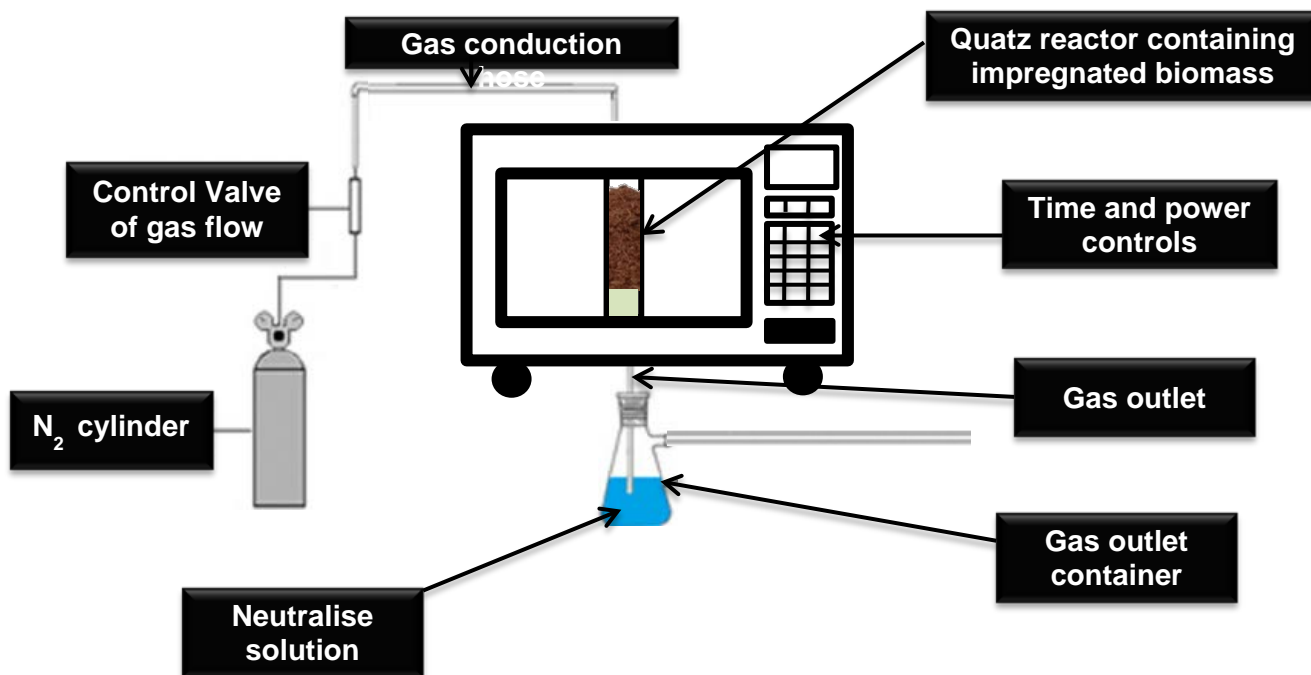**Figure 8.** *Preparation process of MWAC*

Figure 9. *Microwave system*

3.4. Characterization of the activated carbons

The activated carbons were characterized by elemental analysis (EA), nitrogen adsorption-desorption analysis, FTIR, TGA/DTG, SEM, XDR, XRF, diffuse reflectance ultraviolet-visible (DRUV), total acidity and basicity surface functional groups, pH_{zpc} and hydrophobic/hydrophilic ratio.

3.4.1- Nitrogen adsorption–desorption analysis

Nitrogen adsorption-desorption analysis is a very important parameter in the determination of the quality, utility and behaviour of many materials. The BET (Brunauer–Emmett–Teller) method analyzer has been applied in the determination of the surface area and porosity of different adsorbent. In this study the specific surface area and pore structural parameters of the activated carbons were determined by the nitrogen adsorption–desorption isotherms (BET and t-plot methods) at −196°C using a Micromeritics Instrument, TriStar II 3020[98,99]. The pore-size distribution (PSD) was calculated by the Barrett–Joyner–Halenda (BJH) method using the adsorption branch. Before the measurements, samples were outgassed for 16 h at 200°C.

3.4.2- Elemental analysis

Elemental (CHN) analysis has been used to measure the level of organic matter degradation during the carbonization process. It is usually carried out using analytical instruments which operate based on the complete combustion of the material in pure oxygen atmosphere. Elemental analysis (EA) was performed using an elemental analyzer (Perkin Elmer M CHNS/O model 2400). Shortly, 0.05 g oven-dried samples were used to determine total carbon (C), nitrogen (N) and hydrogen (H) contents. Oxygen (O) mass fraction was determined by subtracting the ash, C, N, and H mass fraction from the total mass of the sample.

3.4.3- Thermo gravimetric analysis (TGA) and derivative thermo gravimetric (DTG)

Thermo gravimetric (TGA) is a technique by which the physicochemical properties (moistures, crystalline water, and/or volatile components) of a material can be probed as a function of temperature, whilst the material is subjected to a controlled heating rate. TGA allow studying the thermo stability of the material. In this study, TGA and DTG curves of biomass, pyrolysed materials and activated carbons were obtained on a TA Instruments model SDT Q600 (New Castle, USA) with a heating rate of 10°C min^{-1} at 100 mL min^{-1} of synthetic air flow (White Martins, Canoas, RS, Brazil). Operating temperature was varied from 20°C to 1000°C (acquisition time of 1 point per 5 s) using 10.00 – 15.00 mg of adsorbent[97]. The residual material after the experiment was considered as ash content of that material.

3.4.4- Fourier Transform Infrared (FT-IR) analysis

FT-IR analysis is regarded as a powerful technique for investigating the chemical functionality of carbonaceous materials. A range of different methods, such as, diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy, where the carbon materials are mixed with KBr to form a wafer, and the attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy have been applied in the infrared analysis to characterise carbon materials. In this study, the chemical characterization of functional groups in bulk phase and on the surface of the samples was studied by Fourier Transform Infrared (FT-IR) spectrometer (Bruker, model alpha) in the range of 4000–400 cm^{-1}, using pellets with 0.01 g of samples dispersed in 0.2 g of KBr [100].

3.4.5- Modified Boehm Titration applied to find acidity and basicity

In order to determine quantitatively surface functional groups of the activated

carbons, total acidity and basicity method were applied based on modified Boehm titration[101].
A series of back titrations was performed to determine the concentrations of total acidity (carboxylic, lactonic, and phenolic) and basicity functional groups on activated carbon surfaces.

Activated carbons (ACs) were first dried in an oven at 100 °C for 24h. NaOH and HCl solutions were standardized as described by Oickle[101] *et al.*, 2010 in order to get the exact concentration. In a separate Falcon tube containing 0.15 g of each sample in 25 mL standard solutions of each HCl and NaOH (0.05 M each) were suspended. Na_2CO_3 and $NaHCO_3$ were not used in this study as recommended by Boehm titration because they were found to be highly influenced by dissolved atmospheric CO_2 even after degasification[101]. The solutions were then shaken at a constant temperature for 24 h at 25°C with a shaking speed of 150 rpm. After this time, the slurry was centrifuged (3600 rpm) and heated for about 10 min in order to remove dissolved atmospheric CO_2. 20- mL of 0.05 M HCl or NaOH were added to 10.00 mL of aliquot depending for the original titrant (NaOH or HCl respectively) in order to ensure a complete neutralization of the base or the acid. The acidified or basified solutions were then back-titrated with standardized 0.05 M NaOH or HCl. The back-titration was performed with a digital burette *Titras Pro Instrument* (± 0,0003/50 mL) by using pH measurement while the solution was stirring. The endpoint was found when the pH reached at 7.

The numbers of acidic sites of various types were calculated under the assumption that NaOH neutralizes carboxylic, phenolic, and lactonic groups. The number of surface basic sites was calculated from the amount of hydrochloric acid which reacted with the carbon sample. Results are expressed as mmol g^{-1}. The following equation was used to determine the amount of total acidic/basic groups present on the carbons surface.

$$n_{SFG} = \frac{1}{m}([B,A]V_{B,A} - ([HCl]V_{HCl} - [NaOH]V_{NaOH}))\frac{V_{B,A}}{V_a} \qquad (13)$$

where [*B, A*] and $V_{B, A}$ are the concentration and the volume of the reaction base (or acid) mixed with the carbon sample; n_{SFG} (mmol/g) represents the total amount of surface functional groups that react with the reaction base (or acid) during the mixing step; m is the mass of carbon and V_a is the volume of aliquot taken from the filtrates. [HCl] and V_{HCl} are the concentration and the volume of the HCl standard solution; [NaOH] and V_{NaOH} are the concentration of the volume of the NaOH standard solution.

3.4.6- Optical proprieties

The optical characteristics of the biomass and metal-biomass materials were

evaluated by diffuse reflectance ultraviolet-visible (DRUV) and diffuse reflectance on a Shimadzu UV-2450 spectrophotometer using an ISR-2200 Integrating Sphere Attachment.

The optical characteristics of the biomass and metal-biomass materials were evaluated by diffuse reflectance ultraviolet-visible (DRUV) on a Shimadzu UV-2450 spectrophotometer using an ISR-2200 Integrating Sphere Attachment. For the measurements, the samples were treated as powder. The baseline was obtained using $BaSO_4$ (Wako Pure Chemical Industries, Ltd.). Synchronous fluorescence spectroscopy was carried out in a Shimadzu RF-5301PC spectrofluorometer with a solid state holder. The measurements were performed using excitation/emission slits of 1.5 nm/3.0 nm in a spectral range of 220-700 nm. The spectra were obtained through the simultaneous scanning of the excitation and the emission monochromators of the spectrofluorometer, with a fixed wavelength difference ($\Delta\lambda$) of 15, 30 and 60 nm between them. All the measurements were carried out at room temperature.

3.4.7- Scanning Electron Microscopy (SEM)

The SEM has been used in providing information about the structural morphologies of different materials. Furthermore, this technique allows seeing the shape and size of the numerous microspheres at the surface of activated carbon. In this view, the surface texture of the samples were subjected to scanning electron microscopy (SEM) Instrument (JEOL microscope, model JSM 6060) [52].

3.4.8- The point of zero charge (pH_{pzc})

The pH_{pzc} values were determined by a batch equilibrium method[102]. The technique consist in adding 20.00 mL of 0.050 mol L^{-1} NaCl with a previously adjusted initial pH (the initial pH (pH_i) values of the solutions were adjusted from 2.0 to 10.0 by adding 0.10 mol L^{-1} of HCl and NaOH) to several 50.0 mL cylindrical high-density polystyrene flasks (height 117 mm and diameter 30 mm) containing 50.0 mg of the activated carbons, which were immediately securely capped. The suspensions were shaken in an acclimatized shaker at 25°C and allowed to equilibrate for 24 h. The pH_i of the solutions was accurately measured using the solutions that had no contact with the activated carbon; the final pH (pH_f) values of the supernatant after contact with the solid were recorded. The value of pH_{pzc} is the point where the curve of ΔpH (pH_f− pH_i) versus pH_i crosses a line equal to zero.

3.4.9- X-ray Diffractions (XRD) and Fluorescence (XF) analysis

The nature of phases in the samples was analyzed by powder X-ray diffractions (XRD) (Philips X'pert MPD diffractometer, Netherlands). The instrument was operated at 40 kV and 40 mA with Cu K_α radiation (λ = 1.5406 Å). Measurements were done with scanning

step width of 0.03° and time of 1 s, over the 2θ range of 10 – 80°. The chemical composition of the precursor and inorganics were determined using X-ray fluorescence (Shimadzu XRF1800 X-ray Fluorescence Spectrometer, Japan).

3.4.10- Hydrophobic Index (HI)

For hydrophobic-hydrophilic ratio experiments, the activated carbons were oven-dried in 10 ml glasses at 105°C for 24 h. The samples were cooled in a desiccator before determining the accurate weight. Then 0.3 g of each sample was weighed in 10 mL beakers and exposed in a saturated atmosphere with solvent vapor (n-heptane or water) in Erlenmeyer flasks plugged with a ground glass joint, using 60 ml of solvent. The samples inside the beakers were placed in such a way that they were not in contact with the solvent and wall of the Erlenmeyer flask[103]. The experiment was carried out inside of a temperature-regulated chamber at 25°C in static condition. After 24 h, the samples were removed from the Erlenmeyer flasks, dried carefully from the outside with laboratory tissues and weighed again. The vapor amount adsorbed on the activated carbons was obtained by the difference between the final and initial weight and expressed in mg.g^{-1}. The hydrophobic-hydrophilic ratio were calculated by the ratio of the amount adsorbed of n-heptane vapor (mg.g^{-1}) divided by the amount adsorbed of water-vapor (mg.g^{-1}).

$$HI = \frac{adsorbed\ n-heptan\ (\frac{mg}{g})}{adsorbed\ water\ (\frac{mg}{g})} \tag{14}$$

3.5. Adsorption study

In order to evaluate the performance of the activated carbons produced, adsorption studies were carried out for the removal of bisphenol A, paracetamol, caffeine, 2-naphtol, 2-nitro phenol, 4-nitro phenol, resorcinol and hydroquinone from aqueous solutions. A complete adsorption experimental study was carried out for phenol and *o*-cresol in aqueous solution. This includes, equilibrium isotherms, kinetics, thermodynamic, simulation of effluent and desorption study. All the experiment was performed as follow: In a separate 50.0 mL flat-bottom Falcon tube, 30.0 mg of each activated carbon was suspended in 20.0 mL solution of each molecule (at defined experimental conditions). The mixtures were then shaken at a controlled temperature for 24 h with a shaking speed of 150 rpm. Afterwards, the slurry was centrifuged (3600 rpm) for 5 min to separate the adsorbents from the solutions. The

unadsorbed adsorbates were measured using a T90+ PG Instruments spectrophotometer at a maximum wavelength (λ_{max}) of 276.0 nm for bisphenol A, 243.0 nm for paracetamol, 273.0 nm for caffeine, 278.0 nm for 2-nitro phenol, 226.5 nm for 4-nitro phenol, 273.0 nm for 2-naphtol, 273.0 nm for resorcinol, 288.5 nm for hydroquinone, 269 nm for phenol (PhOH) and 270 nm for *o*-cresol. Maximum wavelengths were obtained by scanning the UV-Vis spectra for each adsorbate from 190 to 500 nm.

The adsorbed quantity expressed as a per unit mass of activated carbons of adsorbate removed is given by **Equation 15**:

$$q_e = \frac{C_0 - C_f}{m} \cdot V \qquad\qquad (15)$$

where q_e is the amount of adsorbate adsorbed by the adsorbent (mg g^{-1}); C_o is the initial adsorbate concentration in contact with the adsorbent; C_f is the final adsorbate concentration after the batch adsorption study; m is the mass of adsorbent (g); and V is the volume of the adsorbate solution (L).

3.6. Desorption study

Adsorbent regeneration can be important to reduce the cost of the adsorption process in practical wastewater treatment systems. The regeneration of the activated carbons was examined through desorption experiments, described as follow: The adsorption experiment was first carried out to find the adsorbed amount. Afterward, the solid phase containing adsorbed molecule was put in contact with various solutions for the desorption experiments. The solutions, which served here as eluents were used for the desorption process. The solutions used were NaOH (1.0 – 5.0 M), 10%EtOH + NaOH 5.0 M and 50%EtOH + NaOH 5.0 M. Afterward the mixtures were shaken at 25°C for 24 h with a shaking speed of 150 rpm, the adsorbate amount which desorbed and present in the supernatant was quantified and compared to the adsorbated one. The recovery (%) was calculate by the ratio of the amount adsorbed of molecule (mg.g^{-1}) divided by the amount desorbed of the same molecule (mg.g^{-1}).

3.7. Validation of the equilibrium and kinetic models

The fitness of the kinetic and equilibrium data were done using nonlinear methods, which were evaluated using Simplex method, and the Levenberg–Marquardt algorithm using the fitting facilities of the Microcal Origin 2015 software. The suitableness of the kinetic and equilibrium models was evaluated using a determination coefficient (R^2), an adjusted determination coefficient (R^2_{adj}) and the standard deviation of residues (SD). Standard

deviation of residues measures the differences between the theoretical and experimental amounts of molecule adsorbed. **Equations 16**, **17** and **18** are the mathematical expressions[86] for respective R^2, R^2_{adj} and SD.

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

(16)

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

(17)

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

(18)

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

4. Conclusion and Future works

4.1. Conclusions

The main goal of this study was to prepare and characterize activated carbons from biomass *via* microwave–assisted pyrolysis and evaluate their adsorption capacity into the removal of Emerging Organic Contaminants (EOCs) in aqueous media.

The first two parts (**Annexes 1** and **2**) showed the preparation process, characterization and application of microwave-assisted activated carbons from wood chips for removal of phenol and *o*-cresol from aqueous solution. $FeCl_3$ and $ZnCl_2$ were used as activating agents at different impregnation ratios during the preparation of activated carbons, and was combined with lime ($CaCO_3$ + $Ca(OH)_2$ + CaO) to prevent permeation of aqueous solution in the carbonaceous material. The mixtures were pyrolysed in a microwave system in less than 11 min. Afterwards a 6 mol L^{-1} HCl was used to treat the carbonised materials, under reflux, to eliminate the inorganic components—producing four activated carbons. Characterization results indicated that activated carbons had mesoporous and microporous structure with a high S_{BET} ranging from 647 to 914 m^2 g^{-1}, V_{tot} of 0.34-0.52 cm^3 g^{-1} and V_{mes} between 0.14 and 0.27 cm^3 g^{-1}. The four activated carbons were used at optimize pH 7.0 to adsorb phenol (PhOH) and *o*-cresol from aqueous solutions.

The adsorption kinetic was very fast and equilibrium contact time was attained in the first ten minutes for both molecules. Pseudo first-order, pseudo-second order and Avrami fractional-order kinetic models were used to probe the kinetic of adsorption. Amount the three models; Avrami fractional-order kinetic model best describes the adsorption kinetics of PhOH and *o*-cresol onto the activated carbons.

The maximum amounts of phenol and o-cresol adsorbed onto activated carbons at 25°C were ranging from 233.5 to 667.9 mg g^{-1} and from 183.4 to 222.4 239 mg g^{-1} respectively. The activated carbons tested for simulated effluents, which was a mixture of different phenolic compounds plus organic matter in a medium of high salts concentrations removed not less than 93.0%. The efficiencies of the activated carbons to treat effluents concur with the Liu maximum sorption capacities for phenol molecule. This was directly related with the textural properties of the activated carbons. However, Sips and Freundlich models were more suitable for describing the equilibrium data of the adsorption of *o*-cresol on the four samples.

The interaction of PhOH or *o*-cresol with the activated carbons should be governed by hydrophobic interactions, hydrogen bonds, polar interactions and electron donor-acceptor interaction. Desorption experiment showed that activated carbons can be regenerated easily using a mixture of EtOH (10 or 50%) + NaOH (5 M).

The third part (**Annexes 3**) was related to the effect of first–row transition metals and impregnation ratios on the physicochemical properties of microwave-assisted activated carbons from wood biomass. Four metals salts $CoCl_2$, $NiCl_2$, $CuCl_2$, and $ZnCl_2$ at different impregnation ratios were compared. Several techniques were used to characterize the 16-activated carbons produced. It appears that metals were strongly bound with surface functional groups of the biomass by ionic or covalence interaction. FTIR and UV-Vis DRS spectra of the metals incorporated into the biomass structure revealed that Zn^{2+} and Cu^{2+} formed more complexes during the impregnation step. Co, Ni, Cu and Zn led to AC with wide variation in both physicochemical and sorption properties. As the ratio metal : biomass increased from 0.5:1 to 2:1, the surface areas and total pore volume of the ACs also increased independently of the metal used. Nevertheless, the samples prepared with Zn showed high porosity and surface areas independently of their ratios. This result was in accordance with the first study (**Annex 1** and **2**) carried out in this thesis, which also showed higher porosity for the activated carbon prepared only with Zn than the mixture Zn and Fe. Adsorption experiments carried out with the 16-samples showed a high adsorption capacity for the removal of bisphenol A, paracetamol, caffeine, 2-naphtol, 2-nitro phenol, 4-nitro phenol, resorcinol and hydroquinone from aqueous solution. These results have demonstrated that Sapelli wood sawdust is a promising precursor for preparing AC to remove emerging organic contaminants from aqueous solutions.

4.2. Future works

Although microwave assisted pyrolysis used in the preparation of activated carbons has many advantages over those using conventional heating, further investigations need to be performed. More in-depth research is needed to develop and understand fast heating techniques involving other biomass and metal activating agents. Additionally, a study on temperature versus candle-power should be performed in other to master the heating.

This work showed that ACs produced with Co, Ni and Cu can be used in the removal of some emerging organic contaminants. Nevertheless, complete adsorption experiments need to be performed for terms of application. This should include isotherms, kinetics, simulated industrial effluent, effect of pH of adsorbate solution, and desorption experiments in order to check the reuse of the adsorbents.

Lastly, the activated carbons produced in this thesis was only tested in adsorption experiment, however more application can be done for other areas such as air purification, catalysis or supports, photocatalysis..etc.

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Annex 1

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SUPPLEMENTARY MATERIAL

Microwave-assisted activated carbons from wood chips for removal of phenol from aqueous solutions

Supplementary Table 1. Inorganic chemical composition of Sapelli wood.

Inorganic Composition of Sapelli Wood	% Element
Ca	0.3738
Si	0.1650
Mg	0.0675
Al	0.1064
S	0.0013
Fe	0.0169
K	0.0132
Sr	0.0112
Ni	0.0354

Supplementary Table 2. Inorganic chemical composition of lime.

Inorganic Composition of lime	% Element
Ca	49.5722
Mg	11.4041
Si	0.7969
Fe	0.3787
Al	0.1766
K	0.0772
Mn	0.0684
P	0.0120
C	2.4394

Supplementary Table 3. FTIR vibrational bands of A) ZnCW-1.0; B) ZnCW-1.5;
C) FeZnCW-1.0; D) FeZnCW-1.5. Assignments are based on literature (Smith, 1999)

Band (cm^{-1})	
ZnCW-1.0	**Assignments**
3411	O-H stretch
2921	Asymmetric C-H stretching
2853	Symmetric C-H stretching
1610	Asymmetric stretch of carboxylate
1563, 1452, 1421	Ring modes of aromatic ring
1099	C-O stretch of alcohols
803	CH out of plane bends of aromatic rings
ZnCW-1.5	
3404	O-H stretch
2920	Asymmetric C-H stretching
2852	Symmetric C-H stretching
1572	Ring modes of aromatic ring
1383	C-H bending
1136	C-O stretch of alcohols
885,811	CH out of plane bends of aromatic rings
FeZnCW-1.0	**Assignments**
3384	O-H stretch
2923	Asymmetric C-H stretching
2852	Symmetric C-H stretching
1583	Ring modes of aromatic ring
1379	C-H bending
1167	C-O stretch of alcohols
885,812,752	CH out of plane bends of aromatic rings
FeZnCW-1.5	
3417	O-H stretch
2918	Asymmetric C-H stretching
2853	Symmetric C-H stretching
1617	Asymmetric stretch of carboxylate
1565, 1460	Ring modes of aromatic ring
1383	C-H bending
1259	C-O stretch of phenol
1104	C-O stretch of alcohols
803	CH out of plane bends of aromatic rings
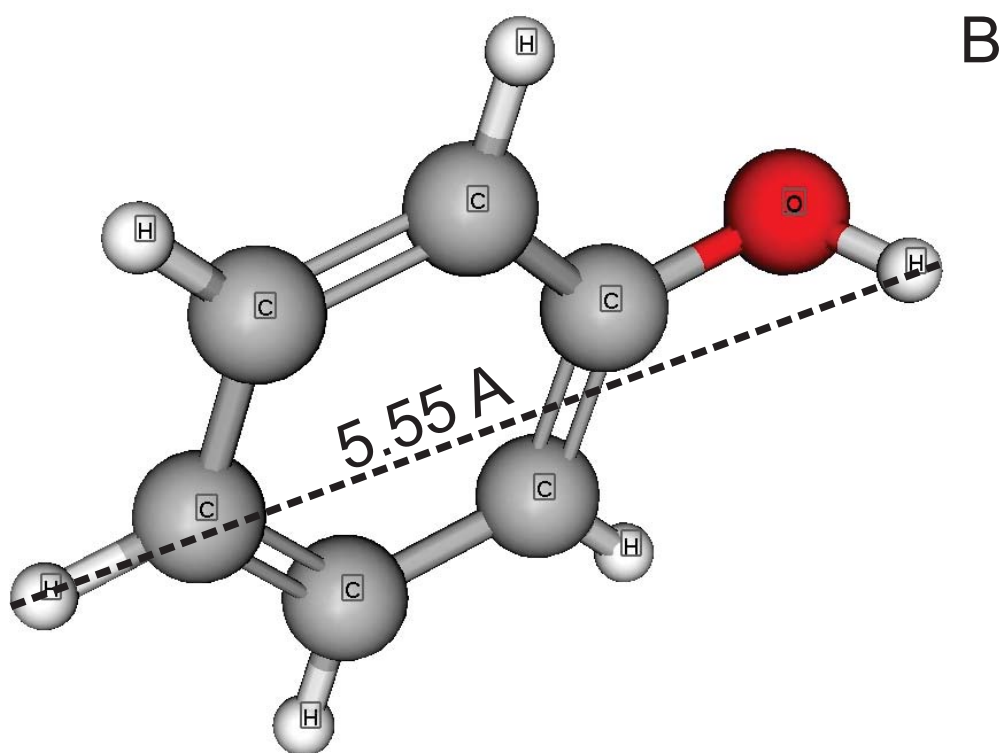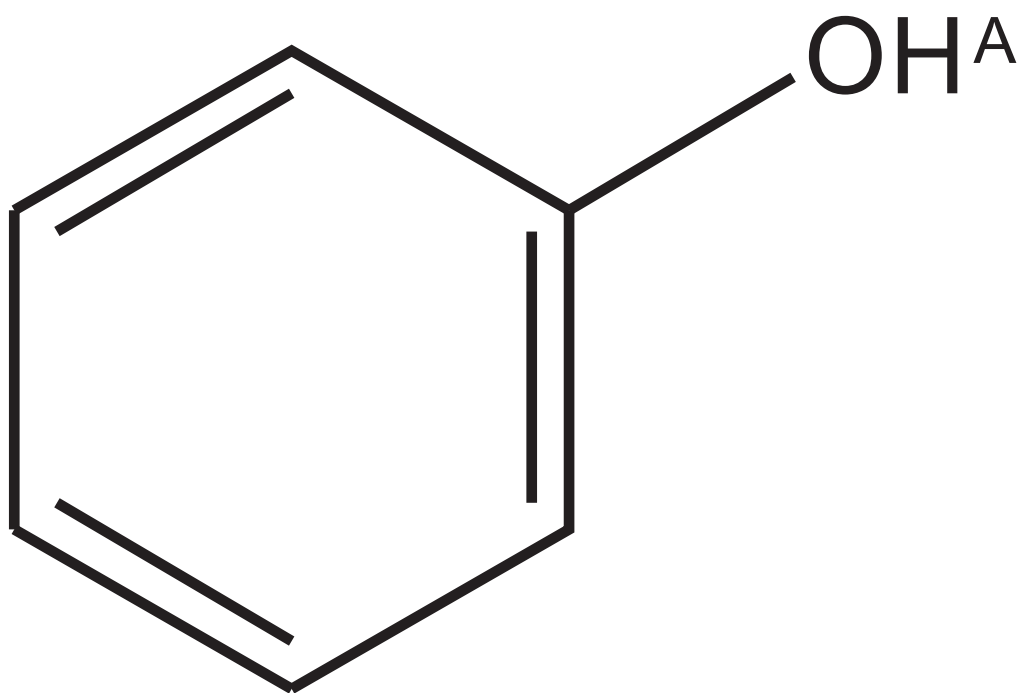
Supplementary Fig 1: (A) Structural formula of PhOH;
(B) Optimized three-dimensional structural formula of PhOH.
The dimensions of the chemical molecule was calculated using
MarvinSketch version 15.6.1.0. Van der Waals surface area
147.21 A^2 (pH 0.0-10.0); Polar surface area 20.23 A^2 (pH 0.0-10.0);
Dipole Moment 2.79 Debye; LogP 1.67.
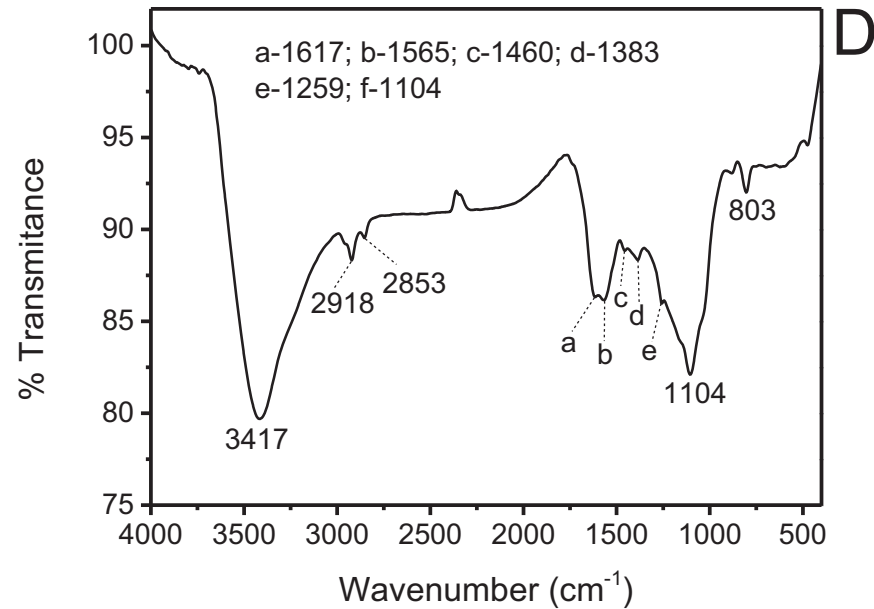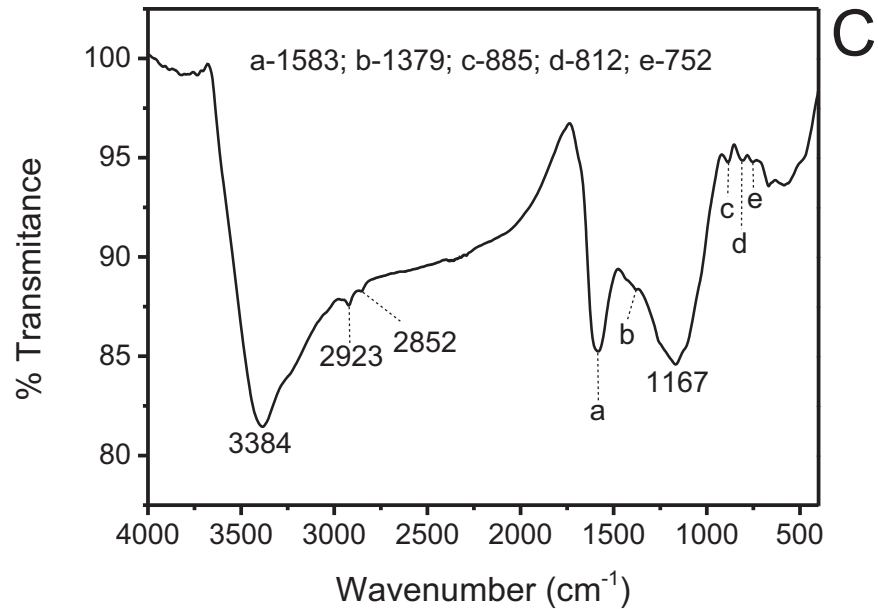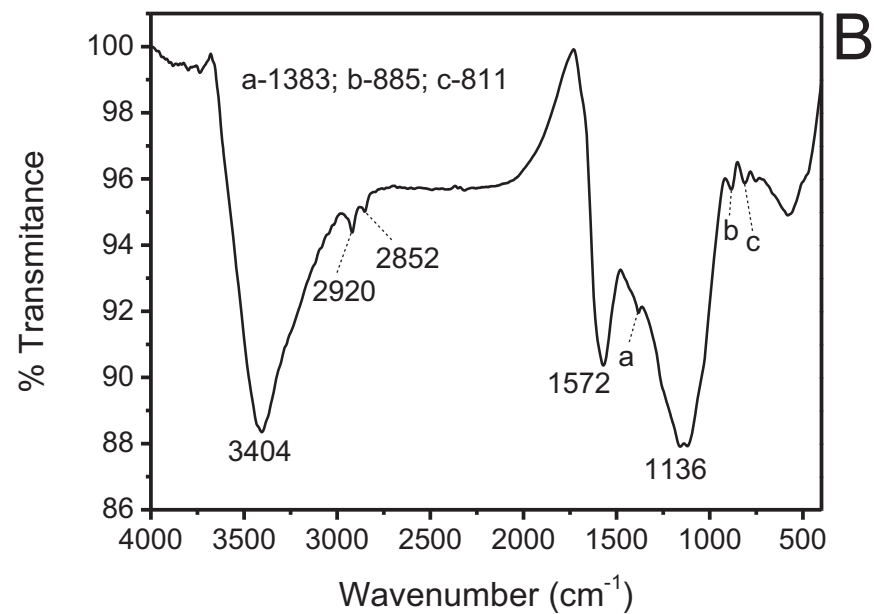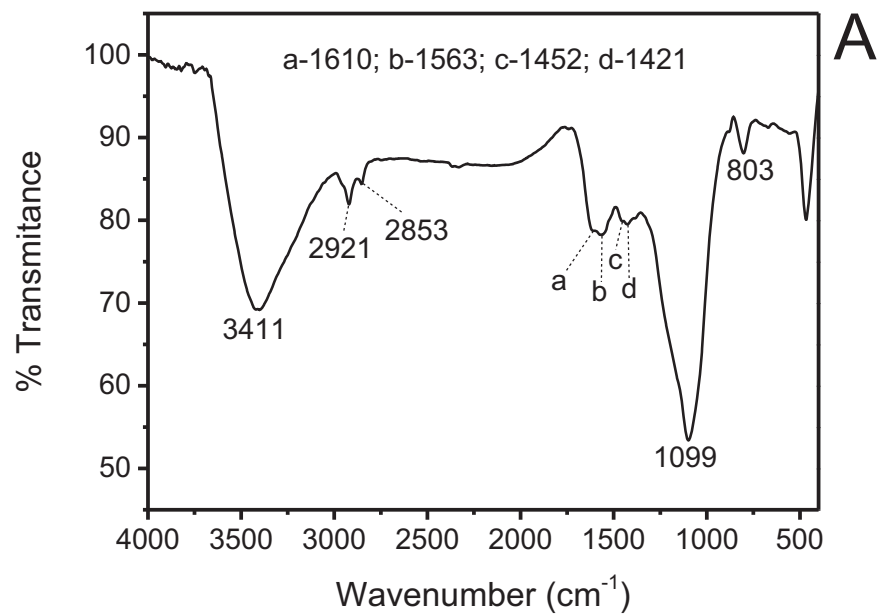
Supplementary Fig 2. FTIR spectra of: **(A)** ZnCW-1.0; **(B)** ZnCW-1.5; **(C)** FeZnCW-1.0; **(D)** FeZnCW-1.5

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	Graph	Graph	Graph	Graph	Graph	Graph	Graph	Graph	Graph	Graph	Graph	Graph	Graph

Supplementary Fig 1. A) Structural formula of o-cresol, B) Optimized three-dimensional structural formula of o-cresol. The dimensions of the chemical molecule was calculated using MarvinSketch version 16.3.14.0. Van der Waals surface area 179.01 A^2 (pH 7.0); Polar surface area 20.23 A^2 (pH 7.0); Dipole Moment 3.01 Debye; LogP 2.18; Log D 2.18;
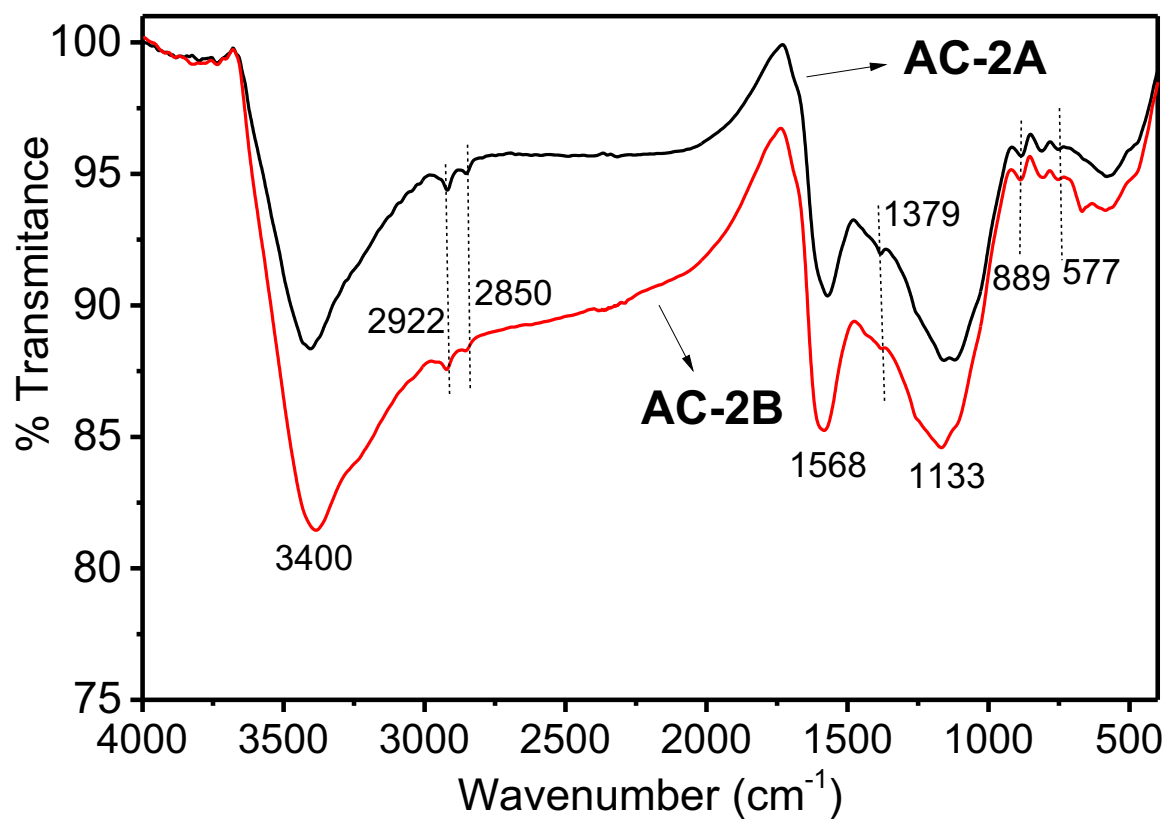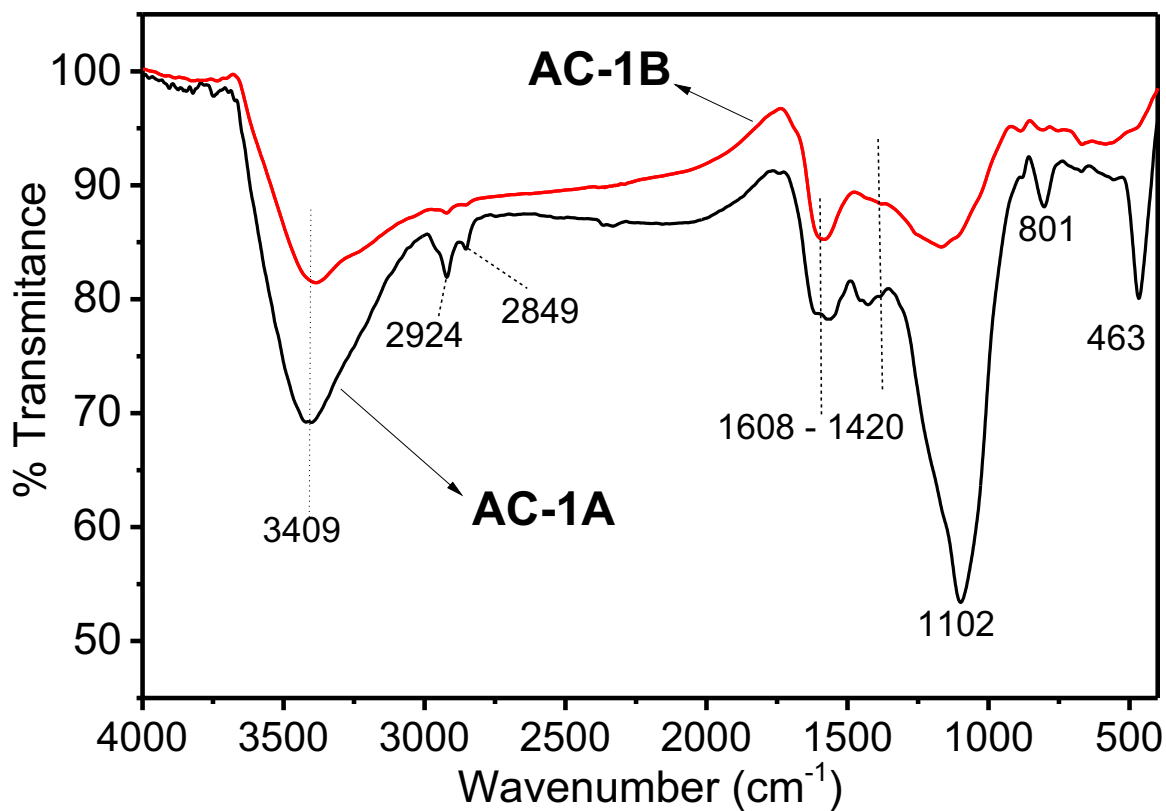
Supplementary Fig 2. FTIR spectra of activated carbons.

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javascript:void(0);

Effects of first–row transition metals and impregnation ratios on the physicochemical properties of microwave-assisted activated carbons from wood biomass

Modified Boehm Titration applied to find acidity and basicity

A series of back titrations was performed to determine the concentrations of total acidity (carboxylic, lactonic, and phenolic) and basicity functional groups on activated carbon surfaces.

Activated carbons (ACs) were first dried in an oven at 100 °C for 24h. NaOH and HCl solutions were standardized as described by Oickle *et al.*, 2010 in order to get the exact concentration. In a separate Falcon tube containing 0.15 g of each sample in 25 mL standard solutions of each HCl and NaOH (0.05 M each) were suspended. Na_2CO_3 and $NaHCO_3$ were not used in this study as recommended by Boehm titration because they were found to be highly influenced by dissolved atmospheric CO_2 even after degasification [36]. The solutions were then shaken at a constant temperature for 24 h at 25°C with a shaking speed of 150 rpm. After this time, the slurry was centrifuged (3600 rpm) and heated for about 10 min in order to remove dissolved atmospheric CO_2. 20- mL of 0.05 M HCl or NaOH were added to 10.00 mL of aliquot depending for the original titrant (NaOH or HCl respectively) in order to ensure a complete neutralization of the base or the acid. The acidified or basified solutions were then back-titrated with standardized 0.05 M NaOH or HCl. The back-titration was performed with a digital burette *Titras Pro Instrument* (± 0,0003/50 mL) by using pH measurement while the solution was stirring. The endpoint was found when the pH reached at 7.

The numbers of acidic sites of various types were calculated under the assumption that NaOH neutralizes carboxylic, phenolic, and lactonic groups. The number of surface basic sites was calculated from the amount of hydrochloric acid which reacted with the carbon sample. Results are expressed as mmol g^{-1}. The following equation was used to determine

the amount of total acidic/basic groups present on the carbons surface.

$$n_{SFG} = \frac{1}{m}([B,A]V_{B,A} - ([HCl]V_{HCl} - [NaOH]V_{NaOH}))\frac{V_{B,A}}{V_a}$$

Where [B, A] and $V_{B, A}$ are the concentration and the volume of the reaction base (or acid) mixed with the carbon sample; n_{SFG} (mmol/g) represents the total amount of surface functional groups that react with the reaction base (or acid) during the mixing step; m is the mass of carbon and Va is the volume of aliquot taken from the filtrates. [HCl] and VHCl are the concentration and the volume of the HCl standard solution; [NaOH] and VNaOH are the concentration of the volume of the NaOH standard solution.

Optical proprieties

The optical characteristics of the biomass and metal-biomass materials were evaluated by diffuse reflectance ultraviolet-visible (DRUV) on a Shimadzu UV-2450 spectrophotometer using an ISR-2200 Integrating Sphere Attachment. For the measurements, the samples were treated as powder. The baseline was obtained using $BaSO_4$ (Wako Pure Chemical Industries, Ltd.). Synchronous fluorescence spectroscopy was carried out in a Shimadzu RF-5301PC spectrofluorometer with a solid state holder. The measurements were performed using excitation/emission slits of 1.5 nm/3.0 nm in a spectral range of 220-700 nm. The spectra were obtained through the simultaneous scanning of the excitation and the emission monochromators of the spectrofluorometer, with a fixed wavelength difference ($\Delta\lambda$) of 15, 30 and 60 nm between them. All the measurements were carried out at room temperature.

Supplementary Table 1. Elemental and Inorganic chemical composition of Sapelli wood chips

Sample	% C	%H	%N	%O*	%Ash
Sapelli wood	46.16	6.17	0.22	37.03	10.42

Inorganic Composition	% Element
Ca	0.3738
Si	0.1650
Mg	0.0675
Al	0.1064
S	0.0013
Fe	0.0169
K	0.0132
Sr	0.0112
Ni	0.0354

*obtained by difference (**%O =**100**% - % C - %H - %N - %Ash)**

OH pKa$_2$ 11.55

OH pKa$_1$ 9.68

Hidroquinone

OH pKa= 9.78

2-Naphtol

OH pKa 6.63

NO$_2$

o-Nitrophenol

pKa$_1$ 9.78

pKa$_2$ 10.39

HO

OH

Bisphenol A

Caffeine, neutral at pH=7

pKa 9.46

HO

Paracetamol

OH pKa 7.07

p-nitrophenol

HO

OH

pK$_{a1}$ 9.26   pK$_{a2}$ 10.73
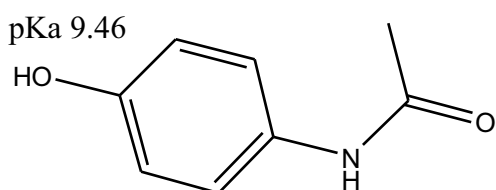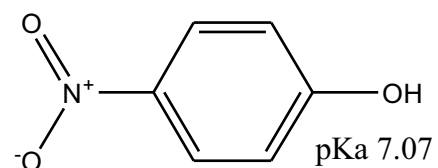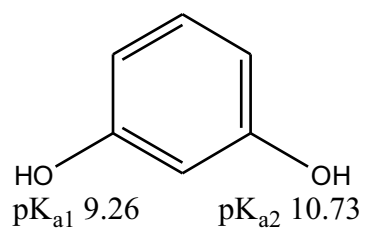
Supplementary Fig.1. Structural formula of phenols and caffeine.
The pKa of the chemical molecule was calculated using MarvinSketch 16.8.22.0
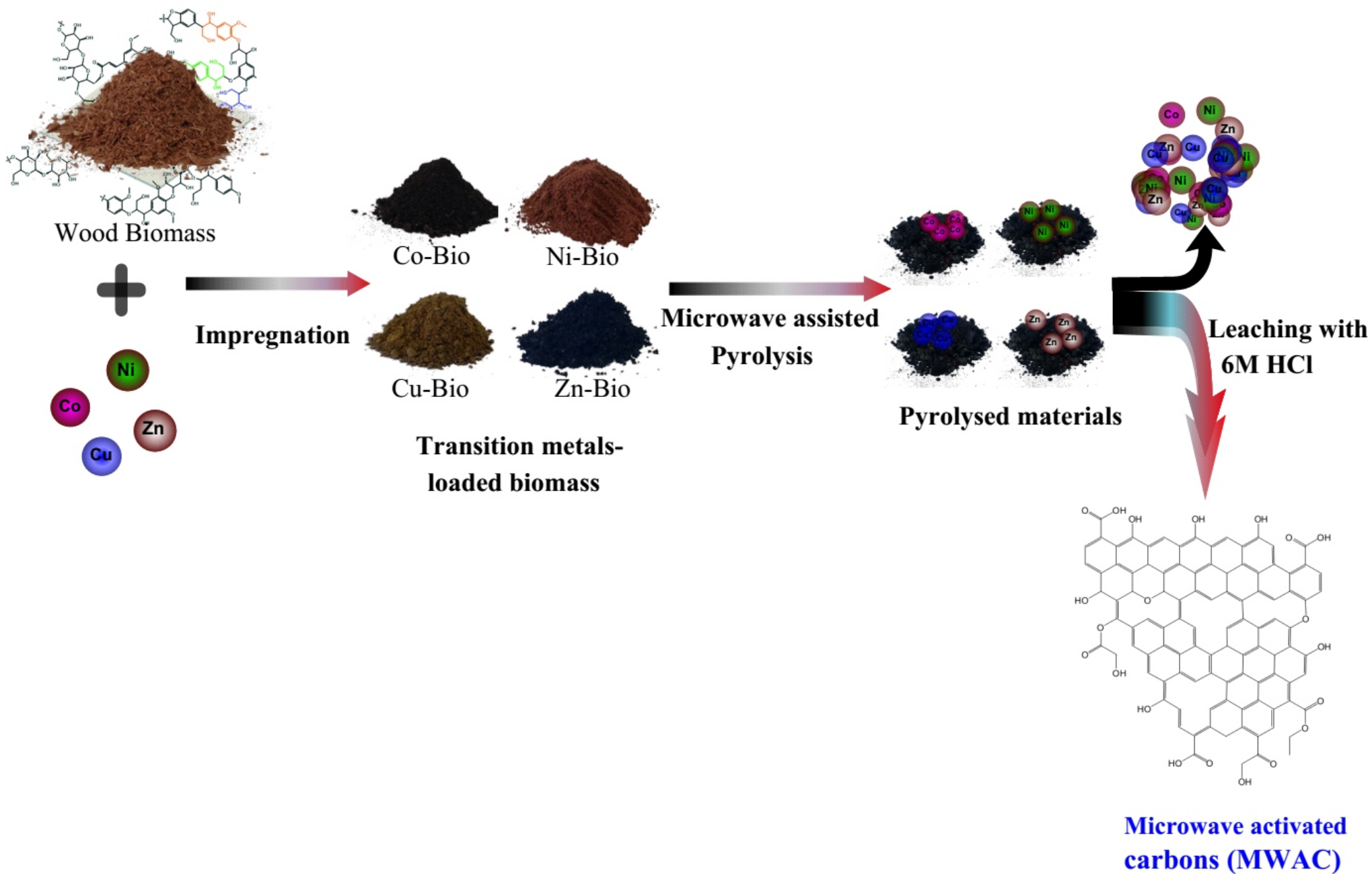
Supplementary Fig.2. Preparation mechanism of MWAC with Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+}
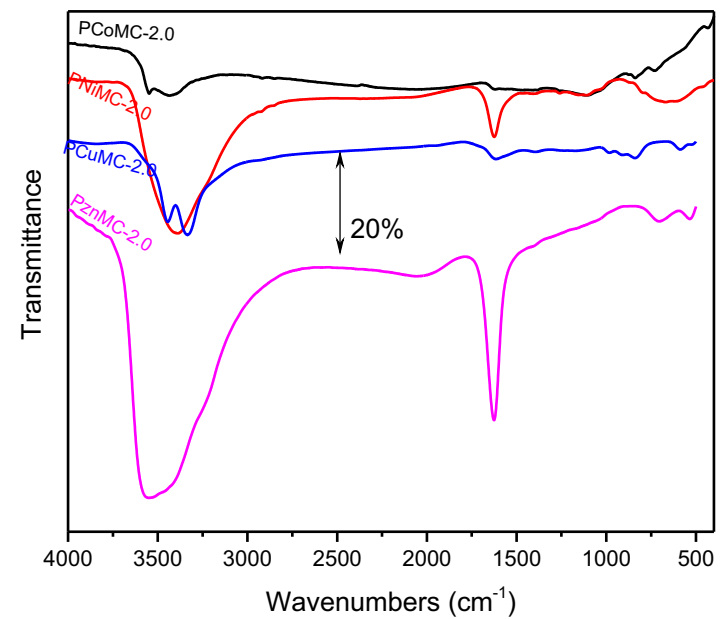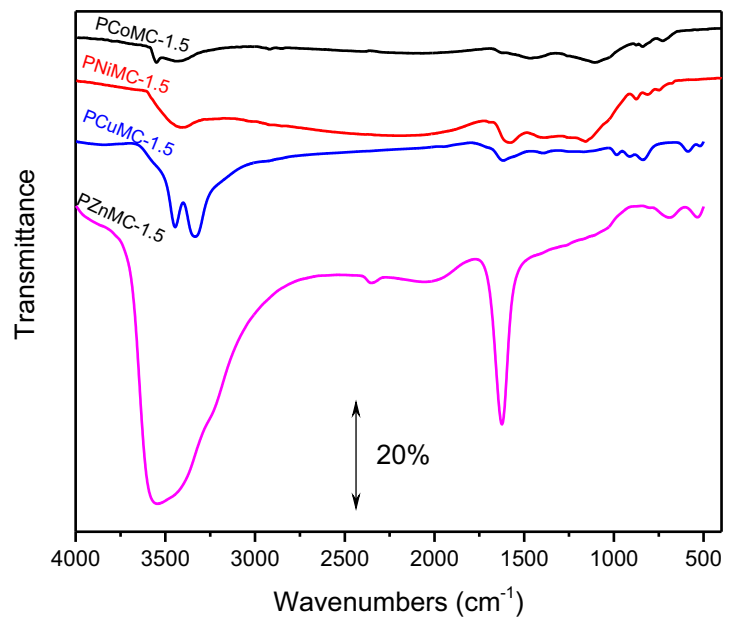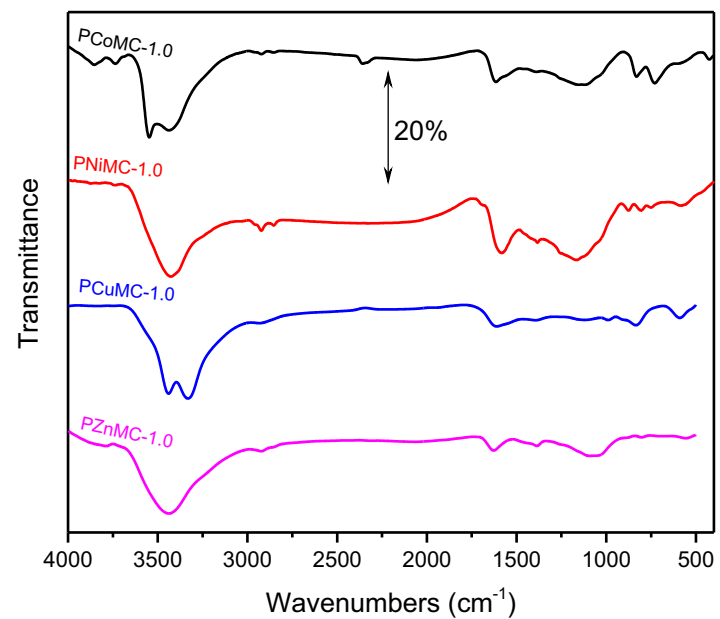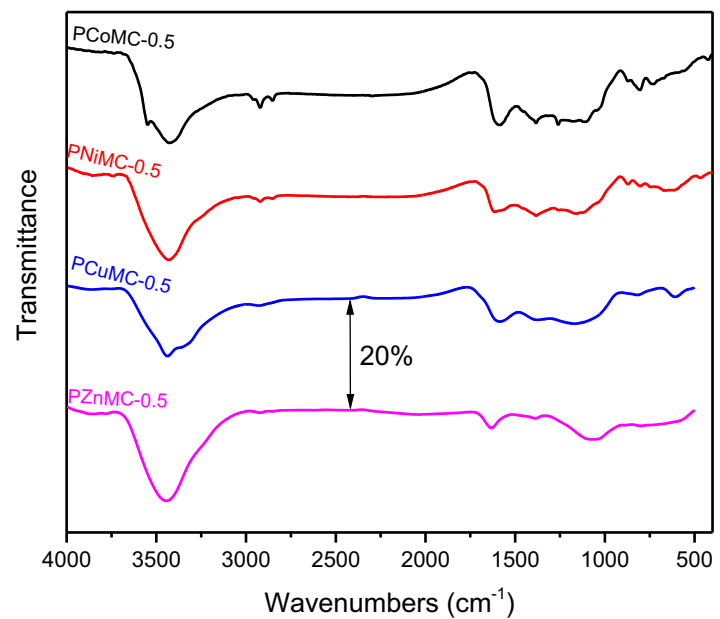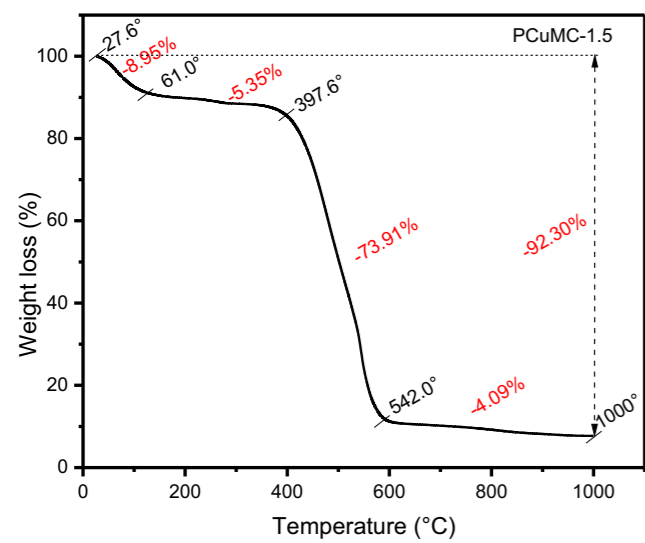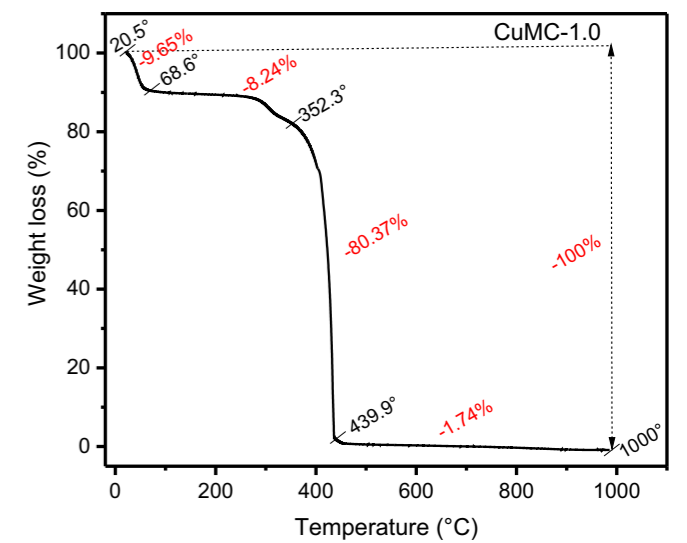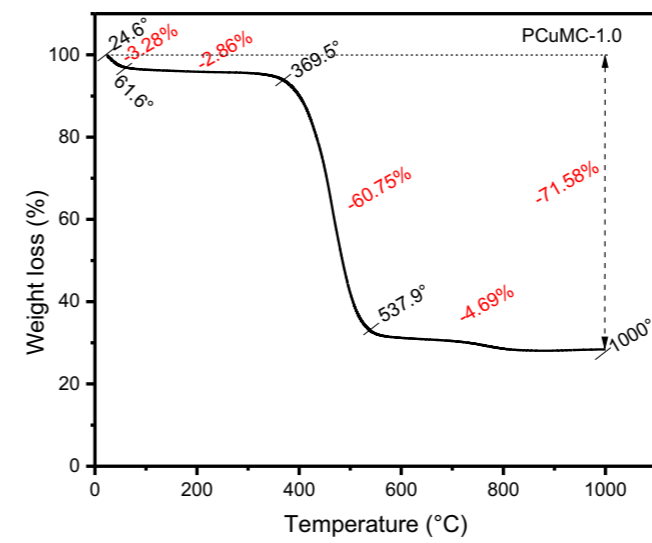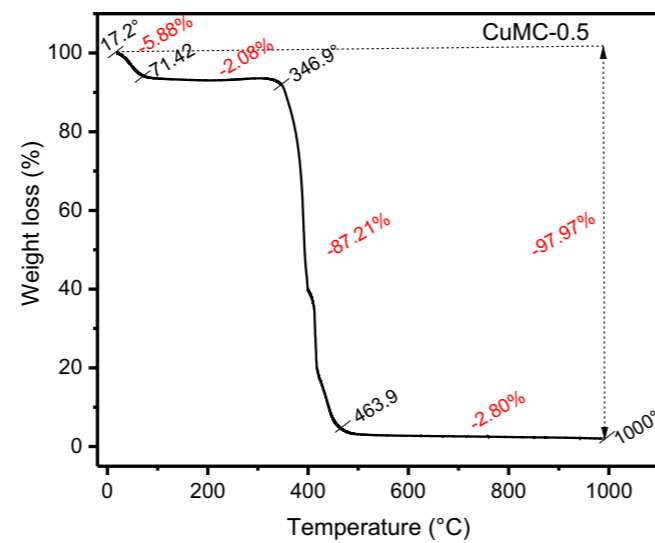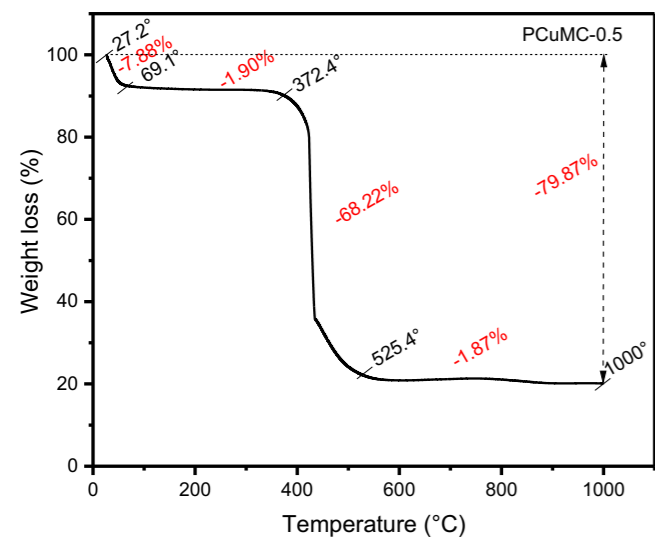
Supplementary Fig. 3. FT-IR spectra of non-leached activated carbons
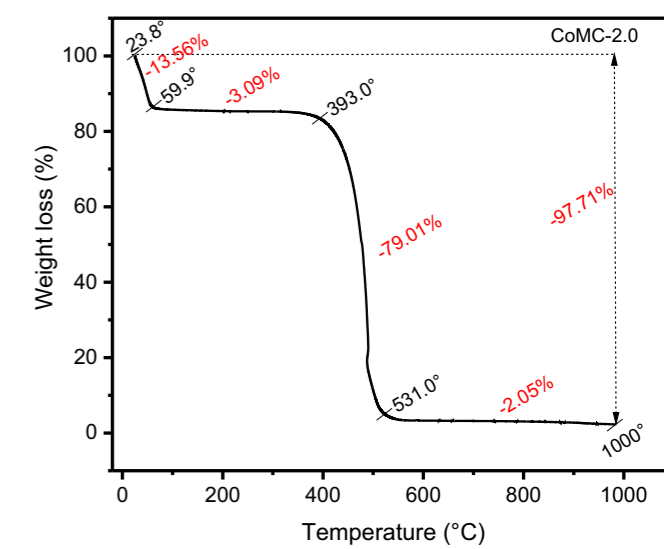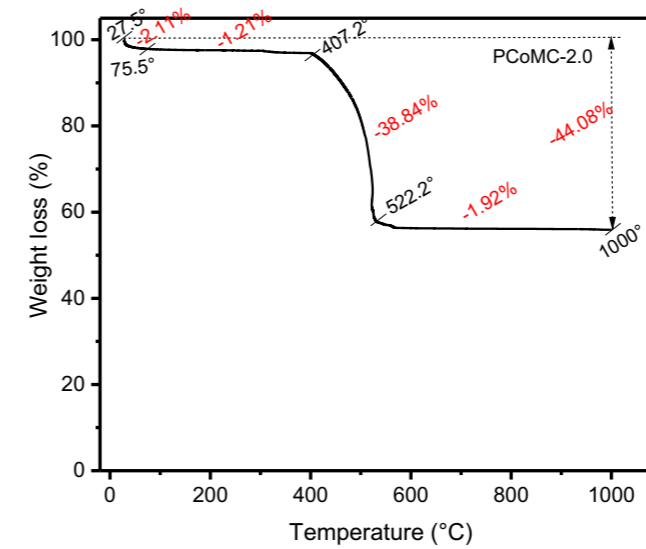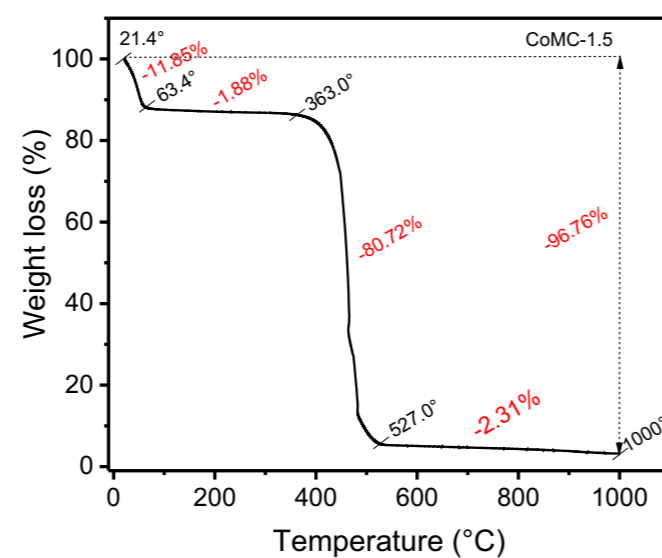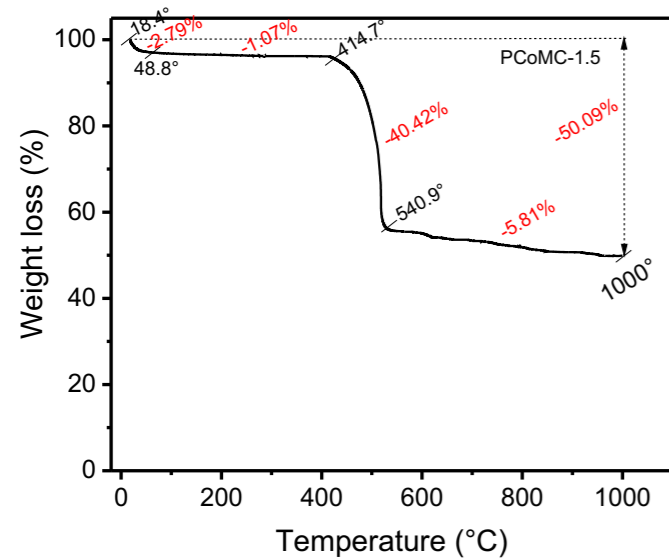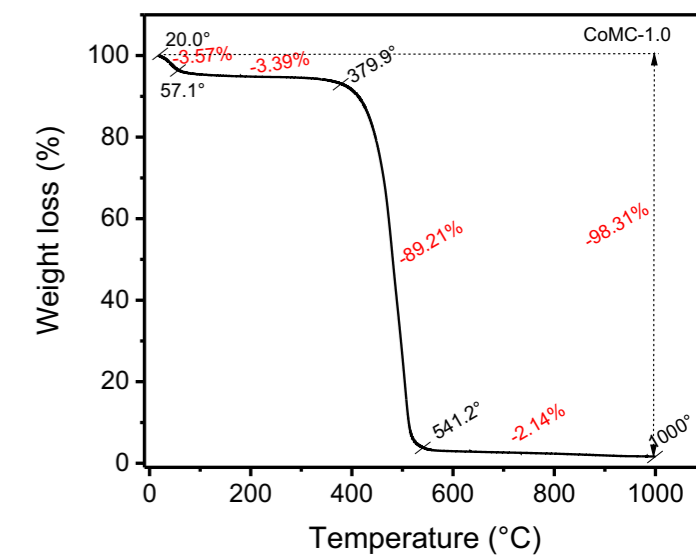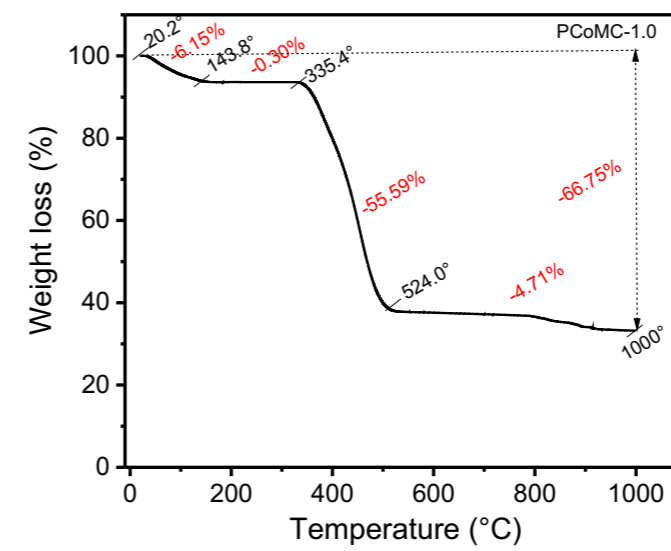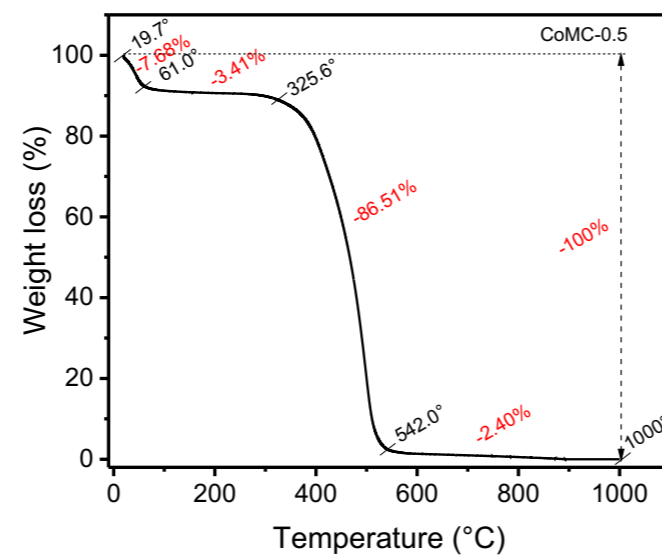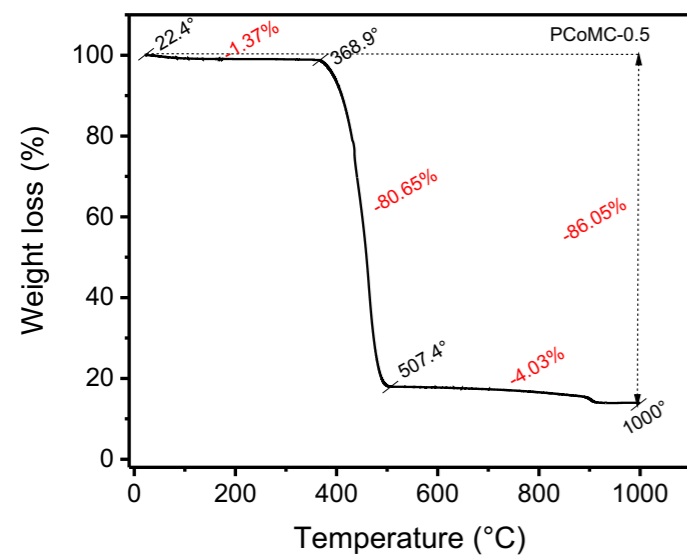
Supplementary Fig.4. TGA curves of the activated carbons modified with Co^{2+} at different ratios.
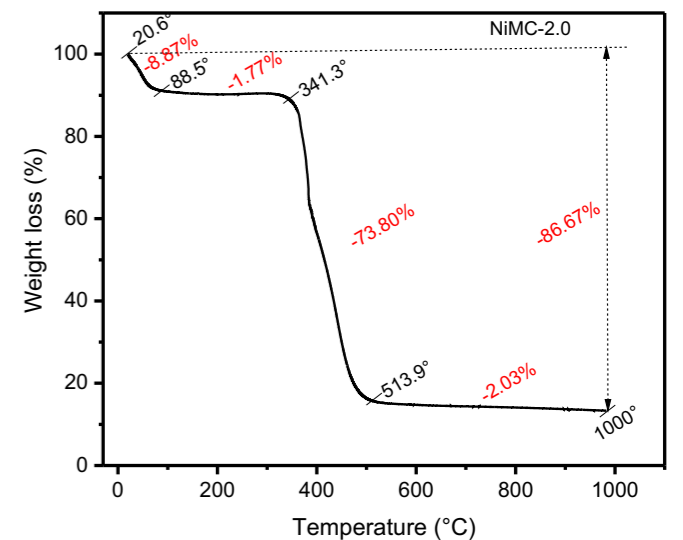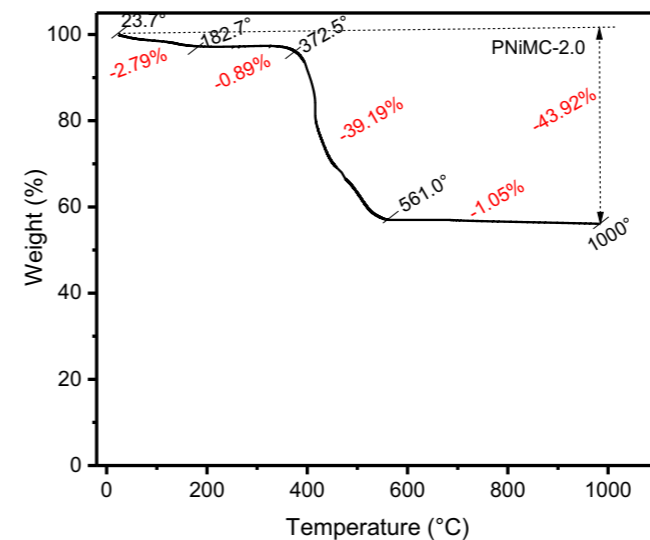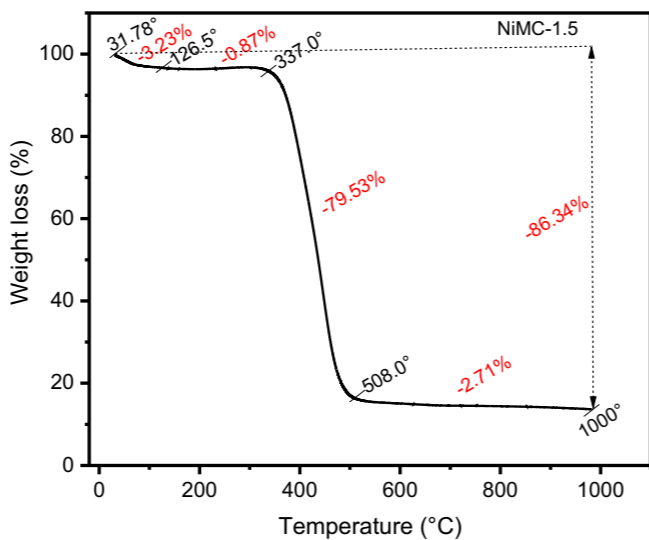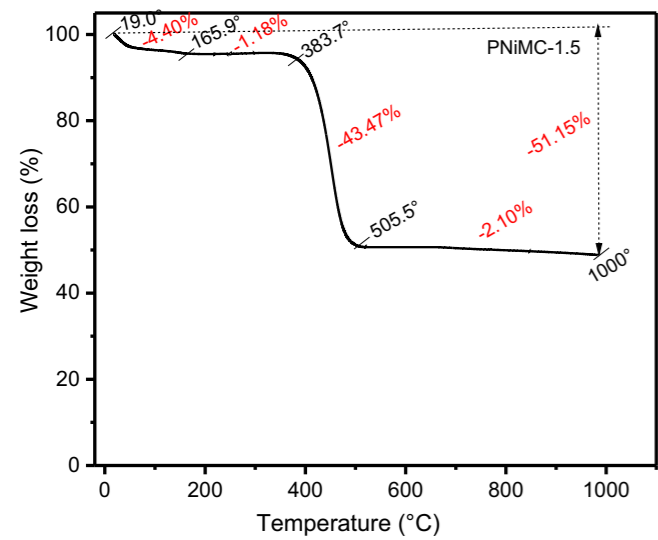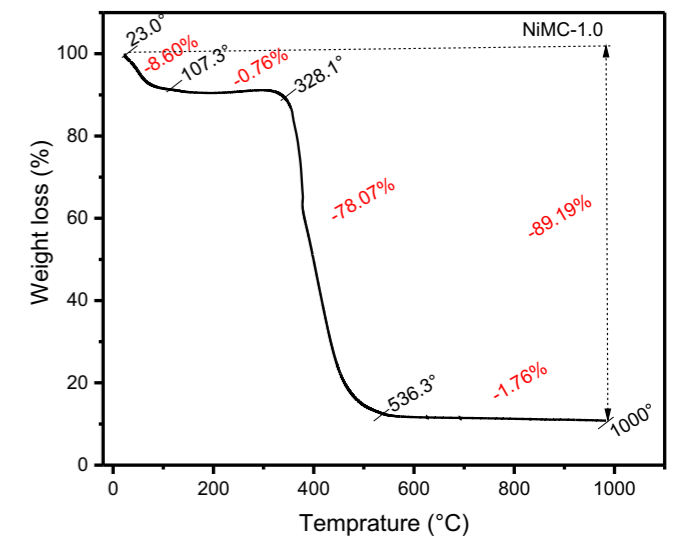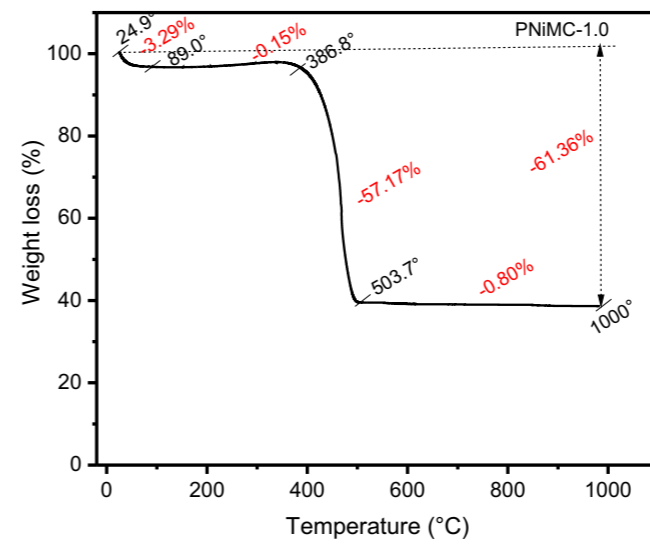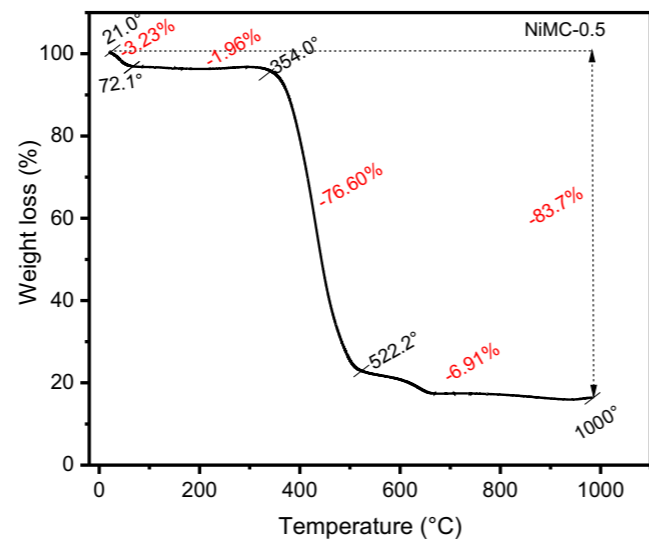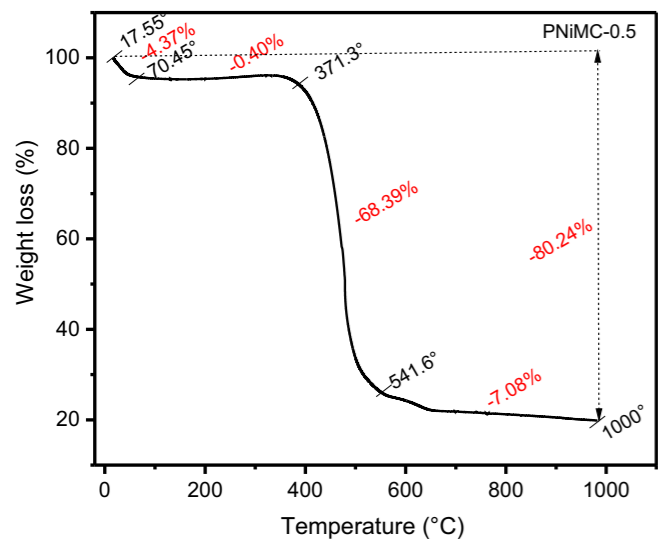
Supplementary Fig.5. TGA curves of the activated carbons modified with Ni²⁺ at different ratios.
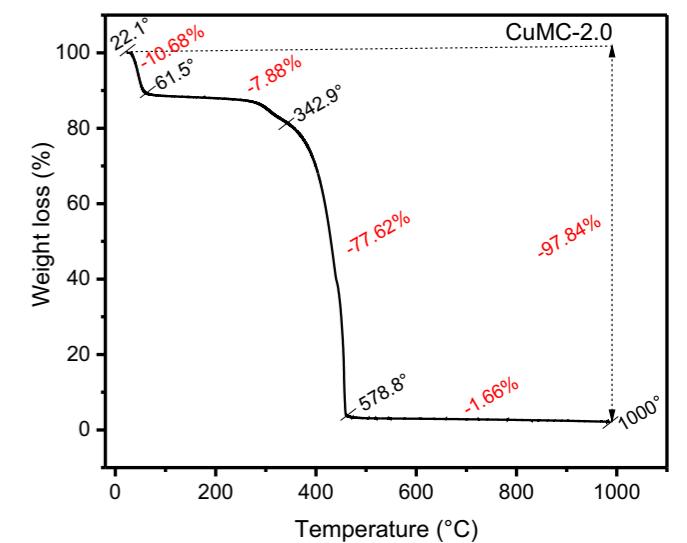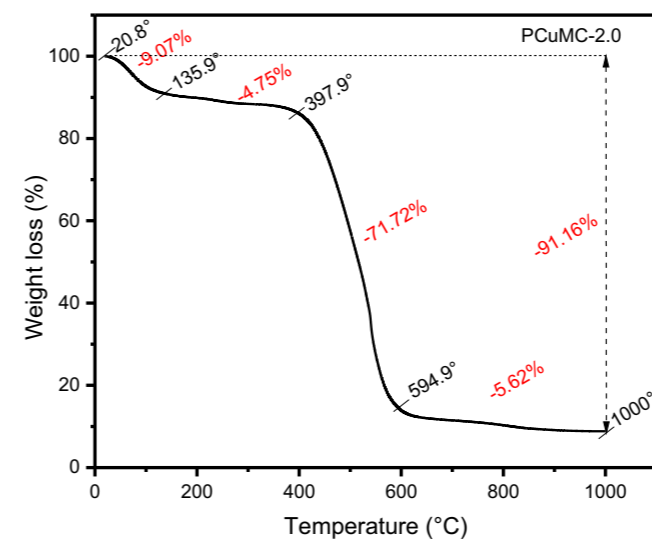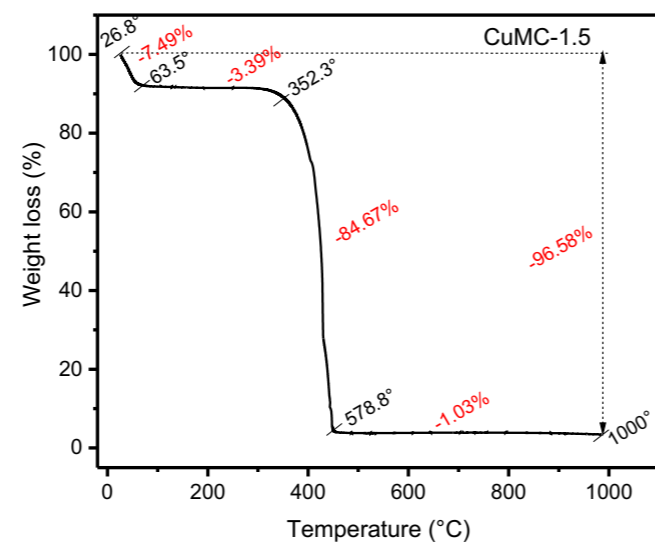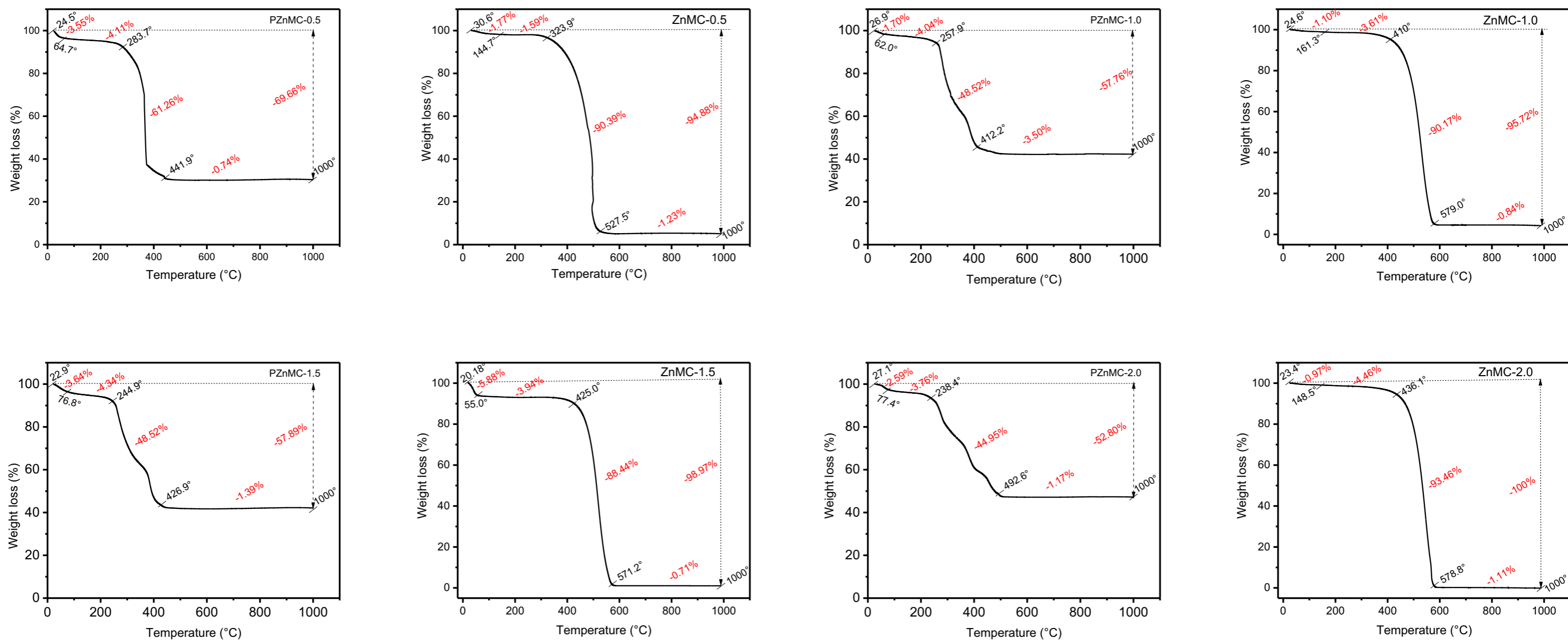
Supplementary Fig.6. TGA curves of the activated carbons modified with Cu^{2+} at different ratios.

Supplementary Fig.7. TGA curves of the activated carbons modified with Zn²⁺ at different ratios.

ERRATUM OF ANNEX 2

This is related to the correction of Table **2** of the second annex of the thesis. The related comments are also provided.

Table 2. Textural properties of activated carbons materials

Sample	BET surface area (m^2 g^{-1})	t-Plot Micropore Area (m^2 g^{-1})	t-plot extern. surface area (m^2 g^{-1})	Total pore volume (cm^3 g^{-1})	t-Plot micropore volume (cm^3 g^{-1})	Mesopore volume (cm^3 g^{-1})	S_{mic}/S_{tot} (%)	V_{mic}/V_{tot} (%)
AC-1A	914.08	518.65	395.43	0.52327	0.25177	0.27151	56.74	48.11
AC-2A	874.72	560.60	314.11	0.55385	0.27025	0.28360	64.09	48.79
AC-1B	805.06	435.17	369.89	0.44205	0.20864	0.23342	54.05	47.20
AC-2B	647.05	405.89	241.15	0.34443	0.20020	0.14424	62.73	58.13

3. Results and discussion

3.1. Characterisation of activated carbons

The chemical activation of the Sapelli wood with inorganics and further pyrolysis assisted by microwaves generated different activated carbons with different adsorption characteristics. Among the main features of the adsorbents, the surface area and porosity are the most influential for adsorption processes. The N_2 adsorption–desorption isotherms and the BJH plots of the AC-1A, AC-1B, AC-2A, and AC-2B samples are listed in Fig 1.

The nitrogen isotherms exhibited by the activated carbons are shown in Fig. 1A. According to IUPAC all these samples are classified all as a mixture of type I and II isotherms which is typical of mesoporous and microporous materials, with pore widths below 2 nm and between 2nm and 50nm [38].

The pore size distribution curves of AC-1A, AC-2A, AC-1B and AC-2B, are presented in Fig 1B-E, respectively. It can be seen that all activated carbons present a mixture of micropores and mesopores, presenting a peak maximum around 40 Å (4 nm).

The effects of the differing types of chemical agents and impregnation ratios on the BET surface area, micropore area, external surface area, total pore volume, micropore volume, and mesopores volume are given in Table 2.

As can be seen from the results of Fig 1A and Table 2, the adsorbed N_2 volume differed depending on the ratio biomass and activation agents used. The highest surface

area was obtained for the AC-1A material (100 g Sapelli wood sawdust + 20 g lime + 80 g $ZnCl_2$) followed by AC-2A (150 g Sapelli wood sawdust + 20 g lime + 80 g $ZnCl_2$), and then AC-1B (100 g Sapelli wood sawdust + 20 g lime + 40 g $ZnCl_2$ + 40 g $FeCl_3$), and lastly AC-2B (150 g Sapelli wood sawdust + 20 g lime + 40 g $ZnCl_2$+ 40 g $FeCl_3$); see Table **2**. The difference in total surface area between AC-1A and AC-2A was only 5.0 %, however, the difference total surface area between AC-1B and AC-2B was 19.62%. From these results, it is possible to infer that the ratio Biomass/Inorganic components is very important for increasing the surface area, as well as pore development in the activated carbon materials [39].

The adsorbents with higher inorganic contents (AC-1A and AC-1B) showed higher surface areas and higher pore volume compared with the adsorbents with lower amounts of inorganics introduced during preparation of the activated carbon (AC-2A and AC-2B) [40,41].

Another analysis that could be convenient with regards to these activated carbons is the ratio $S_{micropore}/S_{total}$ expressed in percentage. These values are 56.74, 54.05, 64.09 and 62.73% for the activated carbons AC-1A, AC-1B, AC-2A and AC-2B, respectively. It can be observed that the micropore structure was created when ratio Biomass/inorganic increased. However, comparing all the results, one can infer that each of the four activated carbon materials presented a mixture of micro- and mesopores with the predominance of micropore structure. The lime + $ZnCl_2$ + $FeCl_3$ activating agent employed in the preparation (AC-1B, and AC-2B) as well as the lime + $ZnCl_2$ activating agent (AC-1A, and AC-2A) can be used to create a predominantely microporous adsorbents.

Furthermore, analyzing these results, it is expected that the sorption capacity of AC-1B would be very close to that of AC-2A, since these materials did not exhibit remarkable differences in surface area (difference of only 8.0 %). Also the inorganic components used to form the paste with the organic precursor (20 g lime + 80 g $ZnCl_2$ or 20 g lime + 40 g $ZnCl_2$ + 40 g $FeCl_3$) presented practically the same performance. Only AC-2B presented worst surface area, being 19.6 % lower than for AC-1B, 26.0 % lower than for AC-2A, and 29.2 % lower than for AC-1A. Use of $ZnCl_2$ as an activating agent is well known in literature [39–41], whereas use of $FeCl_3$ as an activating agent for production of activated carbon is more recent in literature [27].

In addition, the ratio $V_{micropore}/V_{total}$ expressed as a percentage could be another useful parameter for analysis of these activated carbon materials. Its value was 48.11, 47.20, 48.79 and 58.13 % for AC-1A, AC-1B, AC-2A, and AC-2B, respectively. Analyzing these results, only AC-2B (150 g biomass + 20 g lime + 40 g $ZnCl_2$ + 40 g $FeCl_3$) presented a predominance of micropores, because this ratio was slightly higher than 50 %. On the other hand, AC-1A, AC-1B, and AC-2A presented $V_{micropore}/V_{total}$ ratios lower than 50 %, indicating that these materials were predominantly mesoporous. Although this analysis differs from the

analysis of the ratio $S_{micropore}/S_{total}$, for which all the activated carbon materials presented a value higher than 50 %, both analyses indicate that all the activated carbon materials possess micropores and mesopores in their structure, and these pores are responsible for the sorption capacity of the obtained adsorbents [42–45].

In preparation of activated carbon, yield is an important parameter, usually being defined as the final weight of activated carbon produced after activation, washing, and drying, divided by the initial weight of raw material, both on dry basis [27, 46]. The global yield of activated carbon varied in the range from 24 to 35 %, considering the initial mass of sawdust used.
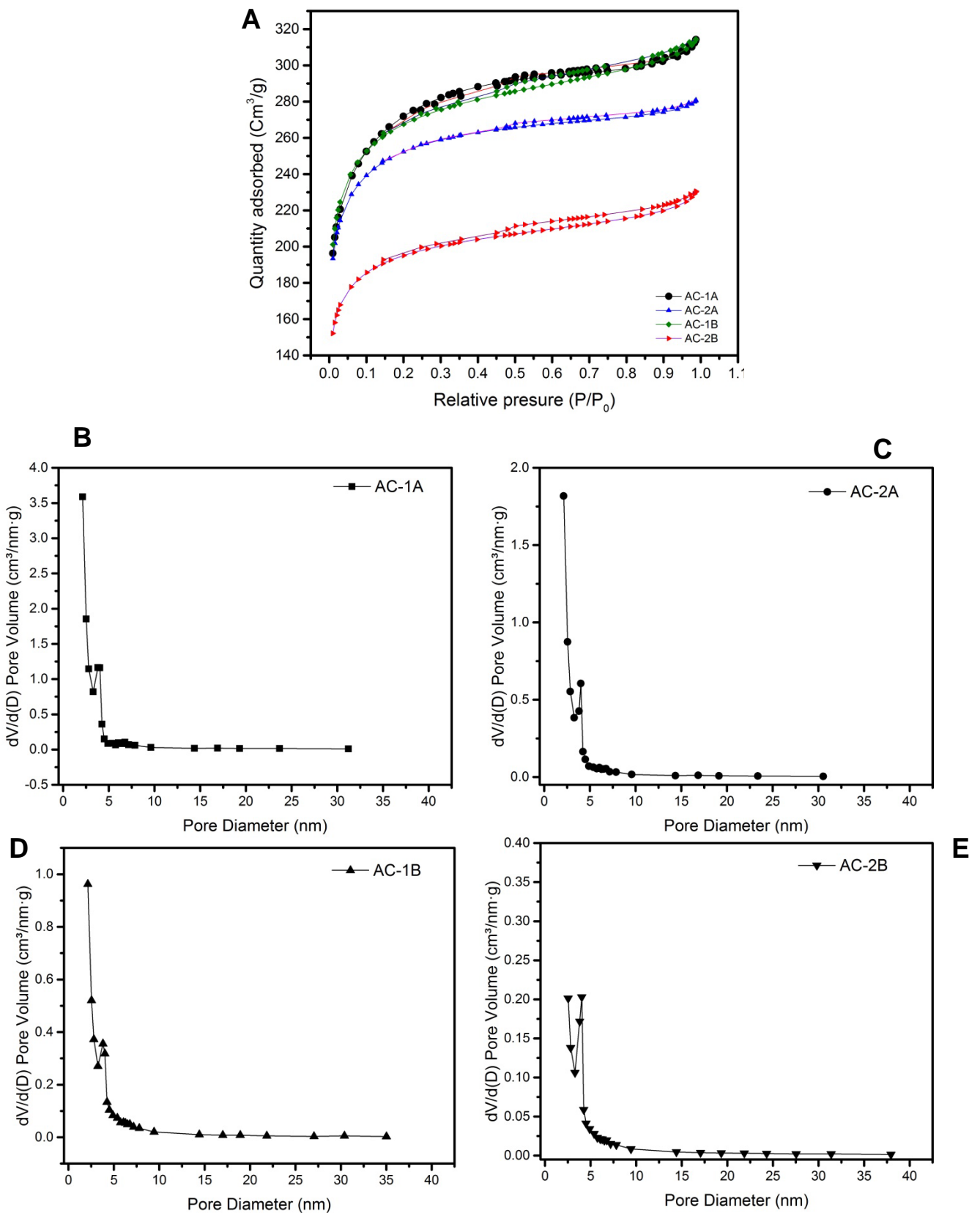
Fig. 1. A) Nitrogen adsorption–desorption isotherms for activated carbons (The compact symbols are for the adsorption branch and the hollow symbols are for the desorption branch). Pore size distribution: B) AC-1A; C) AC-2A; D) AC-1B; E) AC-2B.