UNIVERSIDADE FEDERAL DO RIO GRANDE DO SUL

ESCOLA DE ENGENHARIA

DEPARTAMENTO DE ENGENHARIA QUÍMICA

PROGRAMA DE PÓS-GRADUAÇÃO EM ENGENHARIA QUÍMICA

Análise e Redução do Impacto dos Produtos Químicos de Acabamento Molhado na Carga Poluente dos Efluentes Líquidos de Processo

TESE DE DOUTORADO

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Porto Alegre

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Tese de Doutorado apresentada ao Programa de Pós-Graduação Engenharia Química da Universidade Federal do Rio Grande do Sul como parte dos requisitos para obtenção do título de Doutor em Engenharia Química.

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A Comissão Examinadora, abaixo assinada, aprova a Tese de Doutorado *Análise e Redução do Impacto dos Produtos Químicos de Acabamento Molhado na Carga Poluente dos Efluentes Líquidos de Processo,* elaborado por Éverton Hansen, como requisito parcial para obtenção do Grau de Doutor em Engenharia Química.

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Resumo

A transformação da pele em couro acabado requer adições sequenciais de produtos químicos em meio aquoso, intercaladas por lavagens e operações mecânicas. Os produtos químicos adicionados são parcialmente retidos pelo couro, sendo as frações remanescentes nos banhos de processo descartadas nos efluentes líquidos. Os efluentes líquidos gerados no processo de acabamento molhado encontram-se caracterizados na literatura. No entanto, poucos estudos avaliam como as classes de produtos químicos e suas dosagens individuais aplicadas ao couro impactam na qualidade dos efluentes líquidos do processo. Desta forma, o presente estudo tem por objetivo avaliar o impacto dos produtos químicos utilizados no processo de acabamento molhado do couro nos principais parâmetros de poluição dos efluentes líquidos gerados nesta etapa de processamento. Este estudo foi realizado em quatro partes: (i) estudo de formulações de acabamento molhado publicadas em artigos científicos, (ii) avaliação do impacto dos produtos químicos na carga poluente dos efluentes gerados no acabamento molhado, em um estudo de caso, (iii) ajuste da formulação de acabamento molhado, visando reduzir a carga poluente dos efluentes líquidos gerados, e (iv) revisão sistemática de tecnologias aplicadas para o tratamento dos efluentes líquidos de acabamento molhado. O estudo de formulações de acabamento molhado mostrou um consumo médio de 360,2 kg de produtos químicos por tonelada de couro processado e o consumo médio de água encontrado foi de 8,6 m³/t. Os resultados da avaliação do impacto dos produtos químicos na carga poluente dos efluentes demonstraram que os agentes de recurtimento (taninos vegetais e sintéticos) foram responsáveis pela maior carga de poluição inorgânica nos efluentes, e que os taninos sintéticos foram mais tóxicos que os vegetais. Os óleos foram responsáveis pela maior carga de demanda química de oxigênio nas águas residuais e foram o grupo químico que apresentou a maior citotoxicidade. O agente de fixação e o corante contribuíram com a carga inorgânica dos efluentes líquidos, e a carga de nitrogênio foi relacionada principalmente ao recurtente neutralizante e ao corante. Os resultados do ajuste da formulação, reduzindo a oferta de produtos químicos, mostraram redução da carga poluente dos efluentes líquidos. O couro obtido mostrou qualidade dentro das especificações requeridas e o custo da formulação foi reduzido em 24%. Por fim, a revisão sistemática apresentou as principais condições de operação, inovações e desafios das tecnologias aplicadas ao tratamento de efluentes de acabamento molhado.

Palavras-chave: couro; acabamento molhado; efluentes líquidos; corantes; óleos; recurtentes; citotoxicidade; tratamento de efluentes.

Abstract

The transformation of the hide into finished leather requires sequential additions of chemicals in an aqueous medium, alternated with washing and mechanical operations. These chemicals are partially retained by the leather, and the fractions remaining in the process floats are discharged with the wastewater. Current literature has an extensive number of studies aimed at characterizing tannery effluents. However, few studies have evaluated how groups of chemicals applied to the leather impact the quality of wastewater generated in the process. Thus, this study aims to evaluate the impact of chemicals used in the wet-finishing process of the leather on the main quality parameters of the wastewater generated by this processing step. This study was carried out in four parts: (i) study of wet-finishing formulations published in scientific articles, (ii) evaluation of the impact of chemicals on the pollution load of wet-finishing wastewater, using a case study, (iii) adjustment of the wet-finishing formulation, aiming to reduce the pollution load of the wastewater, and (iv) systematic review of technologies applied to the wet-finishing wastewater treatment. The study of wet-finishing formulations showed an average consumption of 360.2 kg of chemicals per ton of wet-blue leather, and the average water consumption of 8.6 m^3/t was found. The results of the analysis of chemicals impact on the pollution load of wet-finishing wastewater showed that the retanning agents (natural and synthetic tannins) were responsible for the highest inorganic pollution load in the wastewater, and the synthetic tannins were more toxic than the natural ones. The fatliquoring agents were responsible for the highest chemical oxygen demand load in the wastewater and were the chemical group that presented the highest cytotoxicity. The fixing agent and the dye contributed to the inorganic pollution load of the wastewater, and the nitrogen load of the wastewater was mainly related to the neutralizing retanner and the dye. The results of adjusting the formulation, reducing the supply of chemicals, showed a reduction in the pollution load of wastewater. The obtained leather showed quality within the required specifications of the tannery and the formulation cost was reduced by 24%. Finally, the systematic review presented the main operational conditions, novelty, and challenges of the technologies applied to the wet-finishing wastewater treatment.

Keywords: leather; wet-finishing; wastewater; dyes; fatliquoring agents; retanning agents; cytotoxicity; wastewater treatment.

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Capítulo 1

Introdução

A indústria do couro e seus produtos desempenham um papel relevante na economia mundial, com um valor comercial global de aproximadamente 80 bilhões de dólares por ano (SIVARAM e BARIK, 2019). Esta indústria é especialmente importante na economia de países em desenvolvimento (BHARAGAVA e MISHRA, 2018) como Brasil, China e Índia, sendo que o Brasil possui o maior rebanho bovino comercial do mundo (ABQTIC, 2020). De acordo com o Centro das Indústrias de Curtume do Brasil - CICB (2020), o setor de curtumes brasileiro conta com 310 plantas curtidoras e 2.800 indústrias de componentes para couro e calçados, empregando mais de 50.000 funcionários. A indústria brasileira do couro foi responsável pela exportação de mais de 1,1 bilhões de dólares no ano de 2019, sendo o Rio Grande do Sul o maior exportador de couro do país, com receita anual superior a 305 milhões de dólares. O couro acabado é responsável por 59,6% do faturamento (ABQTIC, 2020).

O processamento do couro consiste em uma sequência de operações químicas e mecânicas aplicadas em uma matriz biológica natural (pele), utilizando água e produtos químicos orgânicos e inorgânicos (TENG *et al.*, 2017). Resíduos sólidos e efluentes líquidos são gerados a partir desse processo, o que demanda que a indústria curtidora busque soluções inovadoras que minimizem seus impactos ambientais e atendam a legislação ambiental vigente. De acordo com estudo encomendado por CICB (2013), para 90,3% dos curtumes brasileiros, as questões ambientais fazem parte do planejamento da empresa, e 90,8% fazem um controle diário do volume de efluentes líquidos gerados.

A transformação de uma pele verde em couro acabado envolve um conjunto de etapas agrupadas em: ribeira, curtimento, acabamento molhado, secagem, pré-acabamento e acabamento final. A literatura atual contempla um extenso número de pesquisas sobre o controle e a redução do impacto ambiental dos processos de ribeira e curtimento. Isso não ocorre, com a mesma frequência, para o acabamento molhado e acabamento final do couro (MOREIRA *et al.*, 2019; WU *et al.*, 2018), embora a etapa de acabamento molhado gere cerca de 38% dos efluentes líquidos em um curtume completo (CASSANO *et al.*, 2001) e seja responsável por aproximadamente 30% dos produtos químicos consumidos (RIVELA *et al.*, 2004). O número de publicações no período de 1995 a julho de 2019 na base de dados Scopus contabilizou 1.116 artigos (66%) relacionados ao gerenciamento de efluentes líquidos da etapa de curtimento, 388 artigos (23%) relacionados à ribeira, 141 artigos (8%) relacionados ao acabamento molhado e 44 artigos (3%) relacionados ao acabamento final do couro. A busca foi realizada utilizando as palavras-chave: "beamhouse" OR "soaking" OR "liming" OR "unhairing" OR "tanning" OR "post tanning" OR "wet end" OR "wet finishing" OR "retanning" OR "fatliquoring" OR "dyeing" OR "finishing" AND “leather” AND "wastewater". O número de publicações mostra que existe uma lacuna de informações e estudos sobre o impacto ambiental do acabamento molhado. Por outro lado, um aumento no número de estudos sobre o gerenciamento de efluentes líquidos de acabamento molhado nos últimos dez anos é observado, evidenciando a relevância atual deste tema.

Os curtumes podem ser divididos em (i) curtumes integrados (que processam a pele verde ou conservada até a obtenção de couro acabado), (ii) curtumes de ribeira e curtimento (que processam a pele verde ou conservada até a obtenção de couro wet-blue, que pode ser comercializado como comódite no mercado interno ou exportação) e (iii) curtumes de pós-curtimento e acabamento (que processam couro wet-blue para a obtenção de couros acabados, com diversificação dos tratamentos aplicados para atender às propriedades desejáveis no couro para fabricação do produto final). No estado do Rio Grande do Sul, a maior parte dos curtumes está concentrada nas etapas de acabamento molhado e acabamento final do couro (NUNES *et al.*, 2019). O acabamento molhado tem como objetivo diferenciar o couro wet-blue para obter couros acabados padronizados, conferindo características como aspecto, textura, cor, e propriedades físico-mecânicas. Neste processo, produtos químicos como desacidulantes, taninos vegetais e sintéticos, resinas recurtentes, óleos naturais e sintéticos, surfactantes, corantes, auxiliares químicos e ácidos são utilizados para garantir as propriedades desejadas no couro (AYOUB *et al.*, 2013; ORTIZ-MONSALVE *et al.*, 2019; PICCIN *et al.*, 2016a). Esses produtos químicos não são totalmente absorvidos pelo couro durante o processamento e, portanto, são parcialmente descartados nos efluentes líquidos brutos do curtume (AQUIM, 2009; BHARAGAVA *et al.*, 2018; MOREIRA *et al.*, 2019).

Os efluentes brutos de acabamento molhado já foram caracterizados por diversos estudos, que avaliaram, entre outros parâmetros, demanda química de oxigênio (DQO) (PENA *et al.*, 2018; SUNGUR e ÖZKAN, 2017), demanda bioquímica de oxigênio (DBO) (ISLAM *et al.*, 2014; MELLA *et al.*, 2018), sólidos dissolvidos totais (SDT) (GUTTERRES *et al.*, 2015; SELVARAJU *et al.*, 2017), cromo (PICCIN *et al.*, 2016; RAGHAVA RAO *et al.*, 2003), nitrogênio total Kjeldhal (NTK) (AÇIKEL *et al.*, 2017; PENA *et al.*, 2018), nitrogênio amoniacal (NH_4-N) (GUTTERRES *et al.*, 2015; OLLÉ *et al.*, 2016), condutividade (AÇIKEL *et al.*, 2017; MELLA *et al.*, 2018), cloretos (BASHA *et al.*, 2009; KARTHIKEYAN *et al.*, 2015) e sulfatos (KARTHIKEYAN *et al.*, 2015; RIVELA *et al.*, 2004). Ensaios de toxicidade em efluentes de curtume também já foram conduzidos utilizando peixes (CHAGAS *et al.*, 2019; TAJU *et al.*, 2012), invertebrados (BHATTACHARYA *et al.*, 2016; VERMA, 2011), citotoxicidade em cultura de células (DE PARIS *et al.*, 2019; SHAKIR *et al.*, 2012), bactéria e/ou algas (ORTIZ-MONSALVE *et al.*, 2019; TIGINI *et al.*, 2011). No entanto, existem apenas estudos pontuais avaliando as características químicas e toxicológicas de produtos químicos de acabamento molhado. Estudos realizados por Lofrano *et al*. (2007 e 2008) avaliaram taninos sintéticos, resinas e óleos, Libralato *et al*. (2011) avaliaram o ácido tânico, e Moreira *et al*., (2019) avaliaram um corante e taninos naturais e sintéticos, relacionando as características dos produtos químicos com os seus impactos nos efluentes brutos de curtume e nas técnicas de tratamento dos efluentes.

O tratamento convencional de efluentes de curtume consiste na aplicação das operações de equalização e neutralização, tratamento físico-químico através de coagulação e floculação seguidos de sedimentação, e tratamento biológico, sendo o lodo ativado aplicado mais frequentemente (HASEGAWA *et al*., 2011; KÖRBAHTI *et al*., 2011; KOZIK *et al*., 2019; PAL *et al*., 2020; PENA *et al*., 2020; PICCIN *et al*., 2012; TAMERSIT *et al*., 2018; TRAN *et al*., 2020). No entanto, a literatura aponta a geração de lodo e as baixas eficiências para a remoção de sais e compostos recalcitrantes como vulnerabilidades deste tratamento (KOZIK *et al*., 2019; DE LA LUZ-PEDRO *et al*., 2019; MOREIRA *et al*., 2019; PAL *et al*., 2020; PENA *et al*., 2020; SUTHANTHARARAJAN *et al*., 2004; TAMERSIT *et al*., 2018). Além disso, as legislações ambientais estão cada vez mais restritivas quanto aos padrões de lançamento de efluentes em corpos hídricos, e o tratamento convencional de fim de tubo não atende às exigências para o reuso de efluentes tratados no processo.

Para contornar as vulnerabilidades do tratamento convencional de efluentes de acabamento molhado, novas tecnologias de tratamento vêm sendo estudadas, aplicando processos oxidativos avançados, tratamentos biológicos, adsorção, processos de separação por membrana e coagulação/floculação, além de tratamentos híbridos. No entanto, o tratamento dos efluentes gerados não é a única prática a ser adotada para o gerenciamento de efluentes líquidos industriais. Conceitos de produção mais limpa e prevenção da poluição (EPA, 1988) identificam a necessidade de reduzir ou eliminar em volume, concentração e/ou toxicidade os resíduos na fonte geradora, aplicando uma estratégia ambiental preventiva e integrada aos processos industriais. As medidas de prevenção da poluição e produção mais limpa são benéficas porque reduzem os custos operacionais, diminuem os danos ecológicos decorrentes das operações de extração e beneficiamento das matérias-primas empregadas, reduzem a exposição dos funcionários a substâncias nocivas e melhoram a imagem da empresa (EL-HAGGAR, 2007).

Neste contexto, este trabalho buscou atualizar e discutir os dados disponíveis na literatura sobre o consumo de água e produtos químicos na etapa de acabamento molhado do couro. Este estudo permite uma análise abrangente sobre o uso de produtos químicos no processo de acabamento molhado, considerando que os estudos existentes apresentam frequentemente casos isolados de um curtume ou tecnologia de processamento. Além disso, realizou-se uma caracterização físico-química e citotóxica dos produtos químicos de uma formulação utilizada como estudo de caso em um curtume, uma vez que a relação entre os produtos químicos e a carga de poluição dos efluentes líquidos permanece pouco conhecida. A partir da análise dos produtos químicos e dos efluentes, foi proposta e implementada a redução na oferta de produtos químicos desta formulação, visando reduzir as cargas poluentes dos efluentes de processo. Por fim, foi realizada uma revisão sistemática de tecnologias avançadas aplicadas ao tratamento de efluentes de acabamento molhado, apresentando técnicas adequadas para a remoção dos poluentes presentes neste efluente. Desta forma, o presente trabalho tem o propósito de contribuir para um melhor gerenciamento dos efluentes líquidos, do consumo de água e de produtos químicos nos curtumes, identificando e reduzindo as cargas poluentes e a toxicidade dos efluentes líquidos na fonte geradora, reduzindo os impactos ambientais e os custos do processo.

1.1. Objetivos do trabalho

O objetivo geral deste estudo consiste em analisar e reduzir o impacto dos produtos químicos utilizados no processo de acabamento molhado do couro nos principais parâmetros de qualidade dos efluentes líquidos gerados nesta etapa de processamento.

Os objetivos específicos desse estudo são:

i. Apresentar a situação geral do consumo de água e produtos químicos nas formulações de acabamento molhado;

ii. Indicar valores de referência para o consumo de água e produtos químicos no acabamento molhado, considerando diferentes matérias-primas processadas e artigos de couro produzidos;

iii. Caracterizar os produtos químicos de uma formulação de acabamento molhado quanto a parâmetros físico-químicos e citotoxicidade;

iv. Analisar os efluentes brutos gerados no acabamento molhado, quanto aos parâmetros físico-químicos e citotoxicidade;

v. Analisar o impacto dos produtos químicos na qualidade dos efluentes líquidos gerados no processamento do couro em escala piloto;

vi. Estudar como reduzir a carga poluente dos efluentes brutos gerados, utilizando uma formulação como estudo de caso.

vii. Comparar a eficiência das tecnologias aplicadas para o tratamento dos efluentes de acabamento molhado.

1.2. Estrutura do trabalho

Este estudo está dividido em sete capítulos. No Capítulo 1 está apresentada a introdução do trabalho, abordando a motivação, os objetivos e a estrutura do trabalho. O Capítulo 2 traz a fundamentação teórica, que aborda a pele e seus componentes, o processamento do couro e os produtos químicos utilizados na etapa de acabamento molhado.

A revisão bibliográfica sobre o estado da arte está apresentada na forma de uma análise do consumo de produtos químicos e de água no processo de acabamento molhado do couro, bem como uma caracterização dos efluentes líquidos brutos gerados nesta etapa de processamento (Capítulo 3). Este capítulo apresenta o artigo *Environmental Assessment of Water, Chemicals and Effluents in Leather Post-tanning Process: a Review*, que está publicado no periódico *Environmental Impact Assessment Review*.

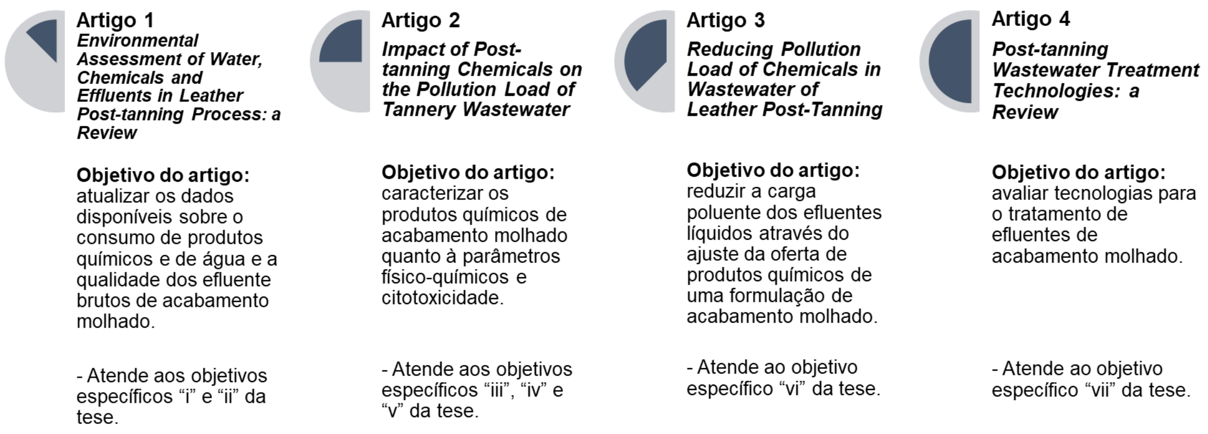
No Capítulo 4 é apresentado o artigo *Impact of Post-tanning Chemicals on the Pollution Load of Tannery Wastewater*, que está publicado no periódico *Journal of Environmental Management*. O artigo aborda a caracterização físico-química e citotóxica dos produtos químicos utilizados em uma formulação de acabamento molhado, avaliando como estes produtos químicos impactam na qualidade dos efluentes brutos de processo.

No Capítulo 5 é apresentado o artigo *Reducing Pollution Load of Chemicals in Wastewater of Leather Post-Tanning*, que está em processo de submissão para periódico. O artigo aborda testes em escala piloto e industrial para redução na oferta de recurtentes e agentes de engraxe, avaliando como a redução na oferta de produtos químicos influenciam na qualidade dos efluentes brutos de processo, na qualidade do couro obtido e nos custos da formulação.

No Capítulo 6 é apresentado o artigo *Post-tanning Wastewater Treatment Technologies: a Review*, que está em processo de submissão para periódico. O artigo apresenta uma revisão sistemática de tecnologias aplicadas ao tratamento de efluentes de acabamento molhado.

No Capítulo 7 são apresentadas as conclusões desta tese de doutorado e as sugestões para trabalhos futuros. A Figura 1.1 apresenta de forma esquemática os quatro artigos que compõem a presente tese, mostrando os objetivos gerais dos estudos e como os objetivos específicos da tese estão organizados nos artigos.

Figura 1.1: Estrutura da tese baseada em artigos



Fonte: autor, 2021.

Capítulo 2

Fundamentação Teórica

Neste capítulo é apresentada a fundamentação teórica do estudo, que aborda a composição e estrutura da pele, as etapas de processamento do couro, a descrição dos grupos de produtos químicos e tecnologias mais limpas aplicadas no acabamento molhado.

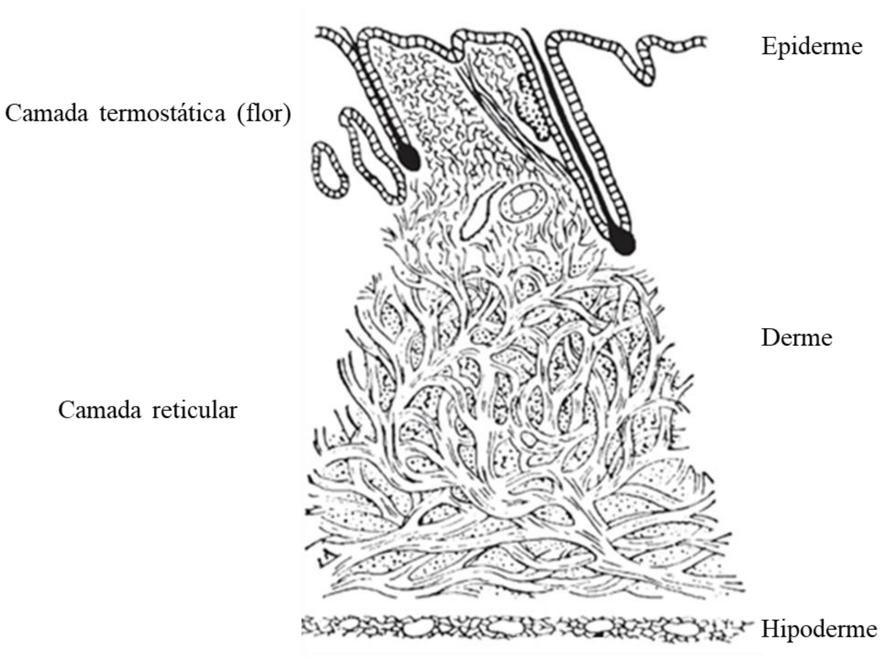
2.1. Pele e seus componentes

A pele é a matéria-prima principal da indústria do couro. A composição aproximada de uma pele fresca é de 60 a 64% de água, 33% de proteínas, 2 a 6% de gorduras e 1% de outras substâncias. Da parcela de proteínas da pele, aproximadamente 94 a 95% é colágeno, 1% é elastina, 1 a 2% é queratina e o restante são proteínas não fibrosas (GUTTERRES, 2008a). As propriedades e o potencial de modificação química do colágeno conferem à pele a possibilidade de transformação no material couro com excelente desempenho, durabilidade e elevado valor comercial.

A cadeia de aminoácidos do colágeno é composta por 1052 restos de aminoácidos, de fórmula básica H_2N-CHR-COOH em forma de unidades repetitivas de tripeptídeos (Gli-X-Y) (GUTTERRES, 2008a), onde a glicina (Gli) está sempre na primeira posição e, no colágeno de peles bovinas, cerca de um terço das posições X e Y são ocupadas por prolina e hidroxiprolina, respectivamente (MANCOPES *et al.*, 2008). As cadeias polipeptídicas têm forma de espiral. Três espirais conformam-se em um eixo comum e fazem ligações de hidrogênio, dando origem a molécula de colágeno (hélice tríplice) (GUTTERRES, 2008a). As tríplices hélices estão unidas através de ligações de hidrogênio entre a glicina e as cadeias vizinhas. A água também é responsável por parte das ligações de hidrogênio existentes na molécula de colágeno, sendo a água parte integrante da estrutura de colágeno (COVINGTON, 2011).

A presença de grupos ácidos e básicos confere ao colágeno um caráter anfótero e, como consequência, a carga global da pele varia com o pH do meio em que se encontra. Em soluções ácidas, os grupos carboxílicos encontram-se na forma não dissociada e os grupos aminas encontram-se na forma dissociada ($^{+}H_3N - COOH$), e a carga total é positiva (caráter catiônico). Em soluções básicas, os grupos carboxílicos estão dissociados e os grupos amina encontram-se na forma não dissociada ($H_2N - COO^{-}$), e a carga total é negativa (caráter aniônico). Desta forma, o pH do meio determina a reatividade da proteína frente aos reagentes químicos usados no processamento da pele (FUCK, 2018). O valor de pH no qual a carga elétrica global da pele é nula é definido como ponto isoelétrico (MACOVESCU *et al.*, 2018). A pele é formada por três camadas: epiderme, derme e hipoderme, conforme ilustrado na Figura 2.1.

Figura 2.1: Estrutura da pele.



Fonte: adaptado de Covington (2011).

A epiderme é a camada mais externa da pele, contribuindo com aproximadamente 1% de sua espessura total, sendo composta principalmente por queratina. A epiderme é removida da pele nos estágios iniciais do processamento (depilação e caleiro) (COVINGTON, 2011).

A derme constitui aproximadamente 85% da espessura total da pele, e apresenta estrutura fibrosa densa. Os couros são obtidos desta camada, após a eliminação das demais camadas constitutivas da pele (DETTMER, 2012). A derme é constituída por sua vez das camadas termostática e reticular. A sub-camada superior (termostática) abrange a espessura que vai da superfície externa superior da pele até a zona da raíz dos pelos. A superfície da camada termostática fica exposta após a etapa de depilação, e também é denominada de camada flor. Esta camada é constituída por um entrelaçado de fibras de colágeno e ainda por fibras de elastina. A sub-camada reticular constitui a parte inferior da derme e apresenta na sua estrutura fibras de colágeno orientadas em todos os sentidos e direções. Tanto a camada termostática quanto a reticular são extremamente importantes no produto final: a primeira é responsável, principalmente, pelo aspecto do couro e a segunda pela resistência à tração e ao rasgo (HOINACKI *et al.*,1994).

A hipoderme é a camada inferior da pele e representa o restante da espessura total da pele fresca. Esta camada une a pele com o corpo animal e apresenta estrutura fibrosa mais frouxa, formada por tecido adiposo, conectivo, vasos sanguíneos, nervos e músculos. A hipoderme é eliminada no princípio do processamento da pele, nas operações de pré-descarne e descarne, anteriormente à etapa de curtimento (PRIEBE, 2016).

A pele recebida de matadouros ou frigoríficos deve ser conservada após o abate, para não entrar em decomposição, devido à produção de enzimas proteolíticas por bactérias (COVINGTON, 2011). No Brasil, o método mais empregado para a conservação das peles bovinas é a salga (MOREIRA, 2016).

2.2. Processamento do Couro

A transformação da pele verde ou salgada em couro acabado requer diversas etapas de processamento, incluindo etapas químicas, com adições sequenciais de produtos químicos, intercaladas por lavagens, realizadas em fulões e processos mecânicos realizados em máquinas apropriadas para cada finalidade. As etapas de processamento da transformação da pele em couro podem ser agrupadas em: operações de ribeira, curtimento, e de acabamento (este por sua vez inclui acabamento molhado, secagem, pré-acabamento e acabamento final). Os conceitos apresentados foram baseados em literaturas clássicas do couro, como: Covington (2011), Gutterres (2008b), Püntener (2000) e Heidemann (1993).

2.2.1. Ribeira

O objetivo das operações de ribeira é limpar a pele, removendo as partes e componentes que não constituem o produto final (couro), entre eles, a epiderme, a hipoderme e o material interfibrilar da derme. A pele conservada é inicialmente submetida ao remolho para recuperar a quantidade de água que tinha antes de sua conservação. As peles são depiladas através de processo químico e/ou enzimático, e a estrutura da fibra é aberta durante o processo de caleiro, em pH 12 (GUTTERRES e MELLA, 2014). O caleiro e a depilação são seguidos das operações mecânicas de descarne (remoção do tecido subcutâneo da pele) e divisão da pele em duas partes: parte superior (composta pela camada flor e parte da camada reticular), e parte inferior (constituída pelo que restou da camada reticular). A divisão pode ser realizada tanto na pele caleirada quanto piquelada, ou ainda após o curtimento. A etapa de desencalagem remove o hidróxido de cálcio (cal) e reverte o inchamento e a etapa de purga promove o tratamento da pele com enzimas proteolíticas visando remover proteínas não colagênicas e material degradado.

2.2.2. Curtimento

A etapa de curtimento do couro integral ou dividido inicia com o píquel, um tratamento salino-ácido que prepara a pele para o curtimento. O curtimento consiste em promover a estabilização irreversível da pele por meio de enlaces químicos transversais das cadeias de colágeno com agentes curtentes. O cromo é o principal agente curtente usado no mundo, com o qual é obtido couro wet-blue, que tem pH em torno de 4,0. Cerca de 80% (GUTTERRES e MELLA, 2014) de todos os couros do mundo são curtidos com cromo. Os taninos vegetais também são usados como agentes de curtimento, fornecendo couro com características diferentes (em geral menos macios e com coloração com tons de castanho). Outros curtentes, como outros metais, taninos sintéticos e aldeídos também são empregados em menores proporções.

2.2.3. Acabamento molhado

O couro curtido wet-blue passa por enxugamento por meio de operação mecânica que visa eliminar o excesso de líquido para facilitar o rebaixamento, quando a espessura do couro é ajustada de forma homogênea de acordo com as especificações de espessura do produto. O processo de acabamento molhado, realizado em fulões, consiste nas etapas de desacidulação, recurtimento, tingimento, engraxe e lavagens. Eventualmente, um banho de recromagem é empregado logo no início do processo de acabamento molhado, com o objetivo de homogeneizar couros wet-blue de diferentes origens, ou diferentes lotes de produção (MOREIRA, 2016).

A desacidulação ajusta o pH do couro wet-blue, que encontra-se próximo de 4,0, elevando para valores entre 5,0 e 6,5, para possibilitar a difusão (penetração para o interior, atravessamento) dos produtos químicos de acabamento molhado (FUCK *et al.*, 2018). A desacidulação é seguida pelo recurtimento que tem por objetivo conferir propriedades específicas e melhorar o desempenho do couro. Essas alterações incluem propriedades de toque, propriedades químicas e físicas, e de aptidão para a aplicação de diferentes tipos de acabamento associadas a aparência do couro (COOPER *et al.*, 2014). O recurtimento requer o emprego de diferentes tipos de produtos químicos recurtentes que visam complementar as propriedades necessárias para o produto final.

O tingimento é a etapa de coloração do material, que visa conferir as características sensoriais do produto final, como tonalidade, intensidade, penetração e uniformidade da cor. O engraxe geralmente ocorre após a etapa de tingimento, ou em conjunto, no mesmo banho. Neste processo, óleos são utilizados na forma de emulsões aquosas. É necessário selecionar óleos com tamanho molecular apropriado para obter a deposição correta na estrutura dérmica (GUTTERRES e MANCOPES, 2013). O engraxe influencia algumas características do couro, como resistência, impermeabilidade, maciez, flexibilidade, toque e elasticidade.

2.2.4. Secagem e pré-acabamento

Após as etapas químicas de acabamento molhado, o couro passa por operações de secagem, que consistem em etapas mecânicas que visam remover a água presente no couro de aproximadamente 60% para até 18%. O couro também passa por operações de pré-acabamento de amaciamento mecânico, estiramento (para aumento de área), aplicação de stuco, lixamento, entre outras.

2.2.5. Acabamento final

O acabamento final consiste na aplicação sobre a superfície do couro de uma série de camadas sucessivas de misturas à base de resinas e pigmentos para garantir a aparência final e propriedades de resistência apropriadas no couro acabado (WINTER *et al.*, 2018). Esta etapa propicia uma ampla gama de artigos diferenciados em função de requisitos de qualidade, de design e moda em couros para os diversos usos (moveleiro, automotivo, calçadista, vestuário, e artefatos diversos).

2.3. Produtos químicos de acabamento molhado

As classes de produtos químicos utilizados em formulações de acabamento molhado do couro são detalhadas a seguir.

2.3.1. Desacidulantes

Desacidulantes como o bicarbonato de sódio, carbonato de sódio e bicarbonato de amônio são utilizados para elevar o pH do couro. Sais mascarantes, como o formiato de sódio e de cálcio e desacidulantes recurtentes também são aplicados ao couro na etapa de desacidulação. O bicaronato de sódio é um desacidulante que, na concentração 1:10, confere um pH 8,0 (COVINGTON, 2011). A desacidulação somente com bicarbonato ou carbonato tende a ser superficial, já que os ânions logo se fixam nas camadas externas do couro, que se encontra com caráter catiônico, impedindo sua ação em profundidade.

O formiato de sódio e de cálcio são classificados como sais mascarantes, que na presença de íons H^+ formam o ácido fórmico, que por ser fraco, encontra-se em grande parte sem ionizar. Quando o formiato entra em contato com o ácido forma um tampão com pH em torno de 4,5 (MOREIRA e TEIXEIRA, 2003).

Os sais de taninos sintéticos também possuem poder suave de neutralização, alguns apresentam efeito complexante. Os desacidulantes recurtentes apresentam hidrólise alcalina ou atuam misturados com produtos alcalinos. Seu ânion é capaz de unir-se ao colágeno modificando com isto o seu ponto isoelétrico (MOREIRA e TEIXEIRA, 2003).

2.3.2. Recurtentes

Os recurtentes químicos modificam as características do couro ao cromo de acordo com o artigo a ser produzido. As características conferidas por diferentes recurtentes são complementares, de modo que a combinação de produtos recurtentes tem sido o caminho utilizado para obter o couro com as características pretendidas (MOREIRA, 2016). Entre os recurtentes estão os taninos vegetais, taninos sintéticos e as resinas. Com o uso de taninos vegetais obtêm-se couros cheios, com decréscimo nas características de elasticidade, alongamento e resistência à luz (MOREIRA e TEIXEIRA, 2003). Os taninos vegetais são moléculas grandes, com peso molecular compreendido entre 500 e 30.000 Da. No entanto, nem todos os taninos são úteis para o curtimento, apenas aqueles com peso molecular inferior a 3.000 Da são eficientes na fabricação de couro, pois grandes moléculas são incapazes de penetrar na estrutura de fibras da pele e tendem a ser insolúveis em água (FALCÃO e ARAÚJO, 2018). Os taninos vegetais são classificados em hidrolisáveis ou condensados. Os taninos hidrolisáveis são sub-divididos em galotaninos e taninos elágicos. Galotaninos são formados por glicose e poliésteres de ácido gálico, liberando ácido gálico quando hidrolisados. Já os taninos elágicos são caracterizados por glicose esterificada com pelo menos uma unidade de ácido hexahidroxidifenil, que é formada pelo acoplamento oxidativo de duas unidades de ácido gálico (AUAD *et al.*, 2019).

Por outro lado, outras misturas polifenólicas presentes nas plantas não sofrem hidrólise, sendo chamadas taninos condensados ou proantocianidinas. São oligômeros ou polímeros da estrutura básica do flavan-3-ol: catequina, epicatequina, galocatequina, epigalocatequina e galato de epigalocatequina (KOLECKAR *et al.*, 2008).

Os taninos sintéticos (sintanos), são tipicamente aromáticos, com grupos sulfônicos e hidroxila (COVINGTON, 2011). Os sintanos são utilizados industrialmente para couros claros, com melhor estabilidade à luz (GIOVANDO *et al.*, 2009). A maioria dos sintanos é fabricada a partir de substâncias aromáticas, por exemplo, cresóis, fenóis e naftaleno (THANKAPPAN *et al.*, 2015), que são sulfonados com ácido sulfúrico e condensados com formaldeído (HEIDEMANN, 1993). Os compostos naftaleno-sulfônicos condensados com aldeídos possuem características de agentes dispersantes e são empregados como auxiliares de dispersão para taninos vegetais ou corantes. Quando aplicados como auxiliares de tingimento, estes compostos competem com os corantes por sítios de ligação, diminuindo a reatividade e aumentando a uniformidade do tingimento. Quando condensados com outros compostos fenólicos, como a dihidroxi-difenil-sulfona, adquirem caráter curtente e então são empregados como recurtentes (COVINGTON, 2011 e HEIDEMANN, 1993).

As resinas recurtentes apresentam indicações variadas e crescentes de uso, sendo sua principal função dar enchimento às partes flácidas do couro. Entre as resinas destacam-se as acrílicas, as aminoplásticas e as estireno-maleicas (MOREIRA, 2016). As resinas acrílicas são polímeros derivados do ácido acrílico e metacrílico, elas não possuem capacidade curtente e demonstram efeito mínimo no aumento da temperatura de retração. As resinas são agentes aniônicos, interagindo com o couro curtido ao cromo na sua forma catiônica (HEIDEMANN, 1993). Com o emprego das resinas acrílicas se conseguem couros sólidos à luz, enchimento, maciez, aptidão para o lixamento e flor lisa (MOREIRA e TEIXEIRA, 2003).

Resinas de base nitrogenada, como as de ureia formaldeído e melamina formaldeído, apresentam boa estabilidade à oxidação e boa ação de preenchimento. Em geral, as amino resinas são sintetizadas usando matérias-primas como melamina, ureia, dicianodiamida, tioureia e formaldeído (SALEEM *et al.*, 2013). As resinas estireno-maleicas são produtos resultantes da polimerização em meio solvente de anidrido maleico e estireno (COVINGTON, 2011).

2.3.3. Corantes

Uma molécula de corante é formada por um grupo cromóforo e um grupo auxócromo. Os grupos cromóforos conferem cor, pois são capazes de absorver a luz na região visível (grupos nitro, azo e quinóides, por exemplo), enquanto os grupos auxócromos são responsáveis pela fixação do corante no couro (BAFANA *et al.*, 2011). Os principais corantes utilizados na indústria do couro podem ser classificados como ácidos, básicos ou diretos, de acordo com a forma de fixação destes ao couro (MOREIRA e TEIXEIRA, 2003).

Os corantes ácidos possuem carga aniônica e tem como característica principal ter um bom atravessamento no couro. Os corantes ácidos empregados na indústria de couro são geralmente azoicos, triarilmetanos ou antraquinônicos, associados a complexos metálicos (PANDI *et al.*, 2019). Os corantes azoicos representam mais de 50% de todos os corantes comerciais utilizados (SINGHA *et al.*, 2019), devido ao seu amplo espectro de tons, maior brilho, intensidade e por conferirem boa uniformidade e estabilidade à cor do produto. Os corantes azoicos possuem grupo cromóforo tipo azo (−N=N−) ligado, geralmente, a radicais fenil e naftil, que, por sua vez, estão ligados em diferentes combinações de grupos funcionais, como amino (NH_2), cloro (Cl), hidroxila (OH), metila (CH_3) e sais de sódio (SO_3Na) (ORTIZ-MONSALVE, 2019).

Os corantes básicos possuem característica catiônica e conferem boa intensidade da cor (MOREIRA e TEIXEIRA, 2003). Esses corantes são formados principalmente por derivados amino ($-NH_2$), frequentemente são da classe do triarilmetano ou xanteno. São comercializados em forma de cloretos, sulfatos ou oxalatos (FUCK, 2018).

Os corantes diretos possuem carga aniônica e proporcionam boa cobertura (MOREIRA e TEIXEIRA, 2003). Como os corantes ácidos, os corantes diretos são sais de ácidos sulfônicos, apresentando, porém, maior massa molecular. Depositam-se na superfície, têm bom poder de cobertura e menor estabilidade à luz que os corantes ácidos. Fixam-se ao couro diretamente, sem necessidade de adição de ácido (COVINGTON, 2011).

2.3.4. Agentes engraxantes

O engraxe consiste em um processo que promove a lubrificação da estrutura fibrosa, contribui com maior nível de maciez, impermeabilidade, resistência à luz e flexibilidade ao couro (LÜ *et al.*, 2011). Esta etapa é normalmente a última do acabamento molhado, podendo ser única, ou com emprego de óleos em diversos momentos como junto com o recurtimento, ou com o tingimento (MOREIRA e TEIXEIRA, 2003). Podem ser empregados óleos naturais (de origem animal ou vegetal) ou sintéticos. De uma maneira geral, os óleos de origem animal possuem boa ação lubrificante, os óleos vegetais geralmente possuem boa fixação, e os óleos sintéticos possuem qualidade constante, peso específico baixo e solidez à luz (SANTOS *et al.*, 2008 e ŻARŁOK *et al.*, 2014).

Os óleos naturais na sua forma original dificilmente são aplicados para o engraxe. Antes de sua aplicação no engraxe esses óleos são modificados para formarem uma emulsão aquosa. Os óleos emulsionáveis em água existem em duas categorias principais: sulfatados e sulfitados. Os sulfatados são óleos quimicamente modificados com ácido sulfúrico, o que regula a afinidade com as fibras curtidas (SANTOS *et al.*, 2008). Os sulfitados são obtidos através de oxidação, seguida de reação com soluções concentradas de bissulfito de sódio. Em uma primeira etapa, os óleos são oxidados, o que transforma a estrutura com ligas duplas em uma estrutura epóxi. Na segunda etapa, os óleos reagem com uma solução concentrada de bissulfito de sódio, sendo, assim, transformados em óleos sulfonados. Os óleos sulfitados possuem essa denominação por serem obtidos através do processo de sulfitação, apesar de apresentarem estrutura sulfonada (COVINGTON, 2011). Esses óleos diferenciam-se dos sulfatados por apresentar partículas menores e maior poder de ligação (SANTOS *et al.*, 2008). Tanto os óleos sulfatados quanto os sulfitados são aniônicos e se ligam aos grupos amino do colágeno (SANTOS e GUTTERRES, 2007). No processo de obtenção dos óleos, agentes emulsificantes também são adicionados para aumentar a estabilidade dos óleos nas emulsões aquosas (LYU *et al.*, 2016).

Agentes de engraxe aniônicos são os comumente empregados por se fixarem quimicamente em couros curtido a cromo, que possuem caráter catiônico (SIVAKUMAR *et al.*, 2008). A emulsão também pode ser obtida pela simples adição de agentes surfactantes ao óleo (NKWOR e UKOHA, 2020). É importante que as gotas de óleo na água permaneçam como emulsão até penetrarem no couro e não se separem como gotas grandes ou como uma camada de óleo, que não penetraria na fibra do couro e resultaria em uma camada oleosa superficial (SANTOS e GUTTERRES, 2007).

2.4. Produção mais limpa aplicada ao acabamento molhado

Para reduzir os impactos ambientais da produção do couro, estudos vem buscando a aplicação de produtos e processos mais limpos neste processo. A Tabela 2.1 apresenta produtos e processos mais limpos propostos para as etapas do acabamento molhado. Entre as alternativas avaliadas está a substituição de taninos sintéticos por recurtentes que apresentam maior biodegradabilidade (SELVARAJU *et al*., 2017), menor toxicidade (LIU *et al.*, 2020), e menor carga poluente (WANG *et al.*, 2019) nos efluentes. Também foram desenvolvidos e testados corantes naturais em substituição aos corantes sintéticos (FUCK *et al.*, 2018; PRIYA *et al.*, 2016; SUDHA *et al.*, 2016), evitando o uso de produtos químicos perigosos, e um óleo essencial de cravo foi testado quanto às suas características biocidas no couro como uma alternativa aos biocidas sintéticos (KOPP *et al.*, 2020). A produção de engraxantes menos poluentes também foi avaliada. Emulsões de óleo em água foram obtidas aplicando-se nano-TiO_2 (LYU *et al.*,

2016) e ultrassom (SIVAKUMAR *et al.*, 2008), evitando o consumo de ácido sulfúrico (para a sulfatação) e agentes surfactantes no processo de obtenção destes produtos químicos.

Durante as etapas químicas de processamento do couro, a transferência de produtos químicos do banho para o interior da estrutura de colágeno é controlada pelo processo de difusão (KANAGARAJ e PANDA, 2011). Desta forma, à medida que os produtos químicos penetram e se ligam à estrutura do couro, o gradiente de concentração diminui até alcançar a concentração de equilíbrio. Alguns estudos buscaram reduzir as concentrações de produtos químicos que permanecem nos banhos ao final do processamento do couro. Estes estudos estão focados na otimização da oferta de produtos químicos (GUTTERRES, 2003; ZHANG *et al.*, 2017) e na maximização da exaustão dos banhos de processo através da otimização de parâmetros como pH, temperatura e duração dos banhos (AYYASAMY *et al.*, 2005; GUTTERRES e SANTOS, 2009; HAROUN, 2005; KANAGARAJ *et al.*, 2016). Os ganhos ambientais relacionados à aplicação destes produtos e processos mais limpos estão principalmente relacionados à redução da carga poluente dos efluentes líquidos gerados no processo.

Tabela 2.1: Produção mais limpa aplicada ao acabamento molhado do couro.

Etapa / produto químico	Produto/processo proposto	Ganho ambiental	Autor
Recurtimento	Substituição de taninos sintéticos por compósito biopolimérico contendo hidroxiapatita inorgânica e copolímero de poli(ácido lático-co-ácido glicólico)	Efluente com maior biodegradabilidade	SELVARAJU *et al.* (2017)
	Redução na oferta de sal de cromo no recurtimento com ajuste das condições operacionais	Redução na concentração de cromo (III) nos efluentes (84,2%)	ZHANG *et al.* (2017)
	Substituição de recurtente sintético a base de glutaraldeído por colágeno modificado com extrato de valonia oxidado	Recurtimento sem uso de compostos tóxicos e reaproveitamento de colágeno do farelo de couro wet-blue	LIU *et al.* (2020)
	Substituição de recurtente comercial por Poliuretano anfotérico enxertado com ácido cromotrópico	Redução nas concentrações de DBO (31,82%), SDT (9,9%) e sólidos suspensos totais (30,8%)	WANG *et al.* (2019)
Biocida	Aplicação de óleo essencial de cravo livre e encapsulado	Substituição de biocidas sintéticos por biocidas naturais	KOPP *et al.* (2020)

Tabela 2.1: Produção mais limpa aplicada ao acabamento molhado do couro (continuação).

Etapa / produto químico	Produto/processo proposto	Ganho ambiental	Autor
Tingimento	Substituição de corante sintético por proteína fluorescente verde	Efluente com menor toxicidade e maior biodegradabilidade	PRIYA *et al*. (2016)
	Ajuste de condições de processo (pH, temperatura e tempo) e uso de auxiliar de tingimento (copolímero de hidrolisado de aparas com amido e álcool polivinílico) para aumentar a exaustão do corante	Redução nas cargas de DBO (44 a 53%) e DQO (60 a 67%) nos efluentes (maior exaustão do banho de tingimento)	KANAGARAJ *et al.* (2016)
	Aplicação de extrato do fungo *Monascus purpureus*	Substituição de corantes sintéticos por corantes naturais, sem uso de produtos químicos perigosos durante a produção	FUCK *et al.* (2018)
	Aplicação de corante obtido a partir do fungo *Penicillium minioluteum*	Substituição de corantes sintéticos por corantes naturais	SUDHA *et al.* (2016)
Engraxe	Substituição do óleo de rícino sulfatado por óleo de rícino com nano-TiO_2	Efluente com maior biodegradabilidade	LYU *et al*. (2016)
	Substituição da gordura animal sulfatada por emulsão de gordura animal em água assistida por ultrassom	Redução da poluição química, eliminando o processo de sulfatação	SIVAKUMAR *et al.* (2012)
	Determinação da oferta necessária de engraxante	Minimização de contaminantes nos efluentes	GUTTERRES (2003)
	Ajuste de condições de processo (pH, temperatura e tempo) para aumentar a exaustão do engraxante	Redução na concentração de óleo e DQO nos efluentes	GUTTERRES e SANTOS (2009)
Acabamento molhado	Processo integrado de recromagem, neutralização e pós-curtimento	Redução nas concentrações de DQO (28%), sólidos totais (34%) e cromo (72%) nos efluentes líquidos. Redução no consumo de água (73%) e geração de efluentes (78%).	AYYASAMY *et al.* (2005)
	Aplicação do recurtimento, engraxe e tingimento em banho único	Redução no consumo de corante na etapa de tingimento	HAROUN (2005)

Fonte: autor, 2021.

O desenvolvimento de uma produção mais limpa também vem sendo pesquisado pela indústria do couro. Um exemplo do envolvimento da indústria neste tema é o conceito de "Kind Leather", desenvolvido pela empresa JBS couros. Neste sistema de produção, apenas as áreas mais desejáveis da pele são utilizadas para a produção de couro. As demais regiões da pele são removidas antes do seu processamento e empregadas como matéria-prima em outras indústrias, como a de cosméticos e produtos farmacêuticos. Como resultados deste processo, a empresa obteve 46% de redução no consumo de água, 28% de redução no consumo de produtos químicos de acabamento e 20% de redução no consumo energético (JBS, 2021).

Para contribuir com uma indústria do couro mais sustentável, a presente tese avaliou o impacto dos produtos químicos utilizados no processo de acabamento molhado do couro nos principais parâmetros de qualidade dos efluentes líquidos gerados nesta etapa de processamento. Nos Capítulos 3, 4, 5 e 6, expostos a seguir, são apresentados os artigos que compõem a presente tese, em língua inglesa. Os artigos são intitulados:

- *Environmental Assessment of Water, Chemicals and Effluents in Leather Post-tanning Process: a Review*;
- *Impact of Post-tanning Chemicals on the Pollution Load of Tannery Wastewater;*
- *Reducing Pollution Load of Chemicals in Wastewater of Leather Post-Tanning*;
- *Post-tanning Wastewater Treatment Technologies: a Review.*

Capítulo 3

Environmental Assessment of Water, Chemicals and Effluent in Leather Post-tanning Process: a Review

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Neste artigo foram analisadas 43 formulações de acabamento molhado publicadas em artigos científicos e disponibilizadas por uma indústria química e um curtume. O artigo está publicado no periódico *Environmental Impact Assessment Review*. Relatório Qualis Capes Engenharias II (2019): A1. Fator de Impacto: 4,135. DOI: https://doi.org/10.1016/j.eiar.2021.106597

Highlights:

- Post-tanning plays an important role in overall environmental impact of a tannery.
- Results showed an average chemical consumption of 360.2 kg/t of leather processed.
- The average water demand of post-tanning is 8.6 m^3/t of leather processed.
- Guideline upper limits for chemical and water consumption were assessed.
- Raw wastewater is poorly biodegradable, with high concentration of salts.

Abstract:

The leather industry has significant consumption of water and chemicals and generates liquid effluents with a high pollution load. This study aims to contribute to the advance of liquid effluents, water, and chemicals management in tanneries since the assessment of these environmental issues for each step of the post-tanning process remains unknown. Forty-three post-tanning formulations were obtained from scientific papers, catalogs from chemical manufacturers and tanneries, and their data were analyzed. Results showed an average chemical consumption of 360.2 kilograms per ton of shaved leather. Retanning and fatliquoring steps are the largest chemical consumers. The average water demand of this process is 8.6 cubic meters per ton of shaved leather, with washing responsible for the highest consumption. The raw wastewater is poorly biodegradable, with high conductivity and elevated concentration of salts. The results obtained in this study contribute to reduce the environmental impacts of leather post-tanning, guiding future studies aiming to optimize this process.

Keywords: Leather chemicals; Water Consumption; Wastewater; Leather process; Post-tanning.

3.1. Introduction

Leather industry and its products play a relevant role in the world's economy, with a global trade value of approximately US$100 billion per year (UNIDO, 2010). Currently, leather industry is especially important in the economy of several developing countries (Bharagava and Mishra, 2018), having Brazil, China and India the largest cattle herds in the world (ABQTIC, 2018).

Leather manufacturing is a chemical process applied on a natural biological matrix (Teng et al., 2017) that uses a huge quantity of inorganic and organic chemicals, besides a great amount of water (Lofrano et al., 2013; Ritterbusch et al., 2019). Approximately 130 different types of chemicals are used for the complete processing of leather (Dandira et al., 2012). Solid and liquid wastes are generated from this process and need to be discharged into the environment after treatment. Some of the agencies responsible for the environmental management consider it as one of the 10 most harmful industrial effluents to the environment (Kumar et al., 2008).

The transformation of a raw hide into finished leather involves a set of steps gathered into: beamhouse, tanning, post-tanning and finishing processes. Current literature has important description of researches about the control and reduction of the environmental impact of beamhouse and tanning processes. This does not occur, with the same frequency, for the post-tanning and finishing of leather (Moreira et al., 2019; Wu et al., 2018). The number of contributions from 1995 to July 2019 in Scopus database counted 1,116 papers (66%) related to environmental issues of tanning step, 388 papers (23%) related to beamhouse, 141 papers (8%) related to post-tanning and 44 papers (3%) related to finishing. Thus, there is a lack of information about post-tanning environmental impact. Global mass balances have already been carried out at the post-tanning stage, indicating that it generates around 38% of the wastewater in a complete leather manufacturing industry (Cassano et al., 2001) and is responsible for approximately 30% of the chemicals consumed (Rivela et al., 2004) however, the stratification of water and chemical inputs and effluent output for each step of post-tanning still needs to be evaluated. In addition, existing papers are often isolated cases of a particular tannery or processing technology. There is no study comparing post-tanning chemicals and water consumption and its impacts with a wide scope.

Tanneries can be divided into (i) integrated tanneries (which process green or preserved hide to obtain finished leather), (ii) beamhouse tanneries (which process green or preserved hide to obtain intermediate materials (e.g. wet-blue leather)), and (iii) post-tanning and finishing tanneries (which process wet-blue leather to obtain finished leather). Thus, post-tanning effluents can be released to wastewater treatment plants either mixed with effluents from different batch processes from an integrated tannery or separately, in post-tanning and finishing tanneries. Besides, in some countries, tanneries are located in clusters where effluents are mixed and sent to common effluent treatment plants (CETPs). Tannery clusters in Italy (Santa Croce, Cuoio Depur and Fuccechino, Arzignano, and Solofra) (Buljan and Kral, 2011), Thailand (Samutprakarn province) (CPCB, 2011), and India (where approximately 85 % of tanneries, especially the small scale, use CETPs) (Pathe et al., 2004) are examples of CETPs application. However, in Brazil, there are 310 tanning industries (CICB, 2020) predominating the use of individual effluent treatment plants. Besides, in the southern region of Brazil (where this study was conducted), post-tanning and finishing tanneries predominate (Nunes et al., 2019), justifying the investigation of the post-tanning stage specifically. Large and medium scale tanneries in India also often apply individual wastewater treatment, with nearly 200 individual tannery effluent treatment plants in this country (Sabumon, 2016). Either way, whether the post-tanning effluent alone or mixed with other tannery effluents, understanding how the chemicals used in post-tanning contribute to the pollution load of tannery effluents is relevant to allow pollution minimization and appropriate wastewater treatment.

Therefore, this paper aims to update and discuss the available data on the main environmental issues related to the leather post-tanning process: chemical consumption, water consumption and the contamination parameters and loads of the generated raw wastewater. Possible correlations between environmental issues and leather articles, raw materials and geographic regions were evaluated by this study. The study was conducted through a survey of scientific articles, chemical manufacturers' catalogs and formulations supplied by local tanneries. Data on the consumption of chemicals and water in leather post-tanning formulations were analyzed as well as the characterization of the raw wastewater generated. Thus, this appears as a way to respond a trend assessment of the current situation of the leather sector, providing an accurate database for an environmental leather guide in post tanning processes and the development of a cleaner leather production.

3.2. Methodology

This research was performed following the steps showed in Figure 3.1**:** and detailed below.

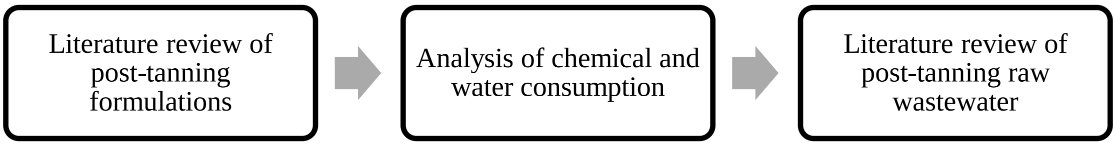

Figure 3.1: The study's methodology stages.

3.2.1. Post-tanning formulation

A literature review of post-tanning formulations published in scientific papers, technical catalogs from chemical manufacturers and formulations provided by local tanneries from southern Brazil was performed. Manuscripts containing post-tanning formulations were searched on Capes database, which includes repositories such as Scopus, Springer, EBSCO and others. Papers published in leather association journals (American Leather Chemists Association and Society of Leather Technologists and Chemists) from 2015 to 2019 have also been consulted.

Forty-three formulations were compiled. From this survey, information on chemical consumption per ton of processed leather (shaved weight), as well as their specific consumption at each processing step were obtained. The number of different chemicals used per formulation was also compiled. Besides, post-tanning water consumption has been verified. Data were organized according to the processing step, type of leather good and raw hide/skin processed. Data were analyzed by one-way Analysis of Variance (ANOVA) followed by Tukey post hoc, and were considered significant when $p < 0.05$. All statistical analyzes were performed using GraphPad Prism software.

3.2.2. Raw wastewater characterization

Physicochemical characterization of liquid effluents from different steps of leather post-tanning process was searched from scientific publications to evaluate the organic and inorganic loads of raw wastewater.

3.3. Theory

The transformation of raw hides and skins into finished leather involves the submission of the hides through a series of physical, physico-chemical and chemical operations, shown schematically in

Figure 3.2. Physico-chemical and chemical operations are performed in aqueous medium (wet operations) using rotating drums and produce liquid effluents. Washings are also performed during wet operations, consuming water and producing additional liquid effluents.

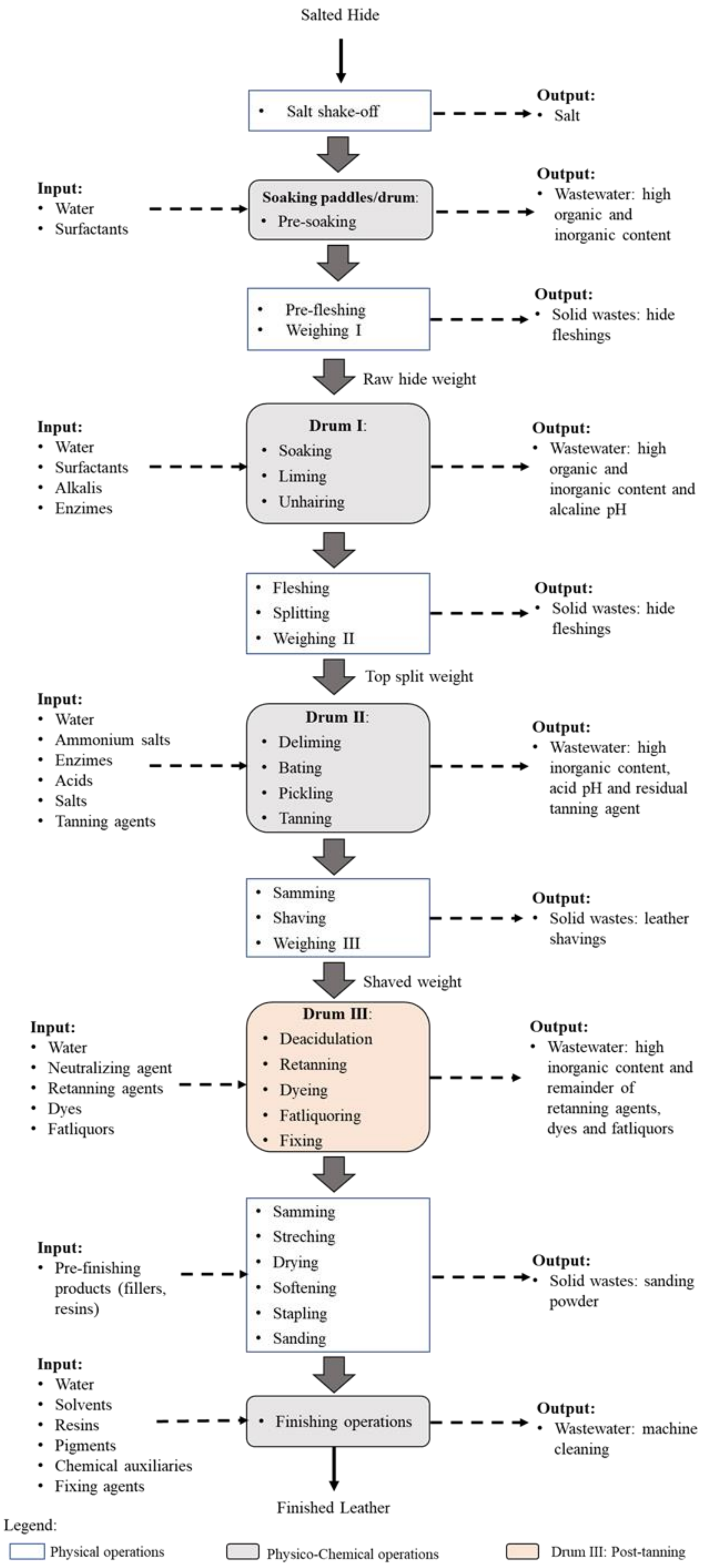

Figure 3.2: Leather processing steps and their respective inputs and outputs.

The processing steps of leather are divided into beamhouse (salt shake-off to bating), tanning (pickling and tanning), post-tanning (deacidulation to fixing), pre-finishing (samming to sanding) and finishing operations. Since this study is focused on chemical and water consumption and wastewater quality, which are related to the physico-chemical operations performed in drums, a description of these processes is presented below.

- Soaking paddle/mixer/drum: when the salted hide is processed, the removal of salt that started in the salt shake-off should continue on properly soaking equipment, such as paddles, mixers or drums. At this stage, the hide rehydration process begins, in contact with water and surfactants. If the green hide is processed, pre-soaking is performed only for washing.
- Drum I: the purpose of this step is to clean and remove all those components of the hides/skins that will not constitute the final product (finished leather), such as globular proteins, salt, soluble substances in contact with water and surfactants, in addition to fats and hair. Soaking cleans and rehydrates the hides in order to interrupt conservation. The fibrous structure of the hide is opened in liming step for cleaning and degreasing (by swelling). The keratin from the hair and epidermis is also removed from the hide by the action of reducing agents, usually sodium sulfide. Chemicals and water are added to this process stage based on the raw hide weight. Beamhouse is responsible (Buljan and Král, 2018) for 85% of Total Kjeldhal Nitrogen (TKN) and 75% of Biochemical Oxygen Demand (BOD) and Chemical Oxygen demand (COD) of the total emission load in raw wastewater of a complete tannery.
- Drum II: This operation removes alkaline substances introduced during the liming step (drum I) by applying washings and using deliming agents, reversing the swelling of the hide. By the bating, enzymes are added to remove residues and produce a clean hide. About 80% - 90% (Bacardit et al., 2015; Gutterres and Mella, 2014) of all leather in the world are tanned with chrome. Pickling prepares collagen for internal diffusion of chromium by acidification of the hide to pH 2.5 – 3.0 in a saline solution (Fuck et al., 2011; Gutterres and Mella, 2014). For tanning, the basic chromium salt is added to the pickled hide in drum II, keeping stirring for 4 - 6 h for its absorption. To promote the final reaction of chromium to collagen the pH of the bath is increased to 3.8 - 4.0 with basifying agents as sodium basic salts or magnesium oxide and temperature elevation to around 50ºC. During chromium fixation the collagen is deprotonated and

the basicity of the chromium sulfate is increased to establish the binding (crosslinking) of the chromium complex with the protein carboxyl groups. Vegetable tannins are also used as tanning agents, providing leather with different characteristics (less softness and brown tones). Other tanners, such as other metals, synthetic tannins, and aldehydes are also used in smaller proportions. Chemicals and water are added to this process based on the hide top split weight. The tanning step is responsible for 70% of chromium and 52% of sulfate ion emission load in a complete leather process (Buljan et al., 2016).

- Drum III (Post-tanning): post-tanning consists of deacidulation, retanning, dyeing, fatliquoring and fixing processing steps. Post-tanning provides texture and structural properties to the leather, touch and color qualities, chemical, physico-mechanical and fastness properties. Chemicals and water are added to this process based on weight after shaving. The outputs from post-tanning steps consists mainly of high COD from incomplete exhaustions of retanning and fatliquoring agents (15% of total COD and BOD total pollution load of a complete leather process). Emissions of inorganic salts present in syntans and chrome tanning agents (from rechroming or leaching of chromium from the main tanning process) accounts for 32% of sulfate ion and 17% of dissolved solids total emission load in a complete leather process (Buljan and Král, 2018).

3.4. Results and Discussion

3.4.1. Post-tanning formulation

Total chemical consumption, the number of different chemicals used in each formulation and total water consumption are shown in Table 3.1. Complete data are presented in the supplementary material, including total chemical consumption and consumption per step (kilograms of chemicals per ton of shaved leather), total water consumption and water consumption per step (cubic meters of water per ton of shaved leather). For a detailed discussion, the raw material, leather assortment, wet-end processing steps, weight basis and manuscript region are also described in the supplementary material. The weight basis used for post-tanning formulations is typically shaved weight. 21 out of 43 formulations (49%) explicitly indicated the use of shaved weight as the basis for water and chemical input. 6 out of 43 formulations (14%) indicated the use of wet-blue weight, without making it clear whether if it was shaved or not, and 16 out of 43 formulations (37%) did not explicitly indicate the weight basis for water and chemical input. The lack of information regarding weight basis in manuscripts makes it difficult to compare the use of chemicals and water, and this information should be further detailed by studies published in the field of leather production. For comparison purposes, this study considers that the weight bases of the formulations are the shaved weight of the leather.

A search for the affiliations of the studies that were the basis of this analysis indicated that 30% of the formulations are from studies carried out by the leather or chemical industry associated with universities. This data shows the relevant participation of manufacturers in the evaluated formulations. 44% of the studies were carried out exclusively by research institutes, 19% of the studies were carried out exclusively by universities, and 7% of formulations involve university and research institutes.

Table 3.1: Compilation of leather post-tanning formulations

Author	Chemicals (kg/t)	Number of chemicals	Water consumption (m³/t)
Alla et al., 2017	360	12	2**
Aravindhan et al., 2014	430	13	7
Bacardit et al., 2014	488	9	10
Bacardit et al., 2014	298	12	9.5
Bacardit et al., 2014	270	11	9.5
Bacardit et al., 2016	488	9	10
Bacardit et al., 2016	309	10	8.8
Bacardit et al., 2016	302	12	9.5
Bacardit et al., 2016	308	13	9
Bacardit et al., 2016	277	11	9.5
Başaran et al., 2008	106	8	9.5
Belay et al., 2019	501	19	10
Buljan et al., 2000	295	7	17
Gari et al., 2016	297	13	3.5
Gomes et al., 2016	284	9	15.5
Haroun, 2005	260	11	3
Haroun, 2005	262.5	11	3
Jayakumar et al., 2016	365	10	6.5
Ji-bo et al., 2018	246	7	20
Karthikeyan and Babu, 2017	410	14	2**
Lai et al., 2017	238	9	2**
Li et al., 2016	418	21	7.3
Local Tannery, 2019a	405.5	19	9.5
Local Tannery, 2019b	613	23	12.5
Lofrano et al., 2008	374.5	17	6
Long-Fang et al., 2017	293	8	12
Marsal et al., 2017	352	11	8.5
Mohammed et al., 2014	458	14	6.5
Mohammed et al., 2014	716	25	4.5
Ollé et al., 2016	500	11	7.1
Ortiz-Monsalve et al., 2019	284	10	12
Ramalingam and Rao, 2018	472	15	6.9
Ramalingam and Rao, 2018	532	15	7.4
Saravanabhavan et al., 2005	270	13	9.5
Sathish et al., 2013	325	11	5.85
Sathish et al., 2016	255	9	6.05
Sathish et al., 2017	370	11	1.6*
Sathish et al., 2017	365	11	1.6*
Sathish et al., 2017	315	12	4.8
Selvi et al., 2018	296	12	4.7
Seta, 2004	479.5	12	5.8
Seta, 2004b	375.5	14	5.8
Zhang et al., 2018	226	6	12.5

* Formulation does not inform water consumption of deacidulation and washing steps.

** Formulation does not inform water consumption of washings.

Total chemical consumption and consumption at each step of leather post-tanning stage are shown in Figure 3.3.

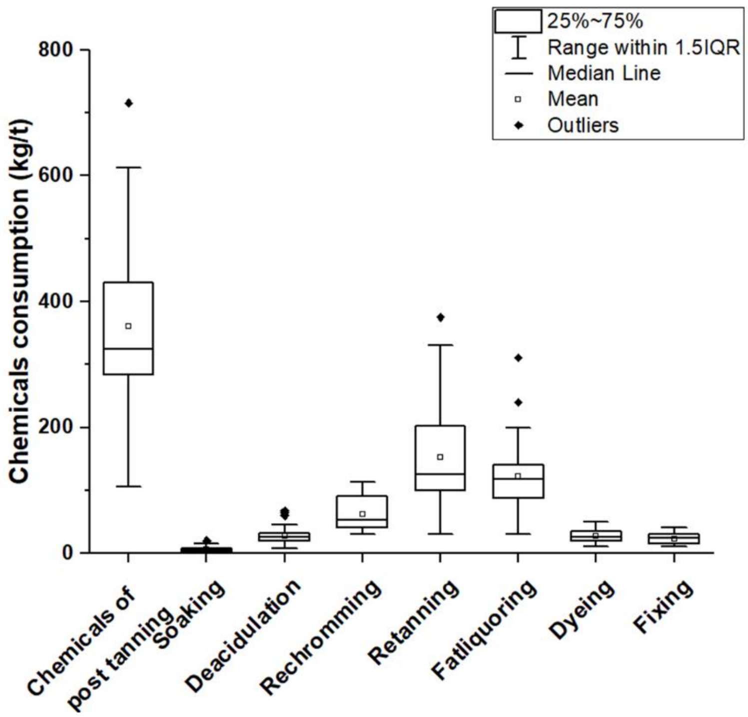

Figure 3.3: Chemical consumption per step of processing.

Average chemical consumption of 360.2 kg/t is observed for a complete post-tanning process, with a large variability (106 to 716 kg/t). Steps presented significantly different chemical consumption ($p<0.0001$). Retanning step requires the highest ($p<0.05$) average chemical consumption (152.2 kg/t, ranging from 30 to 375 kg/t), followed by fatliquoring (average consumption of 122 kg/t, ranging from 30 to 311 kg/t) ($p<0.05$). Therefore, for a cleaner post-tanning process, focus should be placed on evaluating and optimizing retanning and fatliquoring agents' consumption, since they represent the largest amounts of chemicals. On the other hand, wet-blue soaking demands the lowest chemical consumption, 6.6 kg/t on average, ranging from 2 to 20 kg/t.

Chemical consumption below 424 kg/t is found in 75% of the formulations (third quartile). Thus, the consumption of 424 kg of chemicals per ton of shaved leather should be an upper limit for post-tanning process. Processes that consume more than this amount of chemicals should reassess the production formulation to reduce chemical use. Among the formulations with chemical consumption above 424 kg/t, there is a predominance of studies focusing on technological development (seven studies are focused on technological development and two studies are focused on the environmental field). Thus, even if the focus of the study is on technological development, attention should be given to the consumption of chemicals to enable the development of more sustainable processes.

Figure 3.4 shows chemical consumption (kg/t) per leather destination (upholstery, shoe upper and garment leather (not including fur production)) and Figure 3.5 shows chemical consumption (kg/t) per raw material (bovine, sheep and goat).

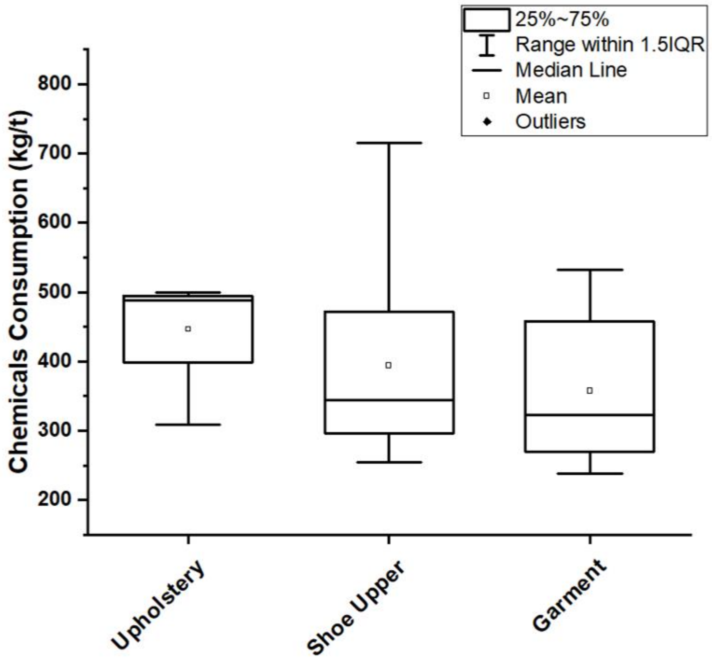

Figure 3.4: Chemical consumption per application.

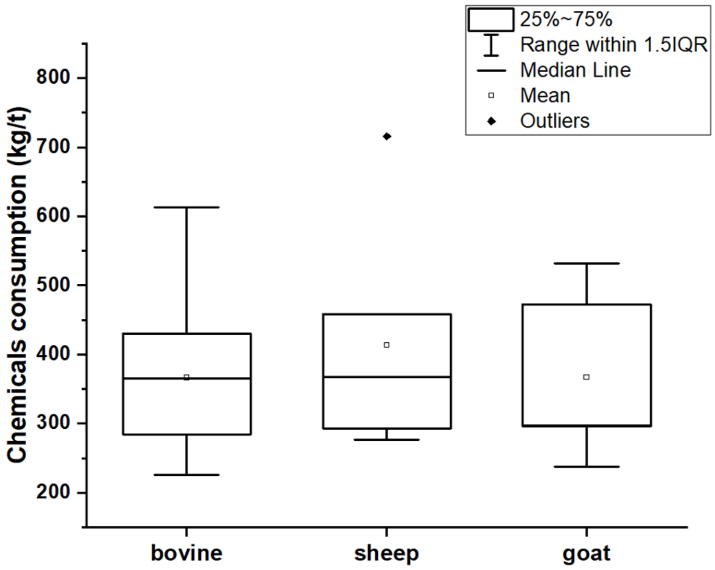

Figure 3.5: Chemical consumption per raw material.

Regarding the different articles produced, upholstery has the highest average chemical consumption (446.3 kg/t), followed by shoe upper (394.1 kg/t) and garment leather (357.5 kg/t), although there is no significant difference among them (p=0.5660). The higher chemical consumption in upholstery leather should be related to the restrictive properties required for this application, such as softness, tensile strength, low fogging and thermal resistance (Zhang and Wang, 2009). It is important to highlight that not all authors indicate which product will be obtained by the formulation. 19 out of the 43 compiled formulations (44%) do not indicate the expected application for the product obtained, reducing the quality of data for systemic literature reviews. Consumption of chemicals varied slightly when different raw materials were used (Figure 3.5). Average consumptions are all within the same range (366.5 kg/t for bovine, 413.2 kg/t for sheep and 367 kg/t for goat leather), without significant difference (p=0.07505).

Figure 3.6 shows the number of different chemicals used per formulation and per application, and Figure 3.7 shows the number of different chemicals used according to the raw material processed. Twelve chemicals are used per formulation, on average, ranging from 6 to 25 chemical products. Upholstery (10 chemical products), shoe upper (14 chemical products) and garment (12 chemical products) leather formulations are on a par with the average number of chemicals used, without significant difference (p=0.3261). The number of chemicals used by raw materials also does not vary significantly (p= 0.8209). Averages are between 12 and 13 chemicals per formulation.

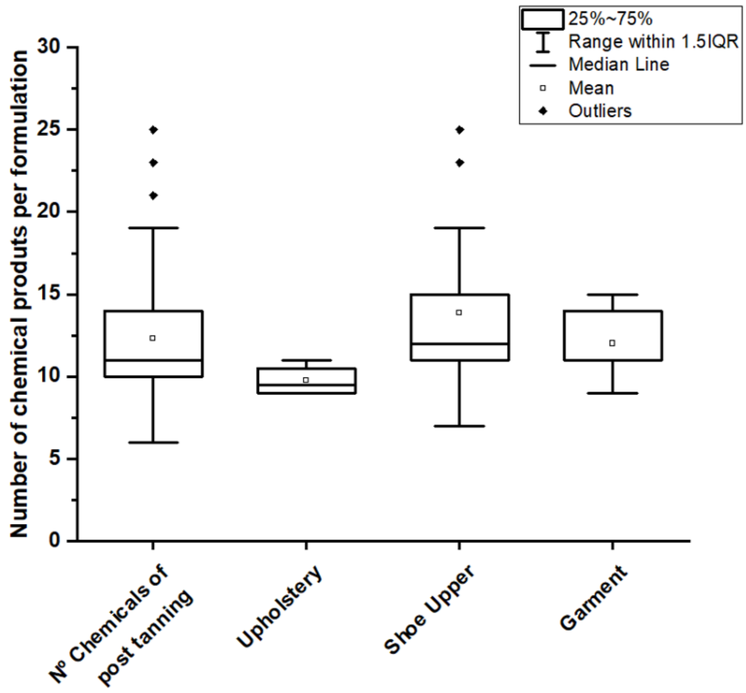

Figure 3.6: Number of chemical products used in post-tanning and per formulation.

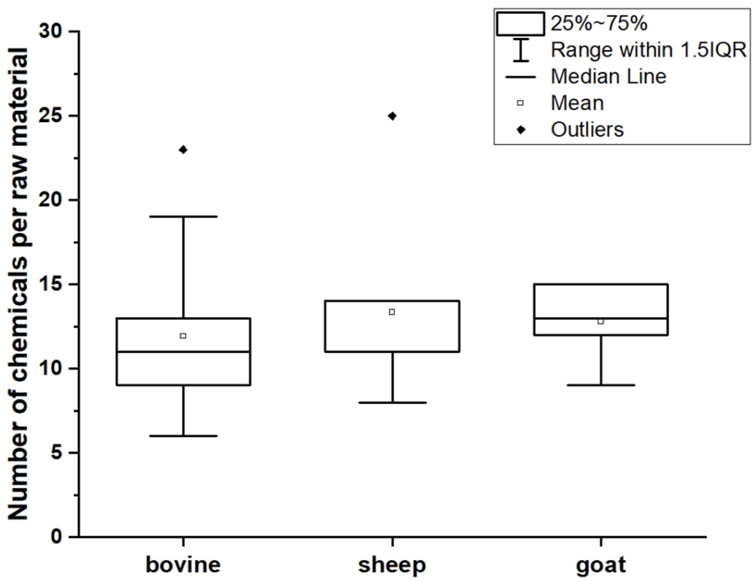

Figure 3.7: Number of chemical products per raw material.

Process water consumption by each processing step is shown in Figure 3.8. The average water consumption in post-tanning is 8.6 m³/t, ranging from 3 to 20 m³/t. Steps presented significantly different water consumption ($p<0.0001$). Washing is the operation that demands the largest ($p<0.01$) amount of water (4.5 m³/t on average) and has great variability in its consumption (1 to 14 m³/t). Thus, optimization of post-tanning water consumption should focus on the minimization of leather washings. Rechromming and deacidulation steps are the lowest water consumers, presenting an average consumption of 1.3 and 1.5 m³/t, respectively.

Water consumption between 6 and 10 m³/t is found in 50% of the formulations (first and third quartiles, respectively). This means that 50% of the formulations show water consumption within this range (central range), 25% of the formulations show water consumption below 6 m³/t, and 25% of the formulations show water consumption above 10 m³/t. Thus, the volume of 10 m³/t should be an upper limit for water consumption in the post-tanning process. This consumption range is similar to the technical guideline published by the International Union of Leather Technologists and Chemists Societies (IUE 6, 2018), which indicates water consumption of 4 to 8 m³/t for bovine leather production under good environmental practice conditions. Among the formulations with water consumption above 10 m^3/t, five studies are focused on environment and four on technological development. Thus, even studies focusing on the environment should consider reducing water consumption in the process.

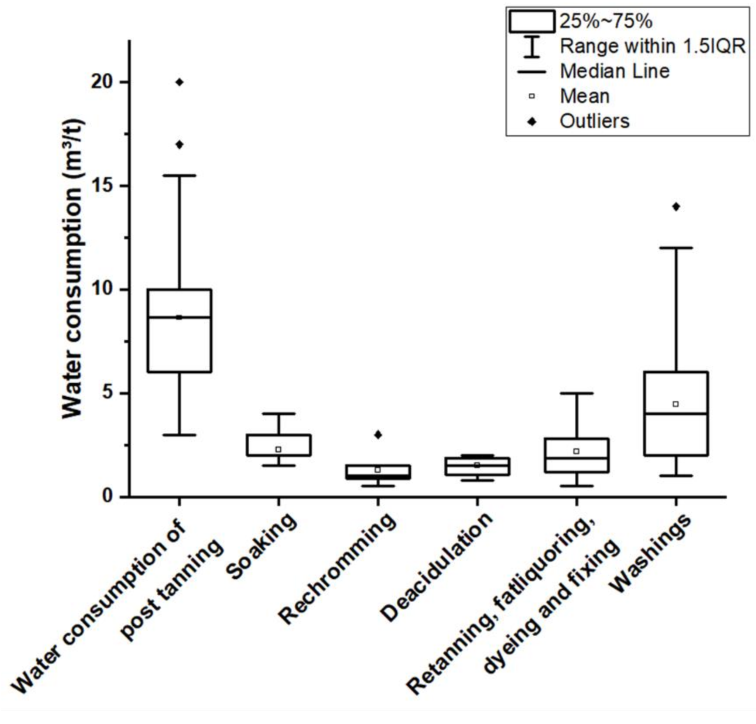

Figure 3.8: Water consumption per step of processing.

Figure 3.9 shows the water consumption according to the leather article produced and Figure 3.10 shows the water consumption according to the raw material processed. Regarding the different applications of leather (upholstery, shoe upper and garment), upholstery leather has the highest water consumption (9 m³/t), followed by garment (8.4

m³/t) and shoe upper leather (8.2 m³/t). The largest water consumption for upholstery leather is consistent with that observed for chemical consumption, although there is no significant difference among them (p=0.8547). Water demand for bovine leather has the highest average (10.6 m³/t), followed by sheep (8.1 m³/t) and goat leather (5.6 m³/t). The bovine hides have greater thickness compared to goat and sheep skins Gascon et al. (2017), thus the bovine leather requires greater amount of water and time for diffusion and penetration of the chemical products, although there is no significant difference among them (p=0.5660) due to the high dispersion of water consumption in the formulation assessed.

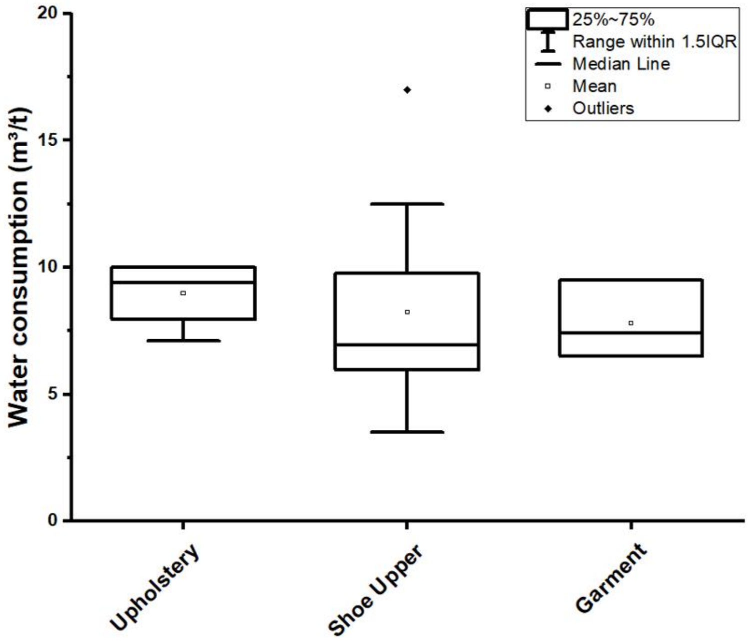

Figure 3.9: Water consumption per application.

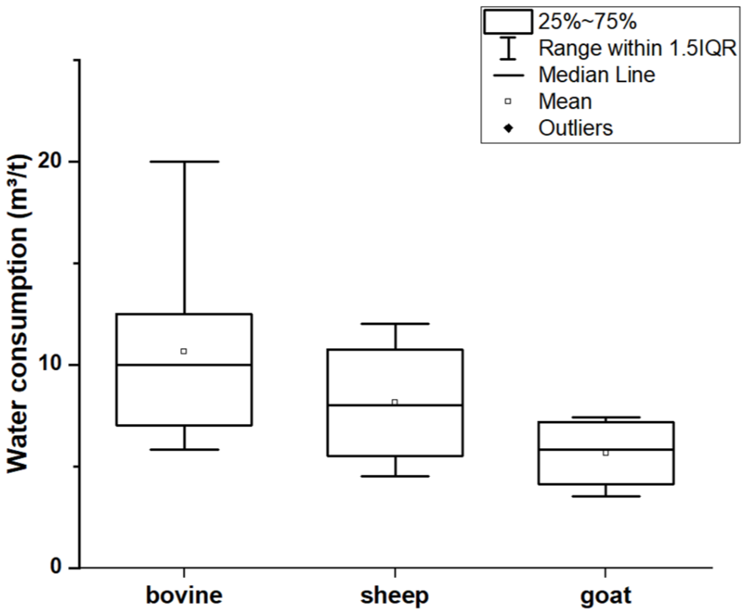

Figure 3.10: Water consumption per raw material.

Formulations according to the study focus and the geographical region of the reports are sorted in Figure 3.11. Among the formulations evaluated there is a greater interest of environmental studies in the European continent, while studies in the Asian continent are more focused on technological development compared to the environmental field. Fewer post-tanning formulations have been identified in South American and African publications, with South American studies focusing on the environment and African studies on technological and economic development.

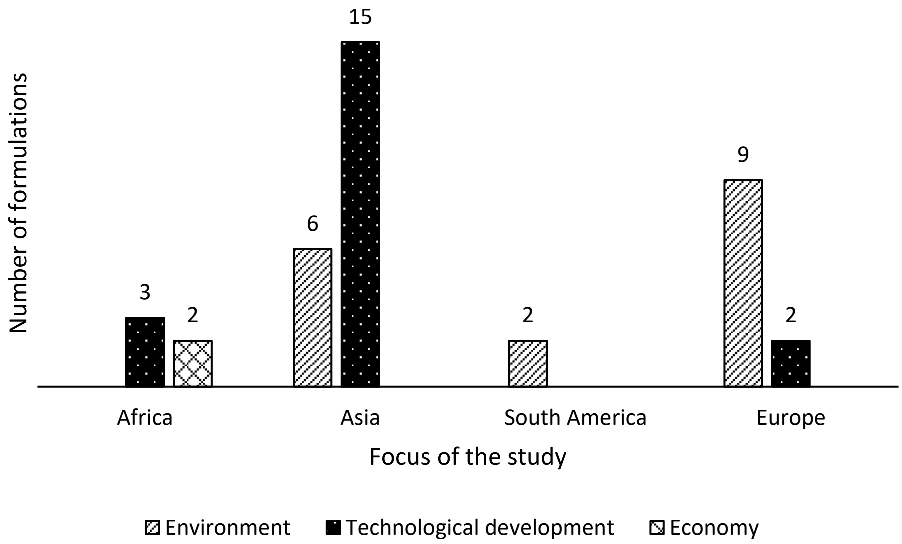

Figure 3.11: Formulations by geographic region and focus of the study.

3.3.2. Raw wastewater characterization

The application of chemicals in aqueous medium during leather processing generates liquid effluents, which mainly consist of chemicals not absorbed and fixed in the leather collagen structure. Although it is less feasible to recycle post-tanning floats, compared to beamhouse and tanning floats (Moreira et al., 2019), it is important to know the characteristics of the wastewater generated in this process, as well as the chemicals used in each step, in order to minimize the pollutant load of the effluents.

The interquartile ranges (first and third quartiles) of concentrations of nine wastewater quality parameters are shown in Table 3.2, to evaluate the dispersion of the data. This means that 50% of the concentrations compiled are within this range, 25% of the concentrations are below the first quartile and 25% of the concentrations are above the third quartile. Complete characterization data are available on supplementary material.

Table 3.2: Characterization of post-tanning raw wastewater.

Parameter	Concentration Range (first quartile to third quartile)	Authors
Conductivity (µS/cm)	12,290 - 19,400	Açikel et al., 2017; Bacardit et al., 2014; Gutterres et al., 2015; Mella et al., 2018; Ollé et al., 2016
Total Dissolved Solids - TDS (mg/L)	5,100 – 14,011	Açikel et al., 2017; Basha et al., 2009; Gutterres et al., 2015; Islam et al., 2014; Karthikeyan et al., 2015; Raghava Rao et al., 2003; Selvaraju et al., 2017
Chloride (mg/L)	997 – 5,002	Basha et al., 2009; Cassano et al., 2001; Gutterres et al., 2015; Karthikeyan et al., 2015; Raghava Rao et al., 2003
Sulfate (mg/L)	693 – 2,409	Basha et al., 2009; Karthikeyan et al., 2015; Rivela et al., 2004
Chemical Oxygen Demand– COD (mg/L)	2,850 - 10,000	Açikel et al., 2017; Bacardit et al., 2014; Basha et al., 2009; Cassano et al., 2001; Gutterres et al., 2015; Islam et al., 2014; Karthikeyan et al., 2015; Mella et al., 2018; Ollé et al., 2016; Pena et al., 2018; Raghava Rao et al., 2003; Rivela et al., 2004; Selvaraju et al., 2017; Sungur and Özkan, 2017
Biochemical Oxygen Demand – BOD (mg/L)	1,000 - 2,067	Açikel et al., 2017; Basha et al., 2009; Cassano et al., 2001; Gutterres et al., 2015; Islam et al., 2014; Karthikeyan et al., 2015; Mella et al., 2018; Pena et al., 2018; Raghava Rao et al., 2003; Rivela et al., 2004; Selvaraju et al., 2017; Sungur and Özkan, 2017
Chromium (mg/L)	43 – 246	Bacardit et al., 2014; Cassano et al., 2001; Gutterres et al., 2015; Piccin et al., 2016; Raghava Rao et al., 2003; Rivela et al., 2004; Sungur and Özkan, 2017
Total Kjeldhal Nitrogen – TKN (mg/L)	228 – 632	Açikel et al., 2017; Bacardit et al., 2014; Gutterres et al., 2015; Karthikeyan et al., 2015; Pena et al., 2018; Piccin et al., 2016
Ammoniacal Nitrogen - NH_4-N (mg/L)	54 – 212	Gutterres et al., 2015; Karthikeyan et al., 2015; Mella et al., 2018; Ollé et al., 2016; Pena et al., 2018; Rivela et al., 2004

A large variation in the concentrations determined by different studies is observed. This was expected as the amount of chemicals and water used in the process changes according to the type of leather goods produced and the raw material processed by each study. Thus, it is more appropriate to establish pollution load (mass) standards for wastewater quality rather than concentration standards. However, since wastewater volume is rarely indicated in manuscripts, this study evaluated the concentrations of pollutants in wastewater. Furthermore, the concentration of pollutants in wastewater is an important parameter that can impact the efficiency of the effluent treatment. The pollutants present in post-tanning effluents can reduce enzymatic activity and biomass production in biological treatments. Dyes, especially azo and metal complexes, fatliquoring agents, and tannins (natural and synthetic) can cause acute and chronic toxicities (Hansen et al., 2020; Mella et al., 2017; Ortiz-Monsalve et al., 2019). In addition, fatliquoring agents reduce oxygen transfer efficiency in the aerobic treatment (Kalyanaraman et al., 2013), and natural and synthetic tannins can cause inhibiting conditions for the biomass in biological treatment (Agustini et al., 2018; Munz et al., 2009).

According to the compiled data presented in Table 3.2, post-tanning raw wastewater shows high conductivity. Half of the characterizations showed conductivity between 12,290 to 19,400 μS/cm (interquartile range). This parameter is related to total dissolved salts, such as chloride and sulphate ions. Post-tanning wastewater have sulfates (693 to 2,409 mg/L) and chlorides (997 to 5,002 mg/L) concentrations within similar levels. Chlorides and sulfates are most likely related to process chemicals such as vegetable and synthetic tannins and deacidulation agents (Hansen et al., 2020). Basic chromium sulfate is also responsible for sulfate pollution load (Gutterres and Mella, 2014). Furthermore, chlorides are also related to the leaching of chemicals from previous steps, due to the supply of salts in pickling and tanning of the hide (necessary to prevent hide swelling) (Mella et al., 2015). Thus, the amount of chemicals used in the process must directly interfere with the presence of salts in raw wastewater.

A higher concentration of COD (2,850 to 10,000 mg/L) in relation to BOD (1,000 to 2,067 mg/L) indicates that there is a predominance of inorganic compounds and refractory substances in the wastewater from this stage of the leather processing, making wastewater difficult to treat (Tigini et al., 2018). Retanning and fatliquoring steps are most likely related to the low wastewater biodegradability. This study showed that the retanning step is the largest consumer of chemicals in post-tanning. In addition, retanning agents have low biodegradability. Natural and synthetic tannins show low BOD/COD ratios due to the complex chemical structures of tannins, composed of an extended set of chemicals such as phenol, naphthalene and formaldehyde (Di Iaconi et al., 2010;

Hassoune et al., 2017; Munz et al., 2009). Fatliquoring step is the second-largest consumer of chemicals in post-tanning. Oils can show different biodegradabilities, which result from varying fatty acid composition. Natural oils typically have higher BOD/COD ratio compared to synthetic oils (Luo et al., 2011).

Chromium concentration in wastewater depends on the tanning agent used in the retanning process. Even when chromium is not the retanning agent, a large number of chrome complexes, from the tanning stage, can be released from collagen and remain in the effluents from soaking, deacidulation, retanning, dyeing and fatliquoring processes (Fuck et al., 2011; Wu et al., 2018).

The presence of total nitrogen compounds (228 to 632 mg/L) is related to several components such as synthetic tannins and azo dyes. Table 3.2 shows low concentrations of ammoniacal nitrogen (54 to 212 mg/L), and its presence is derived mainly from previous processing steps.

Overall, post-tanning effluents show as the main pollutants of concern the presence of dissolved salts and refractory compounds, which cause low biodegradability to the effluent. The biological processes applied to the conventional treatment of tannery effluents have low efficiency in removing salts and recalcitrant compounds (de la Luz-Pedro et al., 2019; Kozik et al., 2019; Tamersit et al., 2018). Thus, advanced effluent treatments may be necessary to reach the effluent discharge standards established by environmental regulations.

The number of analyzes of each parameter evaluated in the raw post-tanning effluent divided by geographic region is shown in Figure 3.12. Parameters most commonly used by compiled manuscripts are COD (14 analyzes), BOD (13 analyzes) and TDS (8 analyzes). Asian studies are more focused on COD, BOD and TDS parameters, which shows that, in addition to the concern with organic contamination (COD and BOD), there is a concern with salinization (TDS) discharged in water bodies. South American studies are more focused on COD, BOD, and NH_4-N parameters. The NH_4-N parameter shows a greater concern with the presence of nutrients and eutrophication of water bodies. European studies are more focused on conductivity, COD, and chromium, showing greater concern with salinity (conductivity) and toxicity (occurring in the case of oxidation of chromium (III) to chromium (VI)) of water bodies.

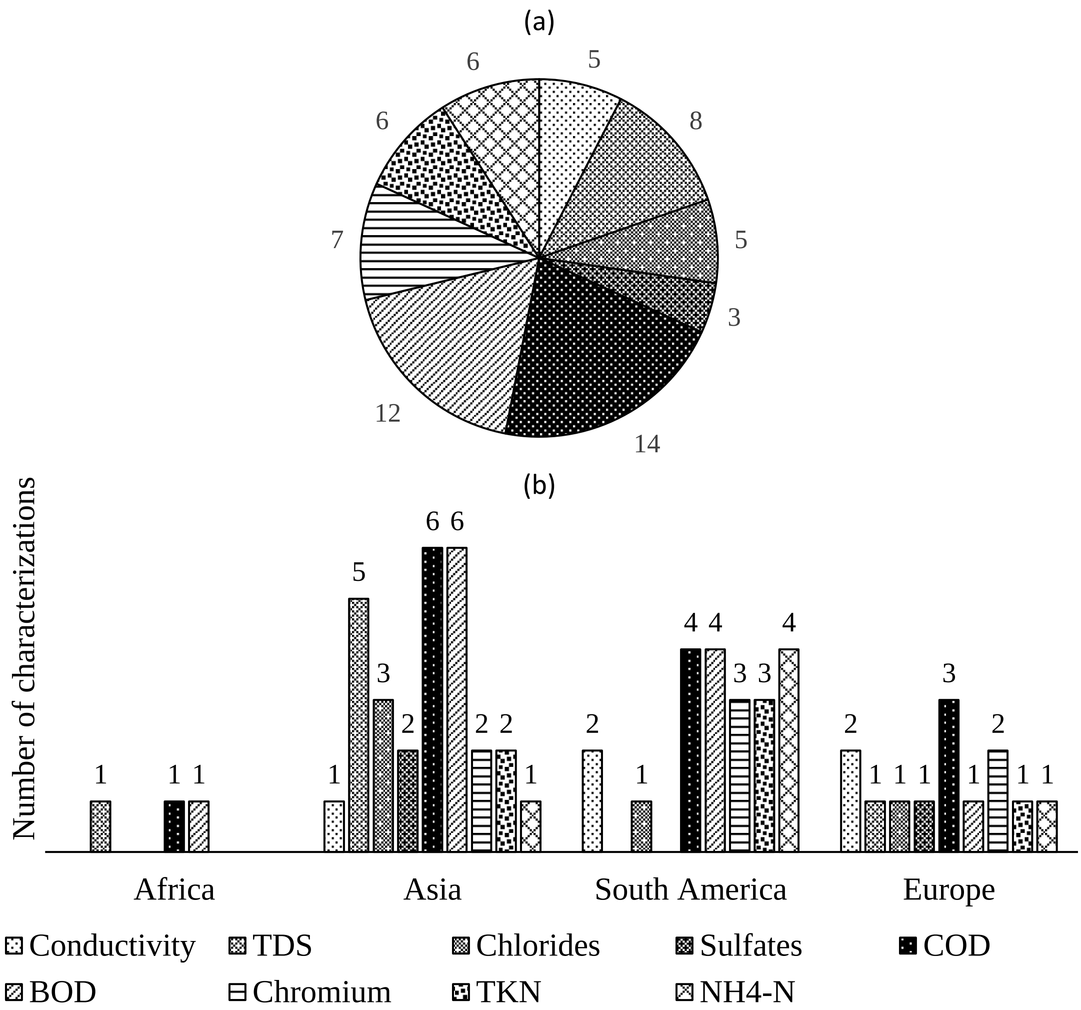

Figure 3.12: Number of analyzes by parameter (a) and by geographic region (b).

3.4. Conclusions

The present study showed that the leather post-tanning process plays an important role in the overall environmental impact of a tannery. The evaluated data included formulations applied by tanneries on an industrial scale and formulations suggested by chemical manufacturers, in addition to formulations obtained from scientific papers, aiming to involve manufacturers and research works in the state of art of post-tanning process.

Post-tanning consumes an average of 360.2 kilograms of chemicals per ton of shaved leather. Retanning and fatliquoring steps have the largest consumers of chemicals, representing on average 152.2 kg/t and 122.0 kg/t, respectively. These steps contribute to the low biodegradability of raw wastewater due to the high amount of chemicals used and their physicochemical characteristics. Scientific literature should provide more accurate information on the volumes of water and effluents involved in the processes in order to compare the final pollutant loads per kg of leather produced.

The average post-tanning water consumption is 8.6 cubic meters per ton of shaved leather. Highest consumption occurs in the washing step, which consumes on average 4.5 m^3/t. Therefore, minimization strategies should focus on this operation step by means of water reuse or recycling.

The upper limits of chemical and water consumption were indicated in this study, in order to be a guideline to reach more sustainable processes. The consumption of 424 kg/t of chemicals and 10 m^3/t of water should be restricted as upper limits for the post-tanning process.

Combination of chemicals used in this process generates a poorly biodegradable effluent, with high conductivity and presence of salts, especially sulfates and chlorides. Thus, the main parameters analyzed in the raw wastewater among the compiled manuscripts are COD, BOD and TDS.

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Supplementary material

Table 3.3: Complete data of leather post-tanning formulations

Table 3.4: Characterization of post-tanning raw wastewater

Table 3.3: Complete data of leather post-tanning formulations

Author	Chemicals (kg/t)	Chemicals per step (kg/t)	Number of chemicals	Water consumption (m³/t)	Water consumption per step (m³/t)	Details of formulation
Alla et al., 2017	360	- Deacidulation: 10 kg/t - Retanning: 140 kg/t - Dyeing: 20 kg/t - Fatliquoring: 120 kg/t - Fixing: 30 kg/t	12	2**	- Deacidulation: 1.0 m³/t - Retanning, dyeing, fatliquoring and fixing: 1.0 m³/t	- Post-tanning recipe for fish skins chrome tanned and retanned using synthetic tannins - Steps of post-tanning: deacidulation, retanning, dyeing, fatliquoring, fixing and washings -Focus of the study:technological development - Weight basis: not explicitly described - Manuscript Region: Asia
Aravindhan et al., 2014	430	- Deacidulation: 20 kg/t - Retanning: 280 kg/t - Dyeing: 20 kg/t - Fatliquoring: 90 kg/t - Fixing: 20 kg/t	13	7	- Deacidulation: 1.5 m³/t - Retanning, dyeing, fatliquoring and fixing: 1.5 m³/t - Washings: 4 m³/t	- Process Recipe for Manufacture of Upper Leather from Wet Blue of Thickness 1.1-1.2 mm - Steps of post-tanning: deacidulation, retanning, dyeing, fatliquoring, fixing and washings -Focus of the study:technological development - Weight basis: shaved weight - Manuscript Region: Asia
Bacardit et al., 2014	488	- Deacidulation: 13 kg/t - Retanning: 300 kg/t - Dyeing: 10 kg/t - Fatliquoring: 140 kg/t - Fixing: 25 kg/t	9	10	- Deacidulation, retanning and dyeing: 2.0 m³/t - Fatliquoring: 2.0 m³/t - Washings: 6 m³/t	- Automotive upholstery retanning of wet blue leather using Tara and synthetic tannins - Steps of post-tanning: deacidulation, retanning, dyeing, fatliquoring, fixing and washings -Focus of the study: environment - Weight basis: shaved weight - Manuscript Region: Europe
Bacardit et al., 2014	298	- Deacidulation: 45 kg/t - Retanning: 110 kg/t - Dyeing: 35 kg/t - Fatliquoring: 85 kg/t - Fixing: 23 kg/t	12	9.5	- Deacidulation and retanning: 1.5 m³/t - Dyeing: 1.0 m³/t - Fatliquoring: 1.0 m³/t - Washings: 6 m³/t	- Shoe-uppers retanning of wet blue leather using Mimosa and synthetic tannins - Steps of post-tanning: deacidulation, retanning, dyeing, fatliquoring, fixing and washings -Focus of the study: environment - Weight basis: shaved weight - Manuscript Region: Europe
Bacardit et al., 2014	270	- Soaking: 5 kg/t - Deacidulation: 42 kg/t - Retanning: 40 kg/t - Dyeing: 50 kg/t - Fatliquoring: 120 kg/t - Fixing: 20 kg/t	11	9.5	- Soaking: 2 m³/ - Deacidulation: 1.5 m³/t - Retanning: 2.0 m³/t - Dyeing: 0.7 m³/t - Fatliquoring: 1.3 m³/t - Washings: 2 m³/t	- Garment retanning of wet blue leather using a chromium-based retanning agent - Steps of post-tanning: retanning, Deacidulation, dyeing, fatliquoring, fixing and washings -Focus of the study: environment - Weight basis: shaved weight - Manuscript Region: Europe
Bacardit et al., 2016	488	- Deacidulation: 13 kg/t - Retanning: 320 kg/t - Dyeing: 10 kg/t - Fatliquoring: 120 kg/t - Fixing: 25 kg/t	9	10	- Deacidulation, retanning, dyeing: 2 m³/t - Fatliquoring: 2 m³/t - Washings: 6 m³/t	- Post-tanning formulation for automotive using tara, phenolic and polimeric retanning agents - Steps of post-tanning: deacidulation, retanning, dyeing, fatliquoring, fixing and washings -Focus of the study: environment - Weight basis: not explicitly described - Manuscript Region: Europe

Author	Chemicals (kg/t)	Chemicals per step (kg/t)	Number of chemicals	Water consumption (m^3/t)	Water consumption per step (m^3/t)	Details of formulation
Bacardit et al., 2016	309	- Deacidulation: 46 kg/t - Retanning: 110 kg/t - Dyeing: 30 kg/t - Fatliquoring: 100 kg/t - Fixing: 23 kg/t	10	8.8	- Deacidulation: 2 m^3/t - Retanning: 0.8 $m^3/$ - Dyeing: 1 m^3/t - Fatliquoring: 1 m^3/t - Washings: 4 m^3/t	- Post-tanning formulation for upholstery using tara, phenolic and polimeric retanning agents - Steps of post-tanning: deacidulation, retanning, dyeing, fatliquoring, fixing and washings -Focus of the study: environment - Weight basis: not explicitly described - Manuscript Region: Europe
Bacardit et al., 2016	302	- Deacidulation: 45 kg/t - Retanning: 140 kg/t - Dyeing: 35 kg/t - Fatliquoring: 55 kg/t - Fixing: 23 kg/t - Washing: 4 kg/t	12	9.5	- Deacidulation and retanning: 1.5 m^3/t - Dyeing: 1 m^3/t - Fatliquoring: 1 m^3/t - Washings: 6 m^3/t	- Post-tanning formulation for shoe uppers using mimosa, phenolic and polimeric retanning agents - Steps of post-tanning: deacidulation, retanning, dyeing, fatliquoring, fixing and washings -Focus of the study: environment - Weight basis: not explicitly described - Manuscript Region: Europe
Bacardit et al., 2016	308	- Deacidulation: 38 kg/t - Retanning: 85 kg/t - Dyeing: 28 kg/t - Fatliquoring: 130 kg/t - Fixing: 26 kg/t - Washing: 1 kg/t	13	9	- Deacidulation: 1 m^3/t - Retanning: 1.5 $m^3/$ - Dyeing: 1 m^3/t - Fatliquoring: 1.5 m^3/t - Washings: 4 m^3/t	- Post-tanning formulation for bovine garment using phenolic and polimeric retanning agents - Steps of post-tanning: deacidulation, retanning, dyeing, fatliquoring, fixing and washings -Focus of the study: environment - Weight basis: not explicitly described - Manuscript Region: Europe
Bacardit et al., 2016	277	- Deacidulation: 42 kg/t - Retanning: 70 kg/t - Dyeing: 50 kg/t - Fatliquoring: 90 kg/t - Fixing: 20 kg/t - Washing: 5 kg/t	11	9.5	- Deacidulation: 1.5 m^3/t - Retanning: 2.0 $m^3/$ - Dyeing: 0.7 m^3/t - Fatliquoring: 1.3 m^3/t - Washings: 4 m^3/t	- Post-tanning formulation for ovine garment using Chromium-containing condensation product of phenolic sulphonic acids and polymeric retanning agents - Steps of post-tanning: deacidulation, retanning, dyeing, fatliquoring, fixing and washings -Focus of the study: environment - Weight basis: not explicitly described - Manuscript Region: Europe
Başaran et al., 2008	106	- Rechromming: 40 kg/t - Deacidulation: 10 kg/t - Retanning: 50 kg/t - Washing: 6 kg/t	8	9.5	- Deacidulation and retanning: 1.5 m^3/t - Washings: 8.0 m^3/t	- Post-tanning recipe using basic chromium sulphate, phenol and naphtalene sulphonic acid condensate retanning agents - Steps of post-tanning: rechromming, Deacidulation, retanning and washings -Focus of the study:environment - Weight basis: wet-blue weight - Manuscript Region: Asia
Belay et al., 2019	501	- Soaking: 6 kg/t - Rechromming: 70 kg/t - Deacidulation: 65 kg/t - Retanning: 150 kg/t - Dyeing: 40 kg/t - Fatliquoring: 140 kg/t - Fixing: 30 kg/t	19	10	- Soaking: 3.0 m^3/t - Rechromming: 1.5 m^3/t - Deacidulation: 1.5 m^3/t - Retanning, dyeing, fatliquoring and fixing: 1.0 m^3/t - Washings: 3.0 m^3/t	- Retanning and Dyeing of Ethiopian Camel Wet blue to Upper Leather. - Steps of post-tanning: soaking, rechromming, Deacidulation, retanning, dyeing, fatliquoring, fixing, cationic toping and washings -Focus of the study:technological development - Weight basis: not explicitly described - Manuscript Region: Africa

Author	Chemicals (kg/t)	Chemicals per step (kg/t)	Number of chemicals	Water consumption (m^3/t)	Water consumption per step (m^3/t)	Details of formulation
Buljan et al., 2000	295	- Rechromming: 50 kg/t - Deacidulation: 30 kg/t - Retanning: 100 kg/t - Dyeing: 20 kg/t - Fatliquoring: 80 kg/t - Fixing: 15 kg/t	7	17	- Deacidulation: 2.0 m^3/t - Retanning, dyeing, fatliquoring and fixing: 1.0 m^3/t - Washings: 14 m^3/t	- Shoe upper leather with rechroming and organic tannins - Steps of post-tanning: rechromming, Deacidulation, retanning, dyeing, fatliquoring, fixing and washings -Focus of the study:environment - Weight basis: shaved weight - Manuscript Region: Asia
Gari et al., 2016	297	- Deacidulation: 7 kg/t - Retanning: 120 kg/t - Fatliquoring: 120 kg/t - Dyeing: 20 kg/t - Fixing: 30 kg/t	13	3.5	- Deacidulation: 1.0 m^3/t - Retanning, dyeing, fatliquoring and fixing: 1.5 m^3/t - Washings: 1.0 m^3/t	- Post-tanning recipe to produce shoe upper leather using ternary solvent medium in wet blue goat skins - Steps of post-tanning: deacidulation, retanning, dyeing, fatliquoring, fixing and washings -Focus of the study:environment - Weight basis: shaved weight - Manuscript Region: Asia
Gomes et al., 2016	284	- Soaking: 4 kg/t - Deacidulation: 25 kg/t - Retanning: 110 kg/t - Dyeing: 40 kg/t - Fatliquoring: 80 kg/t - Fixing: 25 kg/t	9	15.5	- Soaking: 3 m^3/t - Deacidulation: 1.5 m^3/t - Retanning, dyeing, fatliquoring and fixing: 3.0 m^3/t - Washings: 8 m^3/t	- Retanning of wet blue leather using tannins - Steps of post-tanning: soaking, Deacidulation, retanning, dyeing, fatliquoring, fixing and washings -Focus of the study:environment - Weight basis: shaved weight - Manuscript Region: South America
Haroun, 2005	260	- Deacidulation: 10 kg/t - Retanning: 150 kg/t - Dyeing: 40 kg/t - Fatliquoring: 30 kg/t - Fixing: 30 kg/t	11	3	- Deacidulation, retanning, dyeing, fatliquoring and fixing: 2.0 m^3/t - Washings: 1 m^3/t	- Compact dyeing recipe of soft leather - Steps of post-tanning: deacidulation, retanning, dyeing, fatliquoring, fixing and washing -Focus of the study:economic - Weight basis: not explicitly described - Manuscript Region: Africa
Haroun, 2005	262.5	- Deacidulation: 10 kg/t - Retanning: 210 kg/t - Dyeing: 22.5 kg/t - Fixing: 20 kg/t	11	3	- Deacidulation, retanning, dyeing, fatliquoring and fixing: 2.0 m^3/t - Washings: 1 m^3/t	- Compact dyeing recipe of heavy retanned leather - Steps of post-tanning: deacidulation, retanning, dyeing, fatliquoring, fixing and washing -Focus of the study:economic - Weight basis: not explicitly described - Manuscript Region: Africa
Jayakumar et al., 2016	365	- Deacidulation: 20 kg/t - Retanning: 190 kg/t - Dyeing: 30 kg/t - Fatliquoring: 110 kg/t - Fixing: 15 kg/t	10	6.5	- Deacidulation: 1.5 m^3/t - Retanning, dyeing and fatliquoring: 1.0 m^3/t - Washings: 4 m^3/t	- Post-tanning recipe for the manufacture of upper leather from wet blue using synthetic and wattle tannins - Steps of post-tanning: deacidulation, retanning, dyeing, fatliquoring, fixing and washings -Focus of the study:environment - Weight basis: not explicitly described - Manuscript Region: Asia

Author	Chemicals (kg/t)	Chemicals per step (kg/t)	Number of chemicals	Water consumption (m^3/t)	Water consumption per step (m^3/t)	Details of formulation
Ji-bo et al., 2018	246	- Soaking: 3 kg/t - Deacidulation: 28 kg/t - Retanning: 80 kg/t - Dyeing: 20 kg/t - Fatliquoring: 100 kg/t - Fixing: 15 kg/t	7	20	- Soaking: 4.0 m^3/t - Deacidulation: 2.0 m^3/t - Retanning, dyeing and fatliquoring and fixing: 2.0 m^3/t - Washings: 12.0 m^3/t	- Post-tanning recipe for wet blue leather using melamine resin as retanner - Steps of post-tanning: soaking, deacidulation, retanning, dyeing, fatliquoring, fixing and washings -Focus of the study:technological development - Weight basis: shaved weight - Manuscript Region: Asia
Karthikeyan and Babu, 2017	410	- Deacidulation: 25 kg/t - Retanning: 170 kg/t - Dyeing: 20 kg/t - Fatliquoring: 180 kg/t - Fixing: 15 kg/t	14	2**	- Deacidulation: 1.0 m^3/t - Retanning, dyeing, fatliquoring and fixing: 1.0 m^3/t.	- Post-tanning recipe for chicken leg leather using synthetic and vegetable tannins - Steps of post-tanning: deacidulation, retanning, dyeing, fatliquoring, fixing and washings -Focus of the study:technological development - Weight basis: not explicitly described - Manuscript Region: Asia
Lai et al., 2017	238	-Retanning: 105 kg/t - Fatliquoring and dyeing: 120 kg/t - Fixing: 13 kg/t	9	2**	- Retanning: 1.0 m^3/t - Fatliquoring: 1.0 m^3/t	- Process Recipe for Manufacture of Goatskin Garment Leathers using tannins - Steps of post-tanning: deacidulation, retanning, dyeing, fatliquoring, fixing and washings -Focus of the study:technological development - Weight basis: not explicitly described - Manuscript Region: Asia
Li et al., 2016	418	- Deacidulation, retanning and dyeing: 290 kg/t - Rechromming: 30 kg/t - Fatliquoring: 80 kg/t - Fixing: 13 kg/t - Washing: 5 kg/t	21	7.3	- Deacidulation, retanning and dyeing: 4.3 m^3/t - Fatliquoring: 1.0 m^3/t - Washings: 2 m^3/t	- Post-tanning recipe using a new phosphate ester based on nonionic amphiphilic polyurethane as leather fatliquoring agent - Steps of post-tanning: rechromming, deacidulation, retanning, dyeing, fatliquoring, fixing and washings -Focus of the study:technological development - Weight basis: wet-blue weight - Manuscript Region: Asia
Local Tannery, 2019a	405.5	- Deacidulation: 31.5 kg/t - Retanning: 202 kg/t - Dyeing: 25 kg/t - Fatliquoring: 123 kg/t - Fixing: 24 kg/t	19	9.5	- Deacidulation: 1.5 m^3/t - Retanning, fatliquoring, dyeing and fixing: 4.0 m^3/t Washings: 4.0 m^3/t	- Post-tanning recipe for the manufacture of leather for purses from wet blue leather - Steps of post-tanning: deacidulation, retanning, dyeing, fatliquoring, fixing and washings -Focus of the study: not applicable - Weight basis: shaved weight - Manuscript Region: South America

Author	Chemicals (kg/t)	Chemicals per step (kg/t)	Number of chemicals	Water consumption (m^3/t)	Water consumption per step (m^3/t)	Details of formulation
Local Tannery, 2019b	613	- Rechromming: 41 kg/t - Deacidulation: 28 kg/t - Retanning: 330 kg/t - Dyeing: 25 kg/t - Fatliquoring: 149 kg/t - Fixing: 40 kg/t	23	12.5	- Rechromming and Deacidulation: 1.5 m^3/t - Retanning and dyeing: 2.0 m^3/t - Fatliquoring and fixing: 3.0 m^3/t - Washing: 6.0 m^3/t	- Post-tanning process of shoe upper using wet-blue leather - Steps of post-tanning: rechromming, deacidulation, retanning, dyeing, fatliquoring and washings -Focus of the study: not applicable - Weight basis: shaved weight - Manuscript Region: South America
Lofrano et al., 2008	374.5	- Soaking: 15 kg/t - Deacidulation: 28 kg/t - Retanning: 161.5 kg/t - Fatliquoring: 110 kg/t - Dyeing: 30 kg/t - Fixing: 30 kg/t	17	6	- Soaking: 1.5 m^3/t - Deacidulation: 2.0 m^3/t - Retanning, dyeing, fatliquoring and fixing: 3.5 m^3/t	- Retanning applied to process Nappa leather using rechroming and tannins retanning - Steps of post-tanning: soaking, deacidulation, retanning, dyeing, fatliquoring, fixing and washings -Focus of the study:environment - Weight basis: not explicitly described - Manuscript Region: Europe
Long-Fang et al., 2017	293	- Soaking: 15 kg/t - Deacidulation: 28 kg/t - Retanning: 30 kg/t - Dyeing: 25 kg/t - Fatliquoring: 180 kg/t - Fixing: 15 kg/t	8	12	- Soaking: 2.0 m^3/t - Deacidulation: 1.5 m^3/t - Retanning: 1.5 m^3/t - Fatliquoring, dyeing and fixing: 1.0 m^3/t - Washing: 6.0 m^3/t	- Retanning Procedure of wet blue sheepskin - Steps of post-tanning: soaking, deacidulation, retanning, dyeing, fatliquoring, fixing and washings -Focus of the study:technological development - Weight basis: shaved weight - Manuscript Region: Asia
Marsal et al., 2017	352	- Soaking: 8 kg/t - Rechromming: 54 kg/t - Deacidulation: 30 kg/t - Retanning: 120 kg/t - Fatliquoring: 140 kg/t	11	8.5	- Soaking: 3.0 m^3/t - Rechromming: 1.0 m^3/t - Deacidulation: 1.5 m^3/t - Retanning: 0.5 m^3/t - Fatliquoring: 1.0 m^3/t - Washings: 1.5 m^3/t	- Rechroming and vegetable retanning formulation - Steps of post-tanning: soaking, rechromming, Deacidulation, retanning, fatliquoring and washings -Focus of the study:technological development - Weight basis: shaved weight - Manuscript Region: Europe
Mohammed et al., 2014	458	- Rechromming: 55 kg/t - Deacidulation: 68 kg/t - Retanning: 100 kg/t - Dyeing: 40 kg/t - Fatliquoring: 160 kg/t - Fixing: 35 kg/t	14	6.5	- Rechromming: 3.0 m^3/t - Deacidulation and retanning: 3.0 m^3/t - Fatliquoring and fixing: 0.5 m^3/t	- Retanning of sheep garment leather using basic chromium sulphate and Synthetic tannins - Steps of post-tanning: deacidulation, retanning, acidification, rechromming, Deacidulation, dyeing, fatliquoring, fixing and washings -Focus of the study:technological development - Weight basis: shaved weight - Manuscript Region: Africa

Author	Chemicals (kg/t)	Chemicals per step (kg/t)	Number of chemicals	Water consumption (m^3/t)	Water consumption per step (m^3/t)	Details of formulation
Mohammed et al., 2014	716	- Soaking: 20 kg/t - Rechromming: 112.5 kg/t - Deacidulation: 60 kg/t - Retanning: 212,5 kg/t - Fatliquoring: 311 kg/t	25	4.5	- Soaking: 2.0 m^3/t - Rechromming: 0.5 m^3/t - Deacidulation and retanning: 1.5 m^3/t - Fatliquoring: 0.5 m^3/t	- Retanning of sheep upper leather using basic chromium sulphate, synthetic and wattle tannin - Steps of post-tanning: soaking, rechromming, Deacidulation, retanning and fatliquoring -Focus of the study:technological development - Weight basis: shaved weight - Manuscript Region: Africa
Ollé et al., 2016	500	- Deacidulation: 15 kg/t - Retanning: 250 kg/t - Dyeing: 10 kg/t - Fatliquoring: 200 kg/t - Fixing: 20 kg/t - Washing: 5 kg/t	11	7.1	- Deacidulation, retanning and dyeing: 1.1 m^3/t - Fatliquoring: 2 m^3/t - Washings: 4 m^3/t	- Post-tanning recipe for automotive leather using modified tara - Steps of post-tanning: deacidulation, retanning, dyeing, fatliquoring, fixing and washings -Focus of the study:technological development - Weight basis: not explicitly described - Manuscript Region: Europe
Ortiz-Monsalve et al., 2019	284	- Soaking: 4 kg/t - Deacidulation: 25 kg/t - Retanning: 130 kg/t - Dyeing: 35 kg/t - Fatliquoring: 60 kg/t - Fixing: 30 kg/t	10	12	- Soaking: 2 m^3/t - Deacidulation: 2.0 m^3/t - Retanning, dyeing, fatliquoring and fixing: 2.0 m^3/t - Washings: 6 m^3/t	- Retanning of wet blue leather using vegetable and synthetic tannins. - Steps of post-tanning: soaking, deacidulation, retanning, dyeing, fatliquoring, fixing and washings -Focus of the study:environment - Weight basis: wet-blue weight - Manuscript Region: South America
Ramalingam and Rao, 2018	472	- Soaking: 2 kg/t - Rechromming: 110 kg/t - Deacidulation: 25 kg/t - Retanning: 170 kg/t - Dyeing: 15 kg/t - Fatliquoring: 120 kg/t - Fixing: 30 kg/t	15	6.9	- Soaking: 2.0 m^3/t - Rechromming: 1.0 m^3/t - Deacidulation, dyeing, retanning, fatliquoring and fixing: 1.9 m^3/t - Washing: 2.0 m^3/t	- Post-tanning recipe for upper leather processing of chrome tanned goat leather - Steps of post-tanning: soaking, rechromming, Deacidulation, retanning, dyeing, fatliquoring, fixing and washings -Focus of the study:technological development - Weight basis: shaved weight - Manuscript Region: Asia
Ramalingam and Rao, 2018	532	- Soaking: 2 kg/t - Rechromming: 110 kg/t - Deacidulation: 25 kg/t - Retanning: 110 kg/t - Dyeing: 15 kg/t - Fatliquoring: 240 kg/t - Fixing: 30 kg/t	15	7.4	- Soaking: 2.0 m^3/t - Rechromming: 1.0 m^3/t - Deacidulation, dyeing, retanning, fatliquoring and fixing: 2.4 m^3/t - Washing: 2.0 m^3/t	- Post-tanning recipe for garment leather processing of chrome tanned goat leather - Steps of post-tanning: soaking, rechromming, deacidulation, retanning, dyeing, fatliquoring, fixing and washings -Focus of the study:technological development - Weight basis: shaved weight - Manuscript Region: Asia

Author	Chemicals (kg/t)	Chemicals per step (kg/t)	Number of chemicals	Water consumption (m^3/t)	Water consumption per step (m^3/t)	Details of formulation
Saravanabhavan et al., 2005	270	- Deacidulation: 20 kg/t - Retanning: 100 kg/t - Dyeing: 30 kg/t - Fatliquoring: 100 kg/t - Fixing: 20 kg/t	13	9.5	- Deacidulation: 1.0 m^3/t - Retanning, dyeing, fatliquoring and fixing: 0.5 m^3/t - Washings: 8.0 m^3/t	- Retanning using synthetic and mimosa tannins - Steps of post-tanning: deacidulation, retanning, dyeing, fatliquoring, fixing and washings -Focus of the study:environment - Weight basis: shaved weight - Manuscript Region: Asia
Sathish et al., 2013	325	- Deacidulation: 20 kg/t - Retanning: 140 kg/t - Dyeing: 20 kg/t - Fatliquoring: 120 kg/t - Fixing: 25 kg/t	11	5.85	- Deacidulation: 1.7 m^3/t - Retanning, dyeing and fatliquoring: 1.15 m^3/t - Washings: 3.0 m^3/t	- Softy upper crust leather - Steps of post-tanning: deacidulation, retanning, dyeing, fatliquoring, fixing and washings -Focus of the study:environment - Weight basis: not explicitly described - Manuscript Region: Asia
Sathish et al., 2016	255	- Deacidulation: 20 kg/t - Retanning: 100 kg/t - Fatliquoring: 90 kg/t - Dyeing: 20 kg/t - Fixing: 25 kg/t	9	6.05	- Deacidulation: 1.7 m^3/t - Retanning, dyeing, fatliquoring and fixing: 1.35 m^3/t - Washings: 3.0 m^3/t	- Process recipe for the manufacture of softy upper leathers retanned using tara and synthetic tannins - Steps of post-tanning: deacidulation, retanning, dyeing, fatliquoring, fixing and washings -Focus of the study:technological development - Weight basis: shaved weight - Manuscript Region: Asia
Sathish et al., 2017	370	- Deacidulation: 20 kg/t - Retanning: 120 kg/t - Fatliquoring: 200 kg/t - Fixing: 30 kg/t	11	1.6*	- Retanning, fatliquoring and fixing: 1.6 m^3/t	- Post-tanning recipe for sheep wet blue converted into garment leather - Steps of post-tanning: deacidulation, retanning, fatliquoring and washings -Focus of the study:technological development - Weight basis: chrome tanned bovine ear - Manuscript Region: Asia
Sathish et al., 2017	365	- Deacidulation: 15 kg/t - Retanning: 220 kg/t - Fatliquoring: 100 kg/t - Fixing: 30 kg/t	11	1.6*	- Retanning, fatliquoring and fixing: 1.6 m^3/t	- Post-tanning recipe for sheep wet blue converted into upper leather - Steps of post-tanning: deacidulation, retanning, fatliquoring and washings -Focus of the study:technological development - Weight basis: chrome tanned bovine ear - Manuscript Region: Asia
Sathish et al., 2017	315	- Deacidulation: 15 kg/t - Retanning: 90 kg/t - Dyeing: 20 kg/t - Fatliquoring: 160 kg/t - Fixing: 30 kg/t	12	4.8	- Deacidulation: 1.1 m^3/t - Retanning, dyeing and fatliquoring: 1.6 m^3/t - Fixing: 0.1 m^3/t - Washing: 2.0 m^3/t	- Post-tanning recipe for chrome tanned bovine ear leather using synthetic tannins - Steps of post-tanning: deacidulation, retanning, dyeing, fatliquoring, fixing and washings -Focus of the study:technological development - Weight basis: chrome tanned bovine ear - Manuscript Region: Asia

Author	Chemicals (kg/t)	Chemicals per step (kg/t)	Number of chemicals	Water consumption (m^3/t)	Water consumption per step (m^3/t)	Details of formulation
Selvi et al., 2018	296	- Rechromming: 42 kg/t - Deacidulation: 44 kg/t - Retanning: 100 kg/t - Dyeing: 20 kg/t - Fatliquoring: 80 kg/t - Fixing: 10 kg/t	12	4.7	- Rechromming and Deacidulation: 1.5 m^3/t - Retanning, dyeing and fatliquoring: 1.2 m^3/t - Washing: 2.0 m^3/t	- Post-tanning process of goat wet blue using biocolorant - Steps of post-tanning: rechromming, deacidulation, retanning, dyeing, fatliquoring and washings -Focus of the study:technological development - Weight basis: shaved weight - Manuscript Region: Asia
Seta, 2004a	479.5	- Soaking: 2.5 kg/t - Deacidulation: 22 kg/t - Retanning: 375 kg/t - Fatliquoring: 65 kg/t - Fixing: 15 kg/t	12	5.8	- Soaking: 1.5 m^3/t - Deacidulation: 0.8m^3/t - Retanning: 1.6 m^3/t - Fatliquoring: 1.0m^3/t - Washing:1.0 m^3/t	- Post-tanning process of wet-blue leather using vegetable tannins - Steps of post-tanning: soaking, deacidulation, retanning, dyeing, fatliquoring, fixing and washings -Focus of the study: not applicable - Weight basis: shaved weight - Manuscript Region: South America
Seta, 2004b	375.5	- Soaking: 2.5 kg/t - Rechromming: 30 kg/t - Deacidulation: 23 kg/t - Retanning: 220 kg/t - Fatliquoring: 85 kg/t - Fixing: 15 kg/t	14	5.8	- Soaking: 1.5 m^3/t - Rechromming and - Deacidulation: 0.8 m^3/t - Retanning: 1.5 m^3/t - Fatliquoring and fixing: 1.0 m^3/t - Washing: 1.0 m^3/t	- Post-tanning process of wet-blue leather with rechromming - Steps of post-tanning: soaking, rechromming, deacidulation, retanning, dyeing, fatliquoring and fixing -Focus of the study: not applicable - Weight basis: shaved weight - Manuscript Region: South America
Zhang et al., 2018	226	- Soaking: 3 kg/t - Deacidulation: 28 kg/t - Retanning: 80 kg/t - Fatliquoring: 115 kg/t	6	12.5	- Soaking: 2.0 m^3/t - Deacidulation: 2.0 m^3/t - Retanning: 1.5 m^3/t - Fatliquoring: 1.0 m^3/t - Washings: 6.0 m^3/t	- Post-tanning recipe for cattle hides using flame retardant retanning agent - Steps of post-tanning: soaking, deacidulation, retanning, fatliquoring and washings -Focus of the study: technological development - Weight basis: shaved weight - Manuscript Region: Asia

* Formulation does not inform water usage of deacidulation and washing steps.
** Formulation does not inform water usage of washings.

Table 3.4: Characterization of post-tanning raw wastewater

Author		pH	Cond. (µS/cm)	COD (mg/L)	BOD_5 (mg/L)	TDS (mg/L)	Chromium (mg/L)	TKN (mg/L)	NH_4-N (mg/L)	Cl^- (mg/L)	SO_4^{-2} (mg/L)	Observation
Açikel et al. (2017)		3.48	23,100	2,400	1,000	30,200	-	274.4	-	-	-	Wastewater from Dyeing bath of wet blue leather
Bacardit et al. (2014)	I	-	15,183	15,450	-	-	102.5	320	-	-	-	Wet-blue formulation for automotive upholstery
	II	-	17,667	9,150	-	-	ND	220	-	-	-	Wet-bright formulation for automotive upholstery
	III	-	17,970	12,100	-	-	154.9	640	-	-	-	Wet-blue formulation for shoe leather
	IV	-	20,150	10,000	-	-	ND	520	-	-	-	Wet-bright formulation for shoe leather
	V	-	19,400	9,500	-	-	203.9	250	-	-	-	Wet-blue formulation for garment leather
	VI	-	20,640	8,800	-	-	ND	220	-	-	-	Wet-bright formulation for garment leather
Basha et al. (2009)		7.5	-	2,850	900	1,000	-	-	-	550	360	Typical tannery post-tanning effluent
Cassano et al. (2001)		4 - 10	-	15,000 – 75,000	6,000 – 15,000	-	0 - 3000	-	-	5,000 – 10,000	-	Raw wastewater from dyeing, fatliquoring and retanning steps of a wet-blue leather
Gutterres et al. (2014)	IV	6.89	12,290	4,315	2,089	10,301	44*	609	212	2,979	-	Raw wastewater from wet-end steps
	V-Cr	6.73	4,430	6,081	3,137	6,045	-	2,064	24	996	-	Raw wastewater from post-tanning with chromium
	V-Tan	3.96	17,990	54,336	27,038	24,543	-	12,992	42	5,002	-	Raw wastewater from post-tanning with vegetable tannins
	VI	5.49	3,760	2,579	1,327	2,301	56*	265	54	1,056	-	Raw wastewater from wet-end steps
Islam et al. (2014)		4.5	-	3,650	1,450	10,500	-	-	-	-	-	Wastewater from retanning process
Karthikeyan et al. (2015)		6.1	-	1,920	732	36,642	-	746	560	9,458	1,026	Tannery dyeing wastewater
Mella et al. (2018)		4.68	6,670	7,744	1,860	-	-	-	97.715	-	-	Synthetic post-tanning wastewater

Author	pH	Cond. (µS/cm)	COD (mg/L)	BOD_5 (mg/L)	TDS (mg/L)	Chromium (mg/L)	TKN (mg/L)	NH_4-N (mg/L)	Cl^- (mg/L)	SO_4^{-2} (mg/L)	Observation
Ollé et al. (2016)	3.5	14,702	35,120	-	-	-	-	370	-	-	Wastewater of conventional post-tanning process
Pena et al. (2018)	7.68	-	1,045	1,900	-	-	89.91	79.3	-	-	Post-tanning wastewater (75% raw / 25% treated wastewater)
Piccin et al. (2016)	4.02	-	-	-	-	40.53	68.36	-	-	-	Dyeing effluents obtained from pilot-scale reproduction of post-tanning process
Raghava Rao et al. (2003)	3.5 – 4.5	-	2,500 – 7,000	1,000 – 2,000	2,400 – 7,000	40 – 100	-	-	500 – 1,000	-	Raw wastewater from dyeing and fatliquoring
Rivela et al. (2004)	3.9	-	5,058	840	-	462.2	-	58.4	-	3,792	Average Concentrations of retanning baths and washes
Selvaraju et al. (2017) I	-	-	2,950	1,115	9,500	-	-	-	-	-	Conventional retanning of wet blue goat skins with syntan
Selvaraju et al. (2017) II	-	-	2,260	1,346	6,000	-	-	-	-	-	Retanning of wet blue goat skins replacing the retanning agent by synthesized bio-polymeric composite
Sungur and Özkan (2017)	4.23	-	6,740	377	-	372	-	-	-	-	Raw wastewater from pickling, tanning, retanning, fatliquoring and other finishing processes of sheep leather

* Chromium as Cr_2O_3. **Results are in kg/t of raw hide

Capítulo 4

Impact of Post-tanning Chemicals on the Pollution Load of Tannery Wastewater

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Neste artigo é apresentada uma análise sobre a relação entre os produtos químicos e as cargas poluentes dos efluentes de acabamento molhado. O artigo foi publicado no periódico *Journal of Environmental Management*. Relatório Qualis Capes Engenharias II (2019): A1. Fator de Impacto: 5,647. DOI: https://doi.org/10.1016/j.jenvman.2020.110787

Highlights:

- Low exhaustion of post-tanning process shows most chemicals end up in wastewater.
- Deacidulation agents caused high conductivity and dissolved solids in wastewater.
- Retanning agents were responsible for the largest inorganic pollution load.
- Fatliquoring agents released the highest chemical oxygen demand and cytotoxicity.
- Nitrogen pollution is mainly related to the neutralizing retanner and the black dye.

Abstract:

The leather industry uses a large amount of chemicals to transform a raw hide into finished leather. Chemicals are not fully taken up by leather and thus end up in tannery wastewater. Physicochemical and toxicological characterization of tannery effluents has been widely assessed. However, the characterization of processing chemicals and their relation to the pollution load of effluents remains unknown. Thus, this study aimed to assess a physicochemical and cytotoxic characterization of chemicals used in the leather post-tanning process and to evaluate the contribution of each chemical to the pollution load of raw wastewater. This study was performed using a leather post-tanning formulation applied by a large tannery located in Brazil. Deacidulation agents caused high conductivity and dissolved solids in wastewater. Retanning agents (natural and synthetic tannins) were responsible for the largest inorganic pollution load, and synthetic tannins were more toxic than natural ones. Fatliquoring agents released the highest chemical oxygen demand load in wastewater and they were the chemical group that presented the highest toxicity. Fixing agent and black dye provided inorganic pollution load to wastewater, and nitrogen pollution of wastewater was mainly related to the neutralizing retanner and the black dye.

Keywords: Leather chemicals; Leather process; Post-tanning; Physicochemical characterization; Cytotoxicity.

4.1. Introduction

The leather industry is an important economic sector in many developing countries, having Brazil the biggest cattle herd in the world (ABQTIC, 2018). However, it can be a source of environmental pollution due to the discharge of potentially toxic and hazardous polluted wastewater into the environment if not properly treated for decontamination (de Souza et al., 2016; Yadav et al., 2019).

The leather process aims to transform putrescible material (raw hide) into a stable product with significant commercial value (finished leather). This transformation consists essentially of the three following phases of processing: beamhouse (eliminating the interfibrillar matter of the hide), tanning (stabilizing collagen protein), and finishing (adding performance and sensory properties to the leather, divided into post-tanning, drying, pre-finishing and finishing steps). The post-tanning (or also denominated as the wet end or wet finishing) is performed in a water medium in drums aiming to provide properly texture and structural properties to the leather, touch and color qualities, and to impart desired chemical, physicomechanical and fastness properties. Post-tanning consists of the chemical processes of deacidulation, retanning, dyeing, fatliquoring, and fixing.

Approximately 130 different types of chemicals are used by the leather industry (Sawalha et al., 2019). Chemical compounds such as deacidulants, synthetic and natural retanning agents, synthetic and natural oils, surfactants, dyes, chemical auxiliaries, and acids are added during the post-tanning process to ensure the desired properties to the leather (Ayoub et al., 2013; Ortiz-Monsalve et al., 2019; Piccin et al., 2016). These chemicals are not fully taken up by leather during processing and thus end up in tannery wastewater (Bharagava et al., 2018).

Physicochemical characterizations of raw post-tanning effluents have been performed by several studies. Main parameters evaluated are chemical oxygen demand (COD) (Pena et al., 2018; Sungur and Özkan, 2017), biochemical oxygen demand (BOD) (Islam et al., 2014; Mella et al., 2018), total dissolved solids (TDS) (Gutterres et al., 2015; Selvaraju et al., 2017), chromium (Fuck et al., 2011; Piccin et al., 2016; Raghava Rao et al., 2003), total kjeldahl nitrogen (TKN) (Açikel et al., 2017; Pena et al., 2018), ammoniacal nitrogen (NH4-N) (Gutterres et al., 2015; Ollé et al., 2016), conductivity (Açikel et al., 2017; Mella et al., 2018), chlorides (Basha et al., 2009; Karthikeyan et al., 2015), and sulfates (Karthikeyan et al., 2015; Rivela et al., 2004).

Due to the environmental concerns and risks of remains of contaminants released to the water bodies, biotoxicity of tannery effluents have also been assessed in bioassays using fish (Chagas et al., 2019; Taju et al., 2012), invertebrates (Bhattacharya et al., 2016; Verma, 2011), cytotoxicity in cell cultures (de Paris Júnior et al., 2019; Shakir et al., 2012), bacteria and/or algae (Ortiz-Monsalve et al., 2019; Tigini et al., 2011).

Although the characterization of tannery wastewater has been reported in several papers, few studies evaluated the physicochemical and toxicological characteristics of the chemical compounds applied in the leather process and their impacts on raw wastewater. Characterizations already performed in post-tanning chemicals include the determination of COD and BOD of four synthetic tannins (syntans) and three oils (Lofrano et al., 2007); COD, BOD and toxicity (invertebrates, algae and cress seed tests) analyzes on two syntans and two resins (Lofrano et al., 2008); toxicity of tannic acid using algae (Libralato et al., 2011), and the inorganic pollution load (chlorides, sulfates and sodium) of a dye and tannins (natural and synthetic) (Moreira et al., 2019). However, physicochemical and cytotoxic characterizations of several chemicals applied in leather, especially in the post-tanning process, remain unknown. It is necessary to clarify the impact of chemicals inputs on the discharges in raw wastewater.

Therefore, this paper aims to carry out a physicochemical and cytotoxic characterization of chemicals used in the leather post-tanning process and to evaluate the contribution of each chemical (individually and classified according to the application) in the pollution load of raw wastewater generated (untreated). This study was performed as a case study evaluating a leather post-tanning formulation applied by a large tannery located in southern Brazil. The knowledge of the physicochemical and cytotoxic characteristics of the evaluated chemicals can contribute to the identification of the most important sources of pollution in wastewater, allowing the optimization of leather processing.

4.2. Methodology

For this research, a case study was performed following the steps presented in the schema of Figure 4.1.

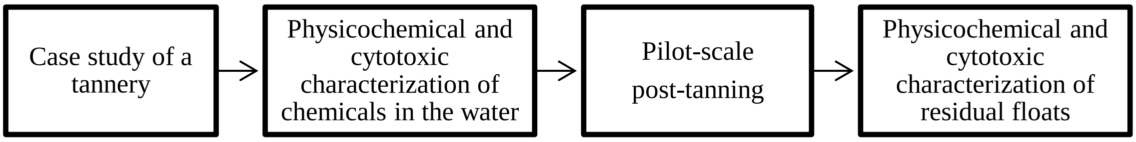

Figure 4.1: The study's methodology stages.

4.2.1. Case study

A case study was chosen to process wet-blue leather (from bovine hide) in a post-tanning formulation (Table 4.1) to produce leather for women bags manufacture. This formulation was chosen from a tannery located in southern Brazil with a production capacity of 750 whole leathers per day to produce daily around 3,000 m² finished leather for a sort of leather goods.

Transformation of wet-blue leather into finished leather is carried out through a series of processes and operations, carried out in steps. In the case study evaluated, these steps are divided into sorting, post-tanning, drying, pre-finishing, and finishing. Among these steps, post-tanning is the most relevant in terms of water and chemical consumption leading to wastewater generation. The post-tanning process consists of the following steps: deacidulation (also known as neutralization), retanning, dyeing, fatliquoring, fixing, samming, and stretching. The leather process is schematically shown in Figure 4.2, highlighting post-tanning operations.

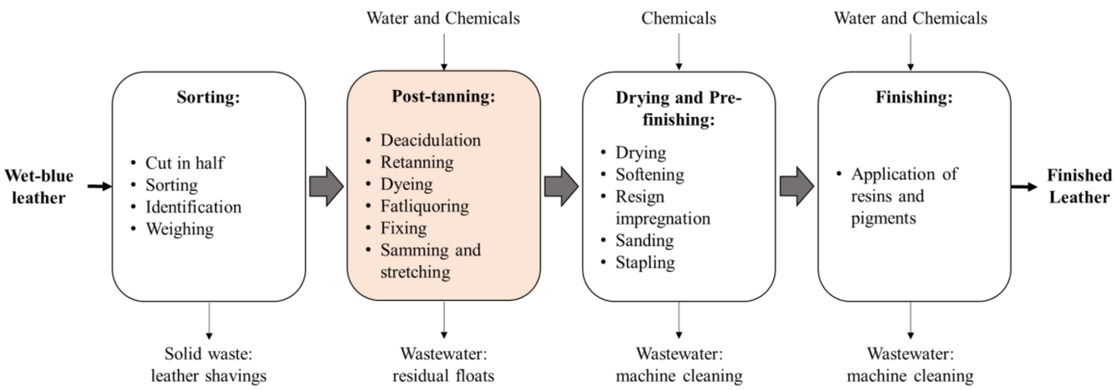

Figure 4.2: Case study processing steps.

Table 4.1: Chemical products in the post-tanning formulation.

Step	Chemical	Role in the process	Addition (%)*
(1) Deacidulation	Water		150
	Neutralizing retanner	Buffering neutralizer	1.5
	Sodium bicarbonate	Deacidulation agent	0.15
	Sodium formate	Deacidulation agent	1.5
Washing I	Water		200
(2) Retanning, fatliquoring and dyeing	Waterproofing agent	Waterproofing (Polymer)	0.2
	Sulphited natural oil 1	Fatliquor (Natural oil)	1
	Synthetic/natural oils 1	Fatliquor (Synthetic and natural oils)	1
	Vegetable tannin 1	Retanner (Acacia tannin)	6
	Syntan 1	Retanner (Syntan)	2
	Syntan 2	Retanner (Syntan)	4
	Sulphited natural oil 2	Fatliquor (Sulphited fish oil)	0.5
	Syntan 3	Retanner (Syntan)	3
	Vegetable tannin 2	Retanner (Acacia tannin)	2
	Black acid dye	Color	2.5
	Acrylic resin	Filler (Acrylic resin)	3
	Water		200
	Fixing agent	Fixation	1.4
Washing II	Water		200
(3) Fatliquoring and fixing	Water		200
	Synthetic/natural oils 1	Fatliquor (Synthetic and natural oils)	3
	Sulphited natural oil 1	Fatliquor (Natural oil)	3
	Synthetic/natural oils 2	Fatliquor (Synthetic and natural oils)	3
	Dyeing auxiliary agent	Fatliquor (Cationic oil)	0.5
	Antioxidant	Cr VI reducer	0.1
	Fungicide	Conservation	0.2
	Fixing agent	Fixation	1.0
Washing III	Water		200

*percentage by shaved wet-blue leather mass.

4.2.2. Physicochemical characterization

Chemicals of the post-tanning step were diluted alone in deionized water to achieve the concentration indicated by the formulation (Table 4.1) and were characterized for the following parameters: pH (Hach hq40d multi-analyzer), conductivity (Hach hq40d multi-analyzer), turbidity (SM 2130 B, 2017), COD (SM 5220 C, 2017), BOD (SM 5210 D, 2017), TKN (SM

4500 Norg, 2017), NH4-N (SM 4500 NH3 C, 2017), chlorides (SM 4110 B, 2017), sulfates (SM 4110 B, 2017), hardness (SM 2340 C, 2017), and TDS (Hach hq40d multi-analyzer).

4.2.3. Cytotoxicity assay

The cytotoxicity of chemicals was evaluated using fibroblast V79-4 cell line from Chinese hamster lung, obtained from Banco de Células do Rio de Janeiro (BCRJ). Cells were maintained in Dullbecco's Modified Eagle Medium (DMEM - Gibco®) modified to contain 4500 mg/L glucose and supplemented with 10% fetal bovine serum (FBS - Gibco®). Cell culture was maintained in a humid atmosphere at 5% CO_2, 37 ºC in a semi-open system.

The medium was prepared using DMEM, sodium bicarbonate, and 2-[4-(2-hydroxyethyl)piperazin-1-yl]ethanesulfonic acid (HEPES – Sigma-Aldrich®) and diluted in each sample. The pH of mediums containing samples was adjusted to 7.4 and the solutions were filtered using a 0.22 µm membrane (Sartorius Biolab®). Cells were seeded in 96-well plates at a density of 2×10^4 cells/well in DMEM 10% FBS. The medium was removed 24 h after cell seeding and replaced with the mediums containing samples and 1% FBS. Each sample was tested in five replicates and the assay was repeated three times in separate experiments for acute (24 h) and chronic (96 h) cytotoxicity.

Two cytotoxicity endpoints (tetrazolium reduction assay (MTT) and sulphorhodamine B (SRB) adsorption) were evaluated at the end of the incubation period. Cell morphologies were observed by an inverted microscope IX75 (Olympus®). MTT assay was performed to evaluate cellular toxicity through mitochondrial functionality. This assay was performed as described by Mosmann (1983). SRB assay was performed as described by Skehan et al. (1990). This assay measures the total biomass, based on cell protein amount colored by SRB dye. Dye adsorption is directly related to the number of cells. Assays with cell survival greater than 70%, compared to the negative control, were considered of low toxicity (Gencoglu et al., 2014).

4.2.4. Pilot-scale of the post-tanning process

Post-tanning of 540 g wet-blue leather with a thickness of 2.3 mm (after shaving) was performed with the same formulation (Table 4.1) in a pilot-scale rotating drum (Tandem GB R 35-6), under 26 rpm. The original and residual floats of the pilot-scale process were collected and characterized:

- Original float 1: deacidulation;
- Original float 2: retanning, fatliquoring, and dyeing;
- Original float 3: fatliquoring and fixing;
- Residual float 1: deacidulation and washing I;
- Residual float 2: retanning, fatliquoring, dyeing, and washing II;
- Residual float 3: fatliquoring, fixing, and washing III.

Each original and residual float was characterized according to the parameters: pH, conductivity, turbidity, COD, BOD, TKN, NH_4-N, chlorides, sulfates, hardness, TDS, and cytotoxicity, using the same characterization methods applied for chemicals. Additionally, chrome (SM 3111 D, 2017) was analyzed in residual floats to quantify some desorption of this metal from the raw material (wet-blue leather).

A mass balance was performed from the characterization of the original and residual floats. The input and output load (kg) of each step of the post-tanning process was calculated, as well as the mass retained by the leather. Mass balance was performed for the parameters COD, BOD, TKN, NH_4-N, chlorides, sulfates, hardness, and TDS using equation 1.

$$m_{accumulated\ j,i} = Cin_{j,i} * Vin_j - Cout_{j,i} * Vout_j \quad (1)$$

Where:

$m_{accumulated,j,\ i}$: accumulated mass of each physicochemical parameter i in step j (kg);

$Cin_{j,i}$: input concentration of physicochemical parameter i in step j (mg/L);

$Cout_{j,i}$: output concentration of physicochemical parameter i in step j (mg/L);

Vin: input volume of original float in step j;

Vout: output volume of residual float in step j.

4.3. Results and Discussion

4.3.1. Chemicals characterization

The impact of each chemical on physicochemical parameters and cytotoxicity of the post-tanning floats is shown in Table 4.2. Results are displayed in ranges.

To discuss the collected data, the main compositions of the evaluated chemicals were obtained from the safety data sheets and are shown on the Supplementary material along with their complete physicochemical and cytotoxic characterizations. Chemicals were divided into the following groups: neutralizing, retanning, fatliquoring, and other chemicals with various functions. Total and ammoniacal nitrogen were not analyzed when not necessary (when the substances do not have nitrogen in their molecule). Additionally, when TKN was not detected, ammoniacal nitrogen was not analyzed. Hardness and cytotoxicity assays were not performed in the Black acid dye due to its interference in colorimetric assays. Results obtained from physicochemical characterization were divided into quartiles, and cytotoxicity results were classified into four ranges (toxicity below 30% (low toxicity), toxicity between 30 and 50%, toxicity between 50 and 80%, and toxicity above 80%), to statistically identify the chemicals that most impact on each of the evaluated parameters.

Table 4.2: Impact of chemicals on the pollution load of raw post-tanning wastewater.

Chemical group	Chemical	Conductivity	Turbidity	COD	BOD	TKN	NH_4-N	Chloride	Sulfate	Hardness	TDS	Cytotoxicity (acute) MTT	Cytotoxicity (acute) SRB	Cytotoxicity (chronic) MTT	Cytotoxicity (chronic) SRB
Deacidulation agents	Sodium bicarbonate	+	-	- -	- -	- -	- -	- -	- -	- -	+	- -	- -	- -	- -
	Sodium formate	+ + +	- -	-	- -	- -	- -	- -	- -	- -	+ + +	+	-	+	+
	Neutralizing retanner	+ +	- -	-	+ +	+ +	+ + +	++	+	+	+ +	- -	- -	+ +	+ +
Retanning agents	Vegetable tannin 1	+	+ +	+ +	+	+	-	+ + +	+ +	+ + +	+	+	+	-	+
	Vegetable tannin 2	-	+ +	+	-	- -	- -	+ + +	-	+ +	-	- -	- -	+	+
	Syntan 1	+	+ + +	-	-	+ +	-	+	+ +	-	+	+	+	+ +	+ +
	Syntan 2	+ +	-	+	- -	- -	- -	+	+	- -	+ +	+ +	+ +	+ +	+ +
	Syntan 3	+	+	+ +	- -	- -	- -	+ +	+ + +	+	+	+ +	+ +	+ +	+ +
	Acrylic resin	-	- -	- -	- -	- -	- -	- -	-	- -	-	+ +	+	+ +	+ +
Fatliquoring agents	Sulphited natural oil 1	-	+ +	+ +	+ + +	- -	- -	- -	-	- -	-	+ +	+ +	+ +	+ +
	Sulphited natural oil 2	- -	+	+	+	- -	- -	-	- -	- -	- -	+ +	+ +	+ +	+ +
	Synthetic/natural oils 1	-	+ +	+ +	+	-	+ + +	- -	+	- -	-	+ +	+ +	+ +	+ +
	Synthetic/natural oils 2	-	+	+ +	+ + +	-	+	-	-	- -	-	+ +	+ +	+ +	+ +
	Dyeing auxiliary agent	- -	+	-	- -	+	+	-	- -	-	- -	+ +	+ +	+ +	+ +
Various functions agents	Waterproofing agent	- -	-	- -	- -	- -	- -	+	- -	- -	- -	- -	- -	+ +	+ +
	Fixing agent	+ + +	- -	- -	- -	- -	- -	+ + +	+ + +	- -	+ + +	- -	- -	-	- -
	Antioxidant	- -	-	- -	- -	- -	- -	+	- -	- -	- -	- -	- -	- -	- -
	Fungicide	- -	- -	- -	- -	- -	- -	-	- -	- -	- -	+ +	+ +	+ +	+ +
	Black dye	+ +	NA	+	- -	+ + +	- -	NA	NA	NA	+ +	NA	NA	NA	NA

Physichochemical: - - concentration below 1 st quartile. - concentration between 1st and 2nd quartile. + concentration between 2 nd and 3 rd quartile. + + concentration above 3rd quartile. + + + top outlier.
Cytotoxic: - - toxicity below 30% (low toxicity). - toxicity between 30 and 50%. + toxicity between 50 and 80%. + + toxicity above 80%.
NA: not analyzed

4.3.1.1. Deacidulation agents

Among the deacidulation agents, high conductivity and TDS were detected, especially in Sodium formate (cond.: 10,860 µS/cm and TDS: 6,040 mg/L) and neutralizing retanner (cond.: 4,700 µS/cm and TDS: 2,480 mg/L). Furthermore, the neutralizing retanner has a high concentration of TKN (680.96 mg/L), especially in the ammoniacal form (582.73 mg/L). Safety data sheet (Supplementary material) informs that it consists of an aromatic sulfone. Possibly, the applied aromatic sulfone has chemically bonded amino groups, given the nitrogen result. Tannery wastewater contains excessive nitrogen concentration, and conventional biological treatment usually achieves unsatisfactory nitrogen removal efficiency, which can cause eutrophication and reduction of dissolved oxygen in water (Lei et al., 2020; Wang et al., 2016). Therefore, minimizing neutralizing retanner consumption can significantly reduce nitrogen pollution load in tannery wastewater, being a cleaner alternative compared to the focus on end-of-pipe treatment.

Regarding the cytotoxicity assay, sodium formate reduced mitochondrial activity and protein content in both acute (MTT: 60.4% and SRB: 43.6% toxicity) and chronic (MTT: 50.9% and SRB: 72.3% toxicity) assays. Neutralizing retanner had a toxic effect only in the chronic exposure assay (MTT: 95.6% and SRB: 95.1% toxicity). Sodium bicarbonate showed no toxic effect in any of the tests performed. This behavior was expected as the cell maintenance medium (DMEM) contains this chemical.

4.3.1.2. Retanning agents

Retanning agents showed high COD and inorganic pollution load (chlorides and sulfates). Vegetable tannin 1 (23,771.97 mg/L) and syntan 3 (21,709.61 mg/L) were the retanners with the highest COD concentrations. Acrylic resin showed lower COD compared to vegetable and synthetic tannins, corroborating with reported results (Lofrano et al., 2008). Nevertheless, these chemicals have low BOD. The low BOD/COD ratios show their low biodegradability, due to the complex chemical structures of natural and synthetic tannins, composed of an extended set of chemicals such as phenol, naphthalene, and formaldehyde (Di Iaconi et al., 2010; Hassoune et al., 2017; Munz et al., 2009). High sulfate and/or chloride were detected on Vegetable tannins 1 and 2 and Syntans 1 and 3. These ions do not chemically bind to the collagen structure of wet-blue leather and therefore their main destination is to remain in the wastewater. Thus, retanning agents are the main source of sulfate and chloride in post-tanning wastewater. High sulfate concentration in syntans was also observed in previous study (Moreira et al., 2019). High hardness of vegetable tannins 1 and 2 suggest that sulfate and chloride ions are associated with calcium or magnesium cations. Also noteworthy is the high turbidity of syntan 1 (10,400.000 NTU). This chemical showed, visually, high presence of suspended solids.

Regarding the cytotoxicity assay, vegetable tannins showed less cytotoxicity than synthetic tannins, corroborating with reported results of De Nicola et al. (2007), which showed higher toxicity of a phenol-based synthetic tannin than mimosa tannin using *Paracentrotus lividus* embryos. Acute SRB assay of vegetable tannins showed about 10% cell toxicity, which indicates low cytotoxicity. While in acute MTT assay vegetable tannin 1 showed a reduction in the mitochondrial activity in 24 h (60.1% toxicity). Cytotoxic effects of vegetable tannins should be related to the presence of gallic acid and other polyphenols (Atif Ali, 2012). On the other hand, exposure to synthetic tannins 2 and 3 resulted in nearby 100% toxicity in both acute and chronic exposure tests. Phenol's (syntan 2) toxicity assessment has been already extensively studied, although no restriction has been set yet for this compound (Dixit et al., 2015), and naphthalene (Syntan 3) is currently classified as a possible human carcinogen, though this classification is under review (Carratt et al., 2016). In chronic assays, although all retanning agents showed toxicity, vegetable tannins showed about 50-60% toxicity, while synthetic tannins and acrylic resin showed toxicity above 90%.

4.3.1.3. Fatliquoring agents

Among the fatliquoring agents there are the highest COD concentrations, especially in sulphited natural oil 1 (22,258.47 mg/L), synthetic/natural oils 1 (24,020.88 mg/L) and synthetic/natural oils 2 (24,836.80 mg/L). Previous characterizations evaluating COD of syntans and oils also found higher COD in oils compared to the other analyzed chemicals (Lofrano et al., 2007). Higher BOD values, comparing to retanning agents, also appear in this chemical group. This shows a greater biodegradability, compared to retanning agents, although they have BOD/COD ratios below 0.20 (Supplementary material), which is usually considered as hardly biodegradable ones (He et al., 2007). Although natural oils typically have higher BOD/COD ratios compared to synthetic oils (Luo et al., 2011), no significant biodegradability differences were observed between synthetic and natural oils in the formulation. Conductivities are among the lowest since they correspond to organic chemicals with low ionization in the presence of water. The higher concentration of ammoniacal nitrogen was detected in synthetic oils compared to natural oils.

Regarding the cytotoxicity assay, all fatliquoring agents showed average cytotoxicity above 90%, presenting cytotoxicity at 24 h and 96 h of exposure. Fatliquoring agents are applied to the leather as oil emulsions, obtained by dispersing the oil in water using surfactants. Surfactants induce curvature stress in cell membranes which causes disordering and, finally, lysis (Nazari et al., 2012), being most likely responsible for the toxicity of this chemical group. Fatliquoring agents are the chemical group that contributes most to the cytotoxicity of the post-tanning wastewater.

4.3.1.4. Various functions agents

Among the various functions agents, the fixing agent has the highest sulfate concentration (highest sulfate concentration in the formulation: 2,824.752 mg/L), in addition to high conductivity (13,630 µS/cm), and TDS (7,620 mg/L). The Black acid dye showed high conductivity (9,020 µS/cm) and TDS (4,880 mg/L). The dye also has low biodegradability and the highest TKN concentration (853.57 mg/L) in the formulation. Nitrogen is present in the chemical structure of this dye with azo chemical groups (−N=N−).

Regarding the cytotoxicity assay, the waterproofing agent increased mitochondrial activity at 24 h and decreased it at 96 h. This is likely to be related to a mitochondrial compensatory response in the first 24 h of stress and not to a proliferative effect since this agent decrease (10%) the protein content at 24 h and was toxic after 96 h of exposition in both MTT and SRB assays. The fixing agent showed low cytotoxicity in all conditions evaluated. This chemical consists of a mixture of organic and inorganic acids. Thus, low cytotoxicity may be related only to cell fixation in the wells since the fixing agent used in the cytotoxicity assay also consists of acid (10% trichloroacetic acid).

Antioxidant had no toxic effect, as expected. Fungicide showed toxic effects in all assays. This effect is most likely related to the presence of chlorobenzene in fungicide composition (according to the safety data sheet), due to the high toxicity of halogenated benzene derivatives (Croute et al., 2002).

4.3.2. Post-tanning wastewater

Characterizations of original and residual floats were applied to the mass balance (equation 1) of each post-tanning step. This procedure was adopted in order to verify if the characteristics of the chemicals are similar to their generated wastewater and the percentage of chemical retention during leather processing. The mass balance is shown in Figure 4.3, where results are expressed in kilograms of pollutants per tonne of wet-blue leather and percentage of chemical retention.

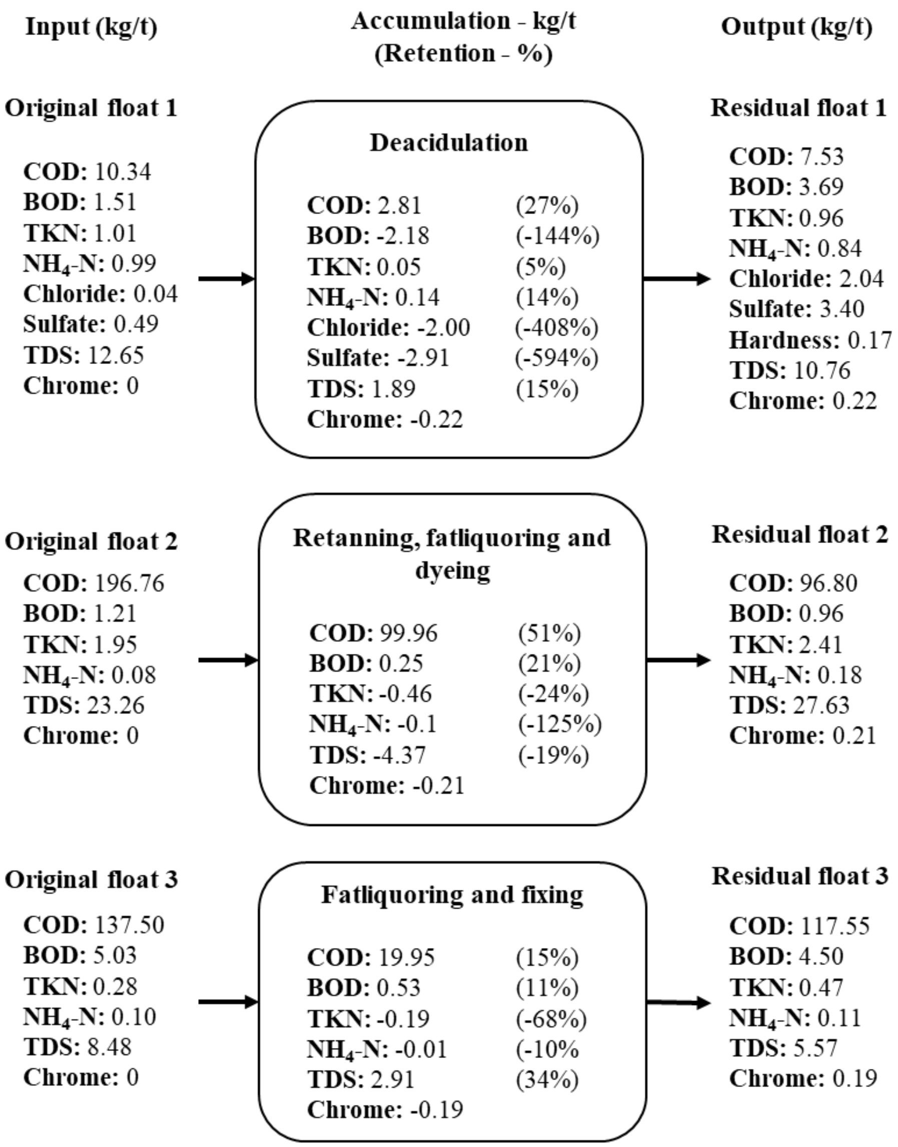

Figure 4.3: Mass balance of post-tanning.

The retention of physicochemical parameters in the post-tanning process is low, ranging from 5% to 51%. The low exhaustions in all process steps (deacidulation, retanning, dyeing, fatliquoring, and fixation) indicate an excess of chemicals applied to the leather processing. Therefore, most chemicals end up in the wastewater.

Negative retentions indicate parameters that are higher in the residual float compared to the original float. This occurs when compounds from previous steps are being removed from the leather. Chromium, for example, comes from the tanning step (Bufalo et al., 2018) and some removal occurs in the post-tanning stages (Black et al., 2013; Fuck et al., 2011).

Biodegradability of residual floats is higher than the original floats in all post-tanning steps, showing the retention of non-biodegradable compounds by leather. The main characteristics of each processing step are presented below.

- Deacidulation step has the highest ammoniacal nitrogen load due to the neutralizing retanner. This step also contributes significantly to TDS in wastewater, mainly due to sodium formate and neutralizing retanner.
- Retanning, fatliquoring, and dyeing step has the highest TDS load of all post-tanning process. The TDS come mainly from tannins, black dye, and fixing agent. A high COD load is observed at this stage, especially caused by tannins. However, chemical retention in leather (51%) reduces the impact of COD in wastewater. The highest TKN load is also observed in residual float 2 (due to the azo dye).
- Fatliquoring and fixing step causes the greatest COD pollution load in wastewater due to the fatliquoring agents.

Some technologies can be applied to wastewater treatment, according to the pollutant to be removed, such as: adsorption for dyes (Aljerf, 2018; Benvenuti et al., 2019; Gomes et al., 2016; Mella et al., 2019, 2017), phenolic substances (Aravindhan et al., 2009; Benvenuti et al., 2018), and chromium removal (Vilardi et al., 2018a); advanced oxidation processes using Fenton for COD removal (Vilardi et al., 2018b), electrochemical treatment for COD (Basha et al., 2009) and chromium removal (Mella et al., 2016), ozonation for COD and color removal (Preethi et al., 2009) and photoelectrochemistry for COD and color removal (Paschoal et al., 2009); membrane process for chromium recovery (Stoller et al., 2018); and biological treatments using fungi for dye degradation (Ortiz-Monsalve et al., 2019), microalgae to reduce nitrogen, phosphorus, ammonium, chemical and biochemical oxygen demands (Pena et al., 2020), and bacteria (Huang et al., 2015; Nachiyar and Rajkumar, 2003; Senthilvelan et al., 2014) to remove COD, BOD, and color.

Cytotoxicity results of the original and residual floats are shown in Figure 4.4. In the deacidulation step, the original float showed acute cytotoxicity for both MTT (71.5% toxicity) and SRB (68.6% toxicity) while the residual float showed low acute cytotoxicity in both tests (MTT: 18.7% and SRB: 22.5% toxicity). After 96 h of exposition, the residual float showed toxicity (MTT: 64,1% and SRB: 37.9% toxicity), although lower than that seen in the original float. This result demonstrates that the retention of chemicals by the leather causes toxicity depletion in residual float compared to the original float.

In the retanning, dyeing, and fatliquoring step there was an interference in the result, especially in the MTT test. This interference is due to the presence of the black dye (caused by its color) and the sedimentation of tannins in the wells, as shown in Figure 4.5. Possibly dye and tannins interference has been reduced in the residual float result due to the retention of these chemicals in the leather. The images obtained from the control, original and residual float (Figure 4.5) confirm their toxicity. Original (b) and residual (c) float samples showed changes in typical fibroblastic morphology, with membrane retraction, spheroid morphology and detachment of cells, with an evident minor number of cells compared to control (a).

Fatliquoring and fixing step (original and residual float 3) were toxic under all conditions studied. This result is consistent with the toxicity of the oil individually assessed.

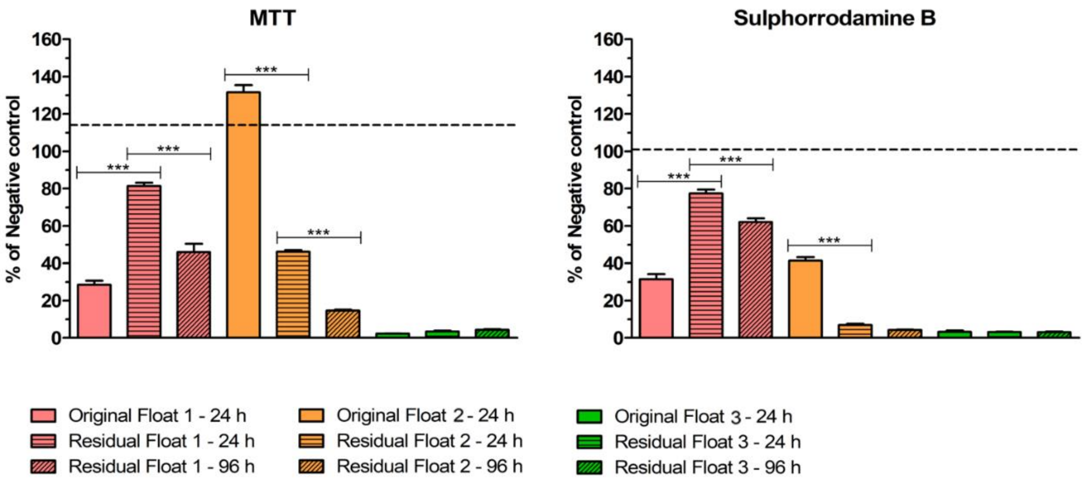

Figure 4.4: Cytotoxicity assays of original and residual floats.

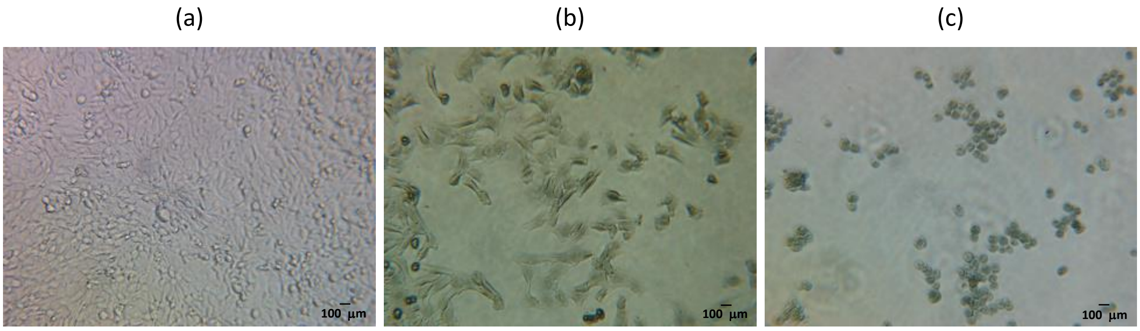

Figure 4.5: Cell morphology of Negative control (a), Original float 2 (b), and Residual float 2 (c).

4.3.3. Technological options to reduce pollution load of post-tanning effluents

Some alternatives have been already evaluated to reduce the impact of post-tanning chemicals on the pollution load of the liquid effluents. An environmental polyurethane was proposed by Wang et al. (2019) to reduce pollution caused by retanning agents, such as free formaldehyde in leather products and BOD, TDS, and total suspended solids in wastewater. The developed retanner could reduce environmental pollution compared to aldehyde retanning agent. Castor oil was prepared using nano-TiO2 as an emulsifying agent by mechanical mixing. The composite fatliquoring agent was easily biodegradable as compared to conventional modified castor oil (Lyu et al., 2016).

The leather industry is also striving to find natural and eco-friendly dyestuffs and auxiliaries since natural dyes are extracted from sustainable sources, and no hazardous chemicals are used while they are produced. Colorant from *Penicillium minioluteum* behaving like an acid dye was identified, extracted, purified, and characterized by Sudha et al. (2016), achieving uniform color diffusion. Monascus purpureus dye was applied to leather dyeing, with 70.6% absorption, good penetration, color homogeneity, and heat fastness (Fuck et al., 2018). Also, the use of microencapsulated essential oils as natural biocide was evaluated, showing the encapsulation gives rise for its bactericidal use in leather, maintaining its properties for more durability and controlled release in leather (Kopp et al., 2020).

A series of green cationic silicon-based gemini surfactants were tested by Bao et al. (2019) in the dyeing process, and showed higher absorption and fixation of dyes, compared to commercial dye-fixing agent, decreasing dye concentration in residual floats. The use of liquid dyes and tannins is also recommended to reduce the presence of sulfate, chloride, and sodium in wastewater, due to the lower amount of salts compared to solid chemicals (Moreira et al., 2019). Changes in processing conditions can also be made, such as the integrated rechroming, neutralization, and post tanning process proposed by Ayyasamy et al. (2005), achieving a reduction in pollution loads of COD (28%), TDS (34%) and chromium (72%).

4.4. Conclusions

The physicochemical and cytotoxic characterizations performed in this study provided important information for a cleaner post-tanning process:

- Deacidulation agents impart high conductivity and TDS to wastewater, and neutralizing retanner is responsible for the highest ammoniacal nitrogen load in post-tanning wastewater.
- Retanning agents (natural and synthetic tannins) are responsible for the largest inorganic pollution load (chlorides, sulfates, conductivity, and TDS) of post tanning wastewater. Regarding cytotoxicity assays, synthetic tannins are more toxic than natural ones.
- Fatliquoring agents release the highest COD load in wastewater and are the chemical group that presented the highest toxicity.

- Among the various functions agents, fixing agent and black dye provide inorganic pollution load to wastewater. Black dye and dyeing auxiliary agent contributes to the presence of TKN in wastewater, and the fungicide presents high cytotoxicity.

Tanneries with issues in meeting wastewater emission standards should implement optimizations in chemicals use, reducing the pollution load to be treated by wastewater treatment plants. The focus of optimization should be on the chemicals that most impact the critical parameters to be met.

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Supplementary material

Table 4.3: Main composition of post-tanning chemicals.

Table 4.4: Physicochemical characterization of post-tanning chemicals

Figure 4.6: Cytotoxicity assays of chemicals.

Table 4.3: Main composition of post-tanning chemicals.

Chemical Product	Main composition
Sodium bicarbonate	Sodium bicarbonate
Sodium formate	Sodium formate
Neutralizing retanner	Aromatic sulfone
Vegetable tannin 1	Modified acacia tannin
Vegetable tannin 2	Bisulfited acacia extract
Syntan 1	Dicyandiamide based synthetic tannin
Syntan 2	4,4'-sulfonyl bis (phenol) bisodium salt
Syntan 3	Synthetic naphthalene sulfonic tannin
Acrylic resin	Acrylic resin
Sulphited natural oil 1	Sulphited natural oils and butylglycol
Sulphited natural oil 2	Distillates (Fischer-Tropsch), heavy hydrocarbons (18 to 50 carbons) branched (cyclic and linear).
Synthetic/natural oils 1	Sulphited natural oil and synthetic oils
Synthetic/natural oils 2	Synthetic and natural oils with synthetic emulsifiers.
Dyeing auxiliary agent	Water-based ethoxylated alkyl derivatives
Waterproofing agent	2-Butenedioic acid, 2-methyl-1-propene and octadecene polymer and sodium salt
Fixing agent	Mixture of organic and inorganic acids
Antioxidant	Benzenopropanoic acid; 3,5-bis (1,1-dimethylethyl) -4-hydroxy-, c7-9-branched alkyl esters
Fungicide	bifenil-2-ol (50% to 70%); 4-cloro-3-metilfenol (30% to 50%); 2-octil-2H-isotiazol-3-ona (5% to 10%); chlorobenzene
Black acid dye	4-amino-6-((4-((4-(2,4-diaminophenyl)azo)phenylsulfamoyl)phenyl)azo) -5hydroxy-3-((4-nitrophenyl)azo)naphthalene-2,7-disulfonate disodium

Table 4.4: Physicochemical characterization of post-tanning chemicals.

Chemical group	Chemical	pH	Conductivity (µS/cm)	Turbidity (NTU)	COD (mg/L)	BOD (mgO$_2$/L)	BOD/COD	TKN (mg/L)	NH$_4$-N (mg/L)	Chloride (mg/L)	Sulfate (mg/L)	Hardness (mgCaCO$_3$/L)	TDS (mg/L)
Deacidulation agents	Sodium bicarbonate	7.93	1,021	1.323	ND	ND	-	NA	NA	2.260	ND	ND	507
	Sodium formate	6.41	10,860	1.147	2,829.25	35	0.01	NA	NA	14.328	6.016	ND	6,040
Retanning agents	Neutralizing retanner	5.92	4,700	0.617	5,556.63	>1,005	>0.18	680.96	582.73	31.857	325.354	197.12	2,480
	Vegatable tannin 1	4.34	2,470	471.333	23,771.97	523	0.02	171.15	7.57	80.524	716.380	733.04	1,253
	Vegetable tannin 2	5.20	958	151.000	13,014.67	462	0.04	23.80	2.87	71.766	54.722	326.48	473
	Syntan 1	7.50	2,500	10,400.000	3,134.29	422	0.13	364.42	15.48	23.365	604.535	187.26	1,264
	Syntan 2	4.77	6,430	3.000	19,337.46	<322	<0.02	ND	NA	26.545	295.331	ND	3,390
	Syntan 3	5.66	4,250	13.500	21,709.61	<322	<0.01	19.50	3.10	31.120	1,274.540	221.76	2,210
	Acrylic resin	6.79	492	0.427	2,202.16	ND	-	ND	NA	11.158	8.995	ND	237
Fatliquoring agents	Sulphited natural oil 1	6.71	388	227.000	22,258.47	2,213	0.10	ND	NA	19.108	33.168	ND	186.6
	Sulphited natural oil 2	5.87	79.5	134.000	5,876.47	543	0.09	ND	NA	20.144	6.487	ND	37
	Synthetic/ natural oils 1	7.41	406	138.000	24,020.88	925	0.04	34.98*	39.34*	19.832	76.284	8.26	196.9
	Synthetic/natural oils 2	7.75	692	37.133	24,836.80	2,364	0.10	24.66	17.20	21.174	14.083	11.57	339
Various functions agents	Dyeing auxiliary agent	6.35	89.7	4.327	2,639.03	27	0.01	61.00	21.62	20.321	4.828	21.16	41.2
	Waterproofing agent	7.35	209.4	1.450	270.06	ND	-	ND	NA	21.986	ND	ND	100.1
	Fixing agent	1.50	13,630	0.370	731.15	210	0.29	ND	NA	51.349	2,824.752	ND	7,620
	Antioxidant	4.85	12.96	3.940	97.46	ND	-	ND	NA	22.288	1.579	ND	5.55
	Fungicide	4.86	13.86	1.193	1,287.05	ND	-	3.94	ND	21.784	ND	ND	6.3
	Black dye	9.39	9,020	NA	10,445.15	ND	-	853.57	4.07	NA	NA	NA	4,880

NA - not analyzed. ND - not detected. *Ammoniacal nitrogen is slightly higher than total kjeldhal nitrogen due to possible presence of interferents in the sample.

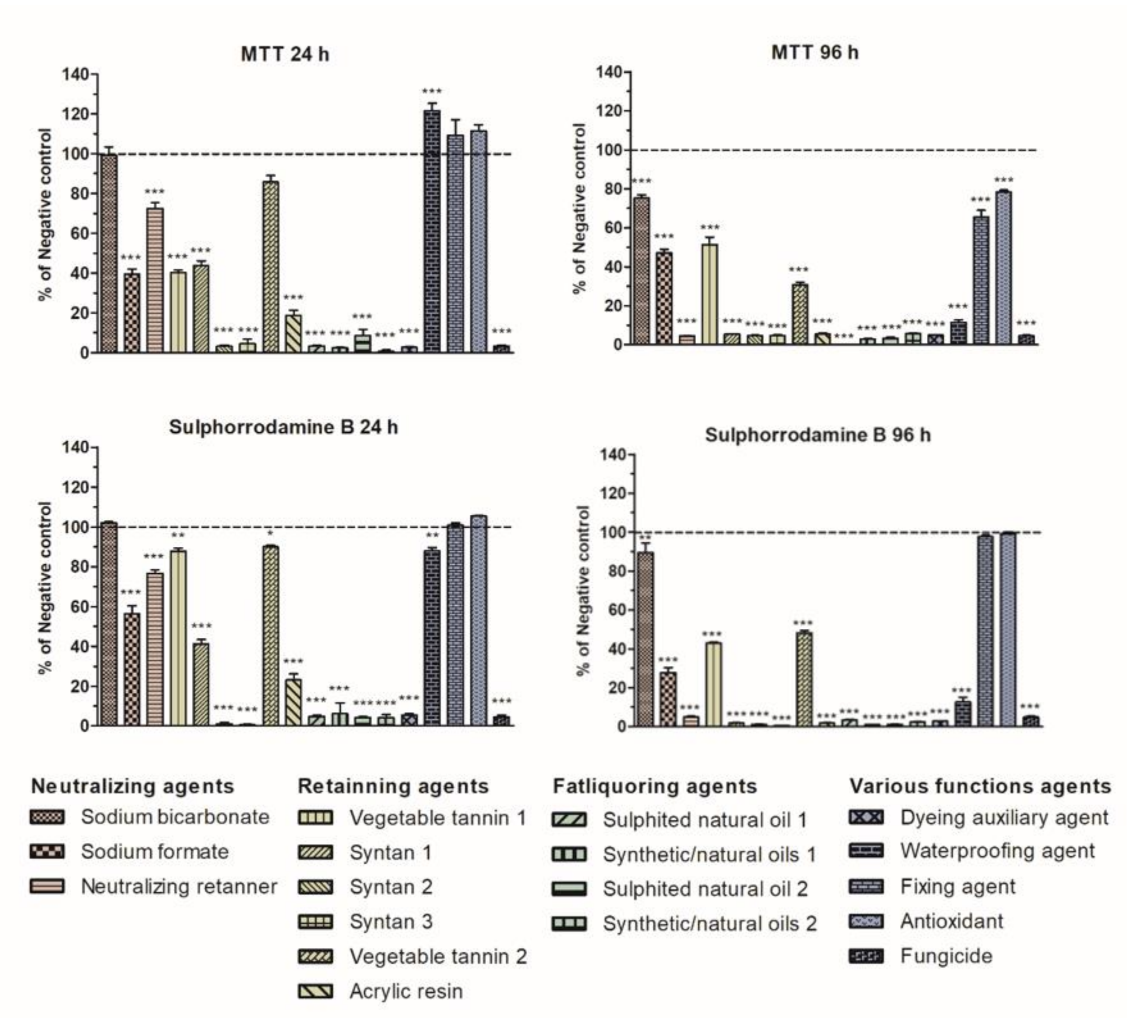

Figure 4.6: Cytotoxicity assays of chemicals.

Capítulo 5

Scale-up Testing for Reducing Pollution Load of Chemicals in Wastewater of Leather Post-Tanning

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Neste artigo são apresentados os testes de redução na oferta de produtos químicos (recurtentes e óleos) no processo de acabamento molhado, visando a redução da carga poluente dos efluentes líquidos bem como dos custos da formulação. Este artigo foi submetido para revisão para ser publicado no periódico *Process Safety and Environmental Protection*. Relatório Qualis Capes Engenharias II (2019): A1. Fator de Impacto: 4,966.

Highlights:

- Adjusting the supply of chemicals was efficient to reduce wastewater pollution load.
- Post-tanning formulation costs were reduced by 24%.
- Reduction in the supply of leather chemicals did not affect the physical-mechanical properties of the leather.
- Scale-up of the adjusted formulation confirmed pilot-scale results.

Abstract:

The leather industry has been looking for alternatives to minimize its environmental impacts, including studies to reduce the pollution load of liquid effluents from the leather process. Although studies reducing the supply of chemicals have already indicated optimized offers of fatliquoring and retanning agents, the effect of the scale-up of these optimized conditions on effluents and the quality of the leather remains unknown. This study aims to reduce the pollution load of post-tanning effluents by reducing leather chemicals supply. Tests were performed on pilot and industrial scales, reducing the offer of retanners and fatliquors in two levels: 19 and 26%. The effluents were tested for pH, conductivity, dissolved solids, sulfate, biochemical oxygen demand, and chemical oxygen demand. The leather was tested for organoleptic properties and physical-mechanical tests. The reduction of chemicals allowed the depletion of the raw wastewater pollution load. The leather obtained showed a quality within the established standards. Besides, post-tanning formulation costs were reduced by 24%.

Keywords: leather chemicals; pollution depletion; retanning; fatliquoring.

5.1. Introduction

Traditional leather production is responsible for a high consumption of water and chemicals to achieve the desired properties of finished leather (Ritterbusch et al., 2019). The leather process consists of four main phases of processing: beamhouse (rehydration, cleaning, and hair removal), tanning (stabilizing collagen protein to transform the hide into leather), post-tanning (provides properly texture, touch, color, and structural properties to the leather), and finishing (adding sensory properties to the leather). The post-tanning stage is performed in a water medium in rotating drums and consists of the chemical processes of deacidulation, retanning, dyeing, fatliquoring, and fixing.

Leather chemicals such as deacidulants, synthetic and natural fatliquoring agents, surfactants, synthetic and natural retanning agents, dyes, chemical auxiliaries, and acids are used during the post-tanning process to ensure the desired properties to the leather (Hansen et al., 2020; Ortiz-Monsalve et al., 2019; Piccin et al., 2016). These chemicals are not fully taken up by leather during processing and are disposed of with wastewater, presenting a significant impact on the efficiency of treatment techniques (Hansen et al., 2021a). Thus, the high concentration of pollutants, low biodegradability (Hansen et al., 2021b; Saxena et al., 2016), and toxicity (Pena et al., 2020; Tasca and Puccini, 2019) of post-tanning wastewater is a major source of environmental concern.

A previous study (Hansen et al., 2020) has already shown the relationship between leather chemicals and the pollution load of wastewater. The study suggested that tanneries with issues in meeting wastewater emission standards should implement optimizations in chemicals use, reducing the pollution load to be treated by wastewater treatment plants. Furthermore, the assessment of the environmental impacts of tannery wastewater and chemicals showed that leather processes in several developing countries require to be optimized for chemical and water consumption (Saxena et al., 2016).

To reduce the environmental impact of tanneries, studies have been looking for cleaner leather production, focused on adjusting process conditions, minimizing leather chemicals use, and replacing polluting chemicals with less polluting ones. Among the alternatives evaluated are the replacement of synthetic tannins by retanning agents that are more biodegradable (Selvaraju et al., 2017), less toxic (Liu et al., 2020), and that causes lower pollution load in effluents (Wang et al., 2019). Natural dyes were also developed and tested to replace synthetic dyes (Fuck et al., 2018; Priya et al., 2016; Sudha et al., 2016), avoiding the use of hazardous chemicals. A clove essential oil was also tested for its biocidal characteristics in leather as an alternative to synthetic biocides (Kopp et al., 2020). The production of less polluting fatliquors was also evaluated. Oil-in-water emulsions were obtained by applying nano-TiO2 (Lyu et al., 2016) and ultrasound (Sivakumar et al., 2008). These processes avoided the consumption of sulfuric acid and surfactant agents to produce oil emulsions.

Studies also aimed to reduce chemicals remaining in the baths at the end of leather processing. These studies focused on optimizing the supply of chemical products (Gutterres, 2003; Zhang et al., 2017) and on maximizing the exhaustion of process baths by optimizing parameters such as pH, temperature, and bath time (Ayyasamy et al., 2005; Gutterres and Santos, 2009; Haroun, 2005; Kanagaraj et al., 2016). The environmental benefits of these cleaner products and processes are mainly related to the reduction of the pollution load of liquid effluents generated in the process.

Although optimized offers of post-tanning chemicals such as fatliquoring and retanning agents have been investigated, tanneries keep using high amounts of chemicals inputs, the effect of reducing chemicals not compromising the quality of the leather after the scale-up process remains unknown. Thus, the objective of this study is to evaluate the reduction in the supply of leather chemicals (pilot and industrial-scale) in leather quality and wastewater in a post-tanning formulation used by a large tannery located in Brazil. The reduction of chemicals consumption aims to minimize the pollution load of wastewater, meeting the desired properties of the leather. The present study is a contribution with a technical alternative and methodology for tanneries aiming to reduce the pollution load of their liquid effluents.

5.2. Methodology

This study was developed using a post-tanning formulation applied by a large tannery company located in Brazil, with a production capacity of 750 whole leather per day corresponding to around 3000 m² finished leather for a sort of leather goods. The methodology steps of this study are shown in Figure 5.1.

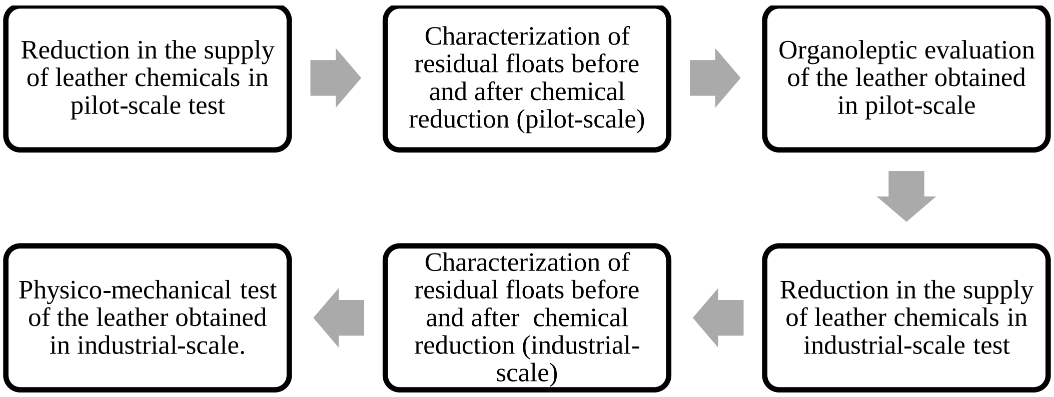

Figure 5.1: Methodology steps.

The post-tanning formulation used in this case study was provided by the tannery and is used to produce leather for women's handbags. The global handbag market size was valued at USD 47 billion in 2018, and leather bags dominated the market and accounted for a 48.5% share of the global revenue (Global Industry Report, 2019). This formulation (Table 5.1) was previously studied to characterize the pollution load of each leather chemical (Hansen et al., 2020) and is the most applied formulation by the tannery. The leather chemicals were characterized by the previous study showing that retanning agents (natural and synthetic tannins) are responsible for the largest inorganic pollution load of post-tanning wastewater, and fatliquoring agents release the highest chemical oxygen demand (COD) load in wastewater. Based on this previous study and considering that the retanning and fatliquoring agents represent the majority of post-tanning chemicals, this study focused on minimizing the consumption of retanning and fatliquoring agents.

Table 5.1: Post-tanning formulation.

*percentage by wet-blue leather mass.

Step	Chemical	Main composition	Role in the process	Addition (%)*	Temp. (°C)	Time (min)
	Water			150	35	
(1) Deacidulation	Neutralizing retanner	Aromatic sulfone	Buffering Neutralizer	1.5		10
	Sodium bicarbonate	Sodium bicarbonate	Deacidulation agent	0.15		
	Sodium formate	Sodium formate	Deacidulation agent	1.5		120
(2) Washing	Water			200	30	10
	Waterproofing agent	2-Butenedioic acid, 2-methyl-1-propene and octadecene polymer and sodium salt	Waterproofing (Polymer)	0.2		
	Sulphited natural oil 1	Sulphited natural oils and butylglycol	Fatliquoring agent	1		
	Synthetic/ natural oils 1	Sulphited natural oil and synthetic oils	Fatliquoring agent	1		10
	Vegatable tannin 1	Modified acacia tannin	Retanning agent (Acacia tannin)	6		
	Syntan 1	Dicyandiamide based synthetic tannin	Retanning agent (Syntan)	2		
	Syntan 2	4,4'-sulfonyl bis (phenol) bisodium salt	Retanning agent (Syntan)	4		20
(3) Retanning, fatliquoring and dyeing	Sulphited natural oil 2	Distillates (Fischer-Tropsch), heavy hydrocarbons (18 to 50 carbons) branched (cyclic and linear)	Fatliquoring agent (Sulphited fish oil)	0.5		
	Syntan 3	Synthetic naphthalene sulfonic tannin	Retanning agent (Syntan)	3		20
	Vegetable tannin 2	Bisulfited acacia extract	Retanning agent (Acacia tannin)	2		
	Black acid dye	4-amino-6-((4-((4-(2,4-diaminophenyl)azo)phenylsulfamoyl)phenyl)azo) -5hydroxy-3-((4-nitrophenyl)azo)naphthalene-2,7-disulfonate disodium	Color	2.5		60
	Acrylic resin	Acrylic resin	Retanning agent (Acrylic resin)	3		
	Water			200	60	
	Formic acid	Formic acid	Fixation	1.4		
(4) Washing II	Water			200	60	10
	Water			200	60	
	Synthetic/natural oils 1	Sulphited natural oil and synthetic oils	Fatliquoring agent	3		
	Sulphited natural oil 1	Sulphited natural oils and butylglycol	Fatliquoring agent	3		
	Synthetic/natural oils 2	Synthetic and natural oils with synthetic emulsifiers.	Fatliquoring agent	3		
(5) Fatliquoring and fixing	Dyeing auxiliary agent	Water-based ethoxylated alkyl derivatives	Fatliquor (Cationic oil)	0.5		
	Antioxidant	Benzenopropanoic acid; 3,5-bis (1,1-dimethylethyl) -4-hydroxy-, c7-9-branched alkyl esters	Cr VI reducer	0.1		
	Fungicide	bifenil-2-ol (50% to 70%); 4-cloro-3-metilfenol (30% to 50%); 2-octil-2H-isotiazol-3-ona (5% to 10%); chlorobenzene	Conservation	0.2		60
	Formic acid	Formic acid	Fixation	1.0		35
(6) Washing III	Water			200	60	

5.2.1. Pilot-scale tests

Tests to reduce the supply of chemicals on a pilot-scale rotating drum (wooden drum with a capacity of 25 kg) (Figure 5.2) were carried out at two levels of reduction (Table 5.2): reduction of 19% and 26% in chemicals supply (focusing on reducing retanning and fatliquoring agents). The objective was to reduce up to approximately a quarter of the chemical supply in the formulation. Three half wet-blue leather (provided by the regular supplier of the tannery) with an average thickness of 1.7 mm were used for each pilot-scale test.

Figure 5.2: Pilot-scale drum.

Leather chemicals were organized in Table 5.2 into three groups: retanning agents, fatliquoring agents, and other chemicals (neutralizing retanner, sodium bicarbonate, sodium formate, waterproofing agent, black acid dye, formic acid, antioxidant, and fungicide). All fatliquoring and retanning agents had the same percentage reduction.

Table 5.2: original formulation and formulations with 19% and 26% chemicals reduction.

Chemicals	Original formulation (%)	19% average chemicals reduction (%)	26% chemicals reduction (%)
Retanning agents	20.00	15.50 (23% reduction)	12.90 (36% reduction)
Fatliquoring agents	12.50	9.30 (26% reduction)	8.90 (29% reduction)
Other chemicals	8.55	8.55	8.55
Sum of chemicals	41.05	33.35	30.35

All percentage values are by wet-blue leather mass.

The offers of fatliquoring (9.3% and 8.9%) and retanning (15.5% and 12.9%) agents of the adjusted formulations are within the range indicated by the literature to ensure good properties to the leather. Fatliquoring supply below 5% offers just sufficient softness (Heidemann, 1993) and above 6% on a dry basis showed a greater softening effect (Gutterres, 2001). On the other hand, the offer of 10% of fatliquors was excessive (Gutterres, 2003; Heidemann, 1993). Regarding retanning agents, the offers in the adjusted formulations considered previous studies that indicates minimum amounts of vegetable and synthetic tannins from 6 to 12%, according to the type of tannin (Stather and Pauligk, 1961), and solutions as high as 20% (Heidemann, 1993).

The residual floats of the original process (with no reduction in chemicals supply) and after chemicals reduction (19% and 26% reduction) in pilot-scale tests were collected. As no reduction in the chemicals supply of deacidulation step (1) was implemented, no reduction in the pollution load of residual floats from this step was expected. Thus, residual floats from deacidulation were not characterized in this study. For each condition (no reduction and 19% and 26% reduction) the floats were collected as it follows:

- Residual floats I: retanning, fatliquoring, dyeing (3) and washing II (4);

- Residual floats II: fatliquoring and fixing (5), and washing III (6).

The residual floats were characterized for pH, total dissolved solids (TDS), and conductivity using Hach hq40d multi-analyzer. The leather obtained from the pilot-scale tests was organoleptically evaluated. Results of hand and visual evaluation method are subjective, although, reliable, since it is performed by experienced technicians (Kanth et al., 2009). This study evaluated softness, filling, grain and visual analysis of resin impregnation of the leather. For this test a scale from 1 to 5, previously evaluated by Ritterbusch et al. (2019), was stablished, 1 being the worse and 5 being the best results. The evaluation was carried out by three technicians of the leather industry, and the average results and standard deviations were calculated. In the impregnation test, technicians observed the process of absorption of acrylic resin by leather. The objective was the complete and uniform absorption of the resin solution by the leather, promoting the leather filling.

5.2.2. Industrial-scale tests

Based on the results of the pilot-scale tests, reduction in the supply of leather chemicals was tested on an industrial-scale in a wooden drum with a capacity of 2,200 kg (Figure 5.3), applying 26% reduction of chemicals supply (reducing retanning and fatliquoring agents).

Figure 5.3: Industrial-scale drum.

The industrial-scale residual floats I and II obtained before and after the reduction in chemicals supply were characterized to verify the impact on the pollution load of liquid effluents. Wastewater characterizations was performed considering the following parameters: pH (SM 4500 H+, 2017), conductivity (SM 2510 B, 2017), TDS (SM 2540 C, 2017), biochemical oxygen demand (BOD) (SM 5210 D, 2017), COD (SM 5220 C, 2017), and sulfate (SM 4110 B, 2017).

Physical-mechanical tests were carried out on finished leather obtained after chemicals reduction in industrial-scale, to verify if the leather produced meets the requirements for the desired application. The tests performed include tear resistance strength (ISO 3377-1:2011, 2011), colorfastness to light (ASTM D1148, 2018), colorfastness to friction (with wool felt wet with water) (ISO 11640, 2012), and colorfastness to friction (with wool felt wet with alcohol) (ISO 11640, 2012), performed in triplicate. During the tear resistance strength tests, leather samples are tested in a dynamometer, where the samples are tensioned until their total tearing occurs. The colorfastness to light consists of determining the color stability of the leather under the action of a 300 W ultraviolet light. The colorfastness to friction consists of determining the color resistance to the action of a frictional force produced by a wool felt in cycles of to-and-fro rubbing. It is expected no damage to the leather and staining of the felt after 100 cycles (Ritterbusch et al., 2014).

To assess the reduction in formulation costs, the costs of leather chemicals were provided by the tannery. The cost of the original formulation was calculated using the dollar rate of 3/15/2020, and the cost of the adjusted formulation was calculated using the dollar rate of 6/30/2020. To preserve the confidentiality of tannery information, costs were normalized, dividing the cost before and after adjusting the process by the cost of the original formulation.

5.3. Results and discussion

5.3.1. Pilot scale tests

Results of pH, conductivity, and TDS of residual floats I and II before and after 19% and 26% chemicals reduction are shown in Table 5.3. Results in parentheses are the percentage reduction of each parameter after the reduced supply of chemicals, compared to the original formulation.

Table 5.3: Evaluation of the residual floats I and II (original process, 19% and 26% chemicals reduction).

Identification of residual float	pH	Conductivity (μS/cm)	TDS (mg/L)
Residual float I (original process)	3.90	1,994	11,580
Residual float I (19% chemicals reduction)	3.81	1,897 (5% reduction)	10,870 (6% reduction)
Residual float I (26% chemicals reduction)	3.75	1,789 (10% reduction)	9,440 (19% reduction)
Residual float II (original process)	3.72	689	3.62
Residual float II (19% chemicals reduction)	3.65	652 (5% reduction)	3.47 (4% reduction)
Residual float II (26% chemicals reduction)	3.62	586 (15% reduction)	3.10 (14% reduction)

Chemicals reduction of 19 and 26% resulted in a depletion in the pollution load of the liquid effluents, with the greatest reduction in chemical inputs (26%) resulting in the lowest pollution load. Results show the high inorganic load in the post-tanning floats, corroborating with results of previous studies (Hansen et al., 2020; Moreira et al., 2019), with most of the dissolved solids consisting of ions that increase conductivity.

To verify if the reduced supply of leather chemicals interferes with the quality of the leather produced, the average results, and the standard deviation of the organoleptic tests are shown in Figure 5.4. It is observed that the average results and standard deviation (SD) of softness, filling, and grain did not change after chemicals reduction compared to the original formulation. Besides, a better average impregnation with a reduction in the supply of chemicals is observed. The improvement in visual analysis of leather impregnation with a lower dosage of chemicals may be related to a better penetration of the dispersion of acrylic resin, due to the lower concentration of other chemicals, which no longer compete in the diffusion into the leather.

These results show that a reduced supply of chemicals does not imply the reduction of organoleptic properties of the leather. Based on these results, the largest reduction in chemicals tested on the pilot-scale tests (26% reduction) was used for the industrial-scale tests.

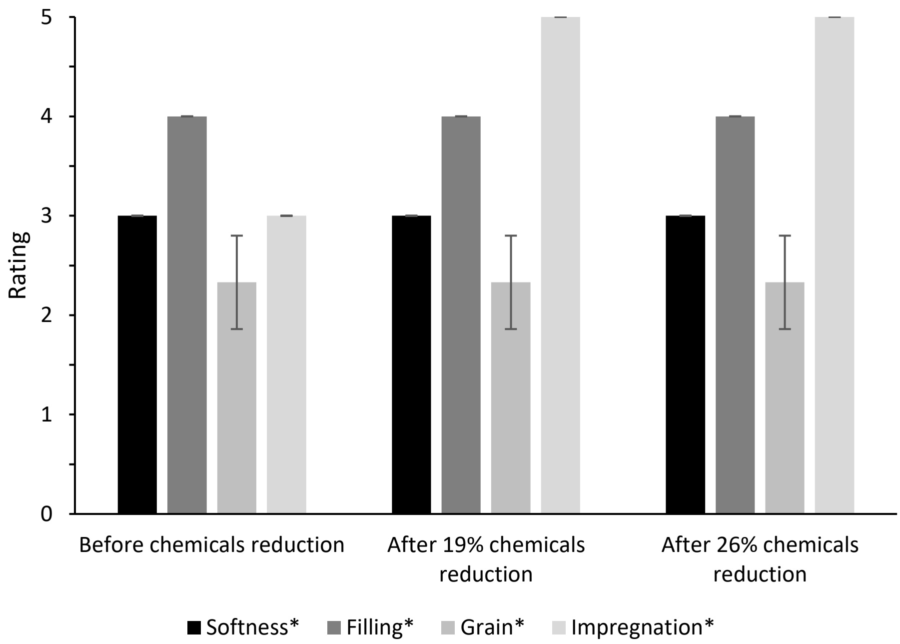

Figure 5.4: Organoleptic evaluation of the leather produced.

5.3.2. Industrial-scale tests

Figures 5.5 and 5.6 present TDS, sulfate, BOD, and COD concentrations of the residual floats I and II before and after 26% reduction in the supply of chemical products. Percentage reductions are also shown in each evaluated parameter. The analytical method used did not allow the comparison of conductivity results due to a low maximum quantification conductivity of 5,000 µS/cm (all results were above 5,000 µS/cm conductivity).

It is possible to observe a reduction in the pollution load of all other parameters of the liquid effluents. TDS (Figure 5a) and sulfate (Figure 5b) behaviors have similar reductions. Retanning agents contribute significantly to these parameters (Hansen et al., 2020). Thus, the higher concentration observed in residual float I, compared to residual float II was expected. Besides, reductions observed in TDS and sulfate (ranging from 13.5% to 20.8%) are consistent with the reduction implemented in chemicals supply (26%). The reduction of the pollution loads of the residual floats do not exactly correspond linearly to the reduction in the chemicals supply (it is slightly below) due to the continuous removal of chemicals from the material (wet blue leather), as is the case of sulfate from the tanning step (from chromium salt), that continues to be removed (Black et al., 2013). On the other side, the uptake of chemicals tends to a limit that is related to the capacity of the collagen structure to interact with the chemicals (Kanagaraj and Panda, 2011).

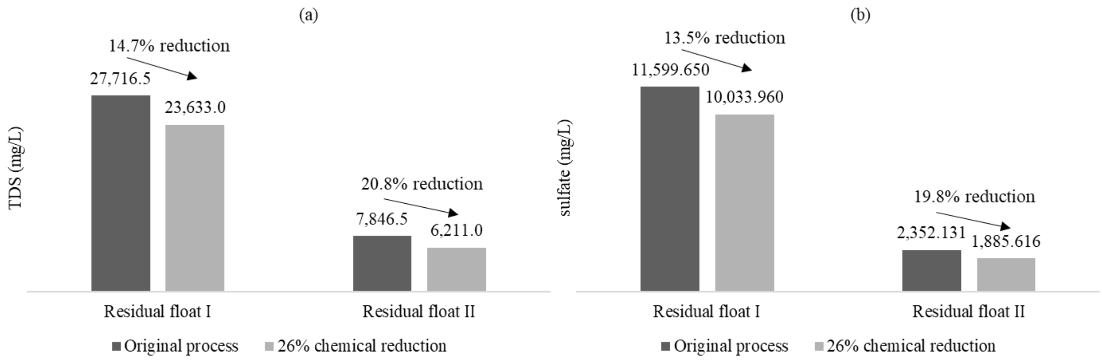

Figure 5.5: TDS (a) and sulfate (b) of residual floats I and II.

BOD (Figure 5.6a) and COD (Figure 5.6b) of the residual float II are higher than those of the residual float I. This behavior was expected since fatliquoring agents are the major contributors to BOD and COD in post-tanning wastewater (Hansen et al., 2020; Lofrano et al., 2013). Besides, residual float I showed lower biodegradability compared to residual float II, since floats containing tannins (residual float I) are hard to biodegrade (Saxena et al., 2016). The high exhaustion observed in the residual float II (89.8% BOD reduction and 46.9% COD reduction) indicates that the reduction in the supply of chemicals improved the diffusion of fatliquoring agents into the leather. Thus, the reduction in the pollution load of BOD and COD were higher than the reduction of chemicals implemented (26%).

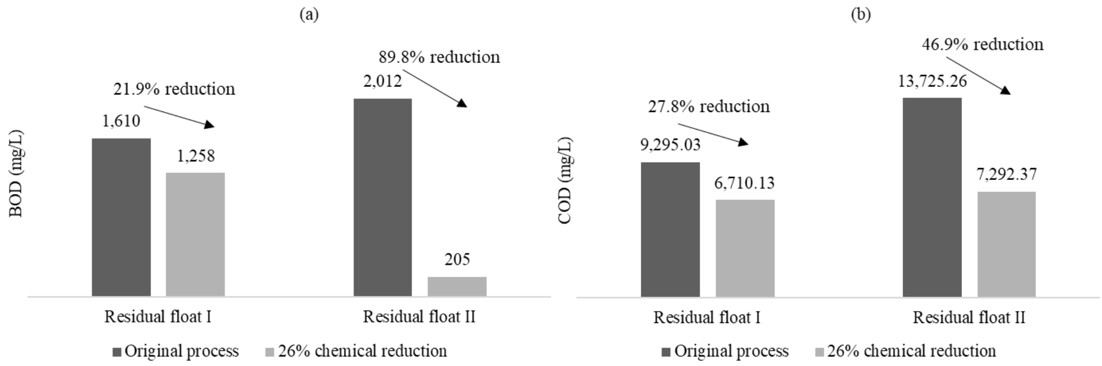

Figure 5.6: BOD (a) and COD (b) of residual floats I and II.

The physical-mechanical tests performed on the leather produced are presented in Table 5.4 (average and standard deviation – SD). Comparing physical-mechanical results with the quality requirements it is observed that all requirements are met.

Table 5.4: Physical-mechanical tests of the finished leather after 26% chemicals reduction.

Physical-mechanical test	Result	Requirement
Tear resistance strenth	107.91	60 N for large handbag ISO 3377-1:2011 (2011)
Colorfastness to light	5	≥ 3 Basf (2005)
Colorfastness to friction - wet	5	≥ 3 Basf (2005)
Colorfastness to friction - alcohol	4 to 5	≥ 3 Basf (2005)

The normalized costs of the original formulation and the formulation after 26% leather chemicals reduction are shown in Figure 5.7.

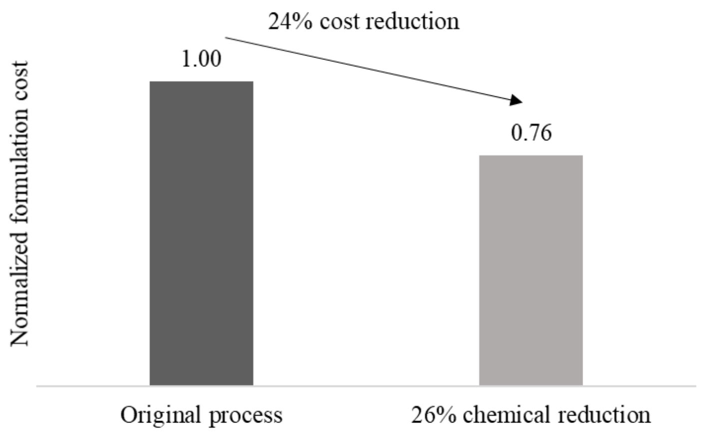

Figure 5.7: Cost reduction of post-tanning formulation.

The adjustment in the supply of chemicals reduced the cost of the formulation by 24%, leading to greater competitiveness for the evaluated tannery. This costs reduction considers only the amount of chemicals saved. Additional savings can be achieved with chemical logistics and costs reduction in the treatment of less polluted wastewater.

5.4. Conclusions

The reduced consumption of leather chemicals was efficient in reducing the environmental impact of the post-tanning process. The residual floats of the pilot-scale tests showed a reduction in the pollution load of conductivity and TDS. Besides, the proposed formulations maintained organoleptic properties in terms of softness, filling and grain and improved impregnation at the two levels of leather chemicals reduction.

With the results of the pilot-scale tests, the highest reduction (26%) of chemicals was implemented on an industrial-scale. The residual floats of the industrial-scale tests showed a reduction in the pollution load of the parameters TDS, sulfate, BOD, and COD. The physical-mechanical tests performed on the leather produced showed that the reduction in the supply of leather chemicals did not affect the physical-mechanical properties of the leather obtained. Besides, post-tanning formulation costs were reduced by 24%.

The study showed that the reduction of leather chemicals can be a technical alternative to reduce the pollution load of raw wastewater. The methodology developed in this study can be replicated in tanneries with issues in reaching wastewater emission standards, reducing the pollution load to be treated by the wastewater treatment plants. The final quality of the leather obtained must be taken into consideration, meeting the established specifications.

Acknowledgements

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Capítulo 6

Current Technologies for Post-Tanning Wastewater Treatment: a Review

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Neste artigo é apresentada a revisão sistemática de tecnologias aplicadas ao tratamento de efluentes de pós-curtimento. O artigo está publicado no periódico *Journal of Environmental Management*. Relatório Qualis Capes Engenharias II (2019): A1. Fator de Impacto: 5,647. DOI: https://doi.org/10.1016/j.jenvman.2021.113003.

Highlights:

- Future perspectives for the treatment of post-tanning effluents are presented.
- Pollution input reduction could increase the efficiency of wastewater treatment.
- Emerging technologies should be focused on recalcitrant pollutants and salts removal.
- The use of real industrial effluents needs to be further explored.

Abstract:

Leather post-tanning is responsible for producing effluents that are difficult to treat due to several recalcitrant pollutants. Dyes, tannins, and fatliquoring agents are mainly related to this characteristic. This study, as the state-of-the-art, attempts to systematically review treatment technologies applied in recent years to the post-tanning effluents. The Scopus database was used to identify articles related to post-tanning pollutants removal. Through the review, Advanced Oxidation Processes (AOPs) and adsorption proved to be good alternatives to increase the effluent biodegradability when applied before biological treatment. AOPs and adsorption were also efficient for the final polishing of the effluents, to reach the regulation standards for disposal, as well as enzymatic treatment. Furthermore, Membrane Separation Processes demonstrated good applicability when the reuse of the treated effluent is aimed.

Keywords: Leather; Post-tanning; Wastewater treatment; Recalcitrant pollutants.

6.1. Introduction

The leather industry and its products play a relevant role in the world economy, with a global commercial value of approximately US$ 80 billion per year (Sivaram and Barik, 2019). This industry is mainly relevant in developing countries (Bharagava and Mishra, 2018), like Brazil, China, and India, with Brazil having the largest commercial cattle herd in the world (ABQTIC, 2020). The transformation of a raw hide into finished leather involves a set of steps grouped into beamhouse, tanning, post-tanning, drying, pre-finishing, and finishing. As these steps are performed, the commercial value of the product increases. In Brazil, for example, finished leather is responsible for 59.6% of the leather exportation revenue (ABQTIC, 2020). As the post tanning process uses several recalcitrant and toxic chemicals, post-tanning wastewater treatment is a worrisome matter of concern that has motivated studies towards new wastewater treatment technologies in hybrid systems.

The post-tanning step processes wet-blue leather to obtain crust leather, applying a diversification of treatments to meet the desirable properties of leather for the manufacture of the many final leather goods. This process uses several chemicals, such as deacidulants, retanning agents, fatliquoring agents, surfactants, dyes, and chemical auxiliaries (Ayoub et al., 2013; Hansen et al., 2020; Ortiz-Monsalve et al., 2019; Piccin et al., 2016). These chemicals are applied in an aqueous medium performed in drums, requiring from 4 to 8 m^3 of water per ton of wet-blue leather processed (IUE 6, 2018), of which about 90% is discharged as effluent (Chowdhury et al., 2013).

Chemicals specific to the post-tanning process as dyes, fatliquoring agents, and tannins make the effluent treatment difficult. The presence of dyes in formulations, as azo and metal complexes, inhibits aquatic life growth (Mella et al., 2017), in addition to induces acute and chronic cytotoxicities (Hansen et al., 2020; Mella et al., 2017; Ortiz-Monsalve et al., 2019). The presence of fatliquoring agents interferes with the oxygen transfer efficiency in the aerobic treatment process (Kalyanaraman et al., 2013a) and causes cytotoxicity due to the presence of surfactants for their solubilization in a water medium (Hansen et al., 2020). Finally, the presence of natural and synthetic tannins can cause inhibiting conditions for the biomass in biological treatment (Agustini et al., 2018; Munz et al., 2009). These compounds contribute to imparting a poorly biodegradable effluent. Post-tanning effluents also show high total dissolved solids (TDS), and suspended solids (SS), nitrogen compounds (organic and ammonium nitrogen (NH3-N)), chemical oxygen demand (COD), and chromium (III) (Hansen et al., 2020; Mannacharaju et al., 2020).

The conventional treatment of effluent from the leather industry is as follow: equalization/neutralization, physical-chemical (coagulation/flocculation followed by sedimentation), and biological treatment (activated sludge) (Hasegawa et al., 2011; Körbahti et al., 2011; Kozik et al., 2019; Pal et al., 2020; Pena et al., 2020; Piccin et al., 2012; Tamersit et al., 2018; Tran et al., 2020). However, the literature indicates some disadvantages of conventional wastewater treatment, including sludge generation (de la Luz-Pedro et al., 2019; Pal et al., 2020; Tamersit et al., 2018) and the low efficiency in removing salts and recalcitrant compounds. This type of treatment results in salty and COD polluted treated waters (de la Luz-

Pedro et al., 2019; Kozik et al., 2019; Moreira et al., 2019; Pena et al., 2020; Suthanthararajan et al., 2004; Tamersit et al., 2018). In addition to these drawbacks, permissible effluent standards are increasingly restrictive (Hasegawa et al., 2011; Tamersit et al., 2018; Zhao and Chen, 2019), and conventional treatment does not meet the criteria for reusing treated waters, which could embrace the circular economy approach (Hansen et al., 2019; Pal et al., 2020).

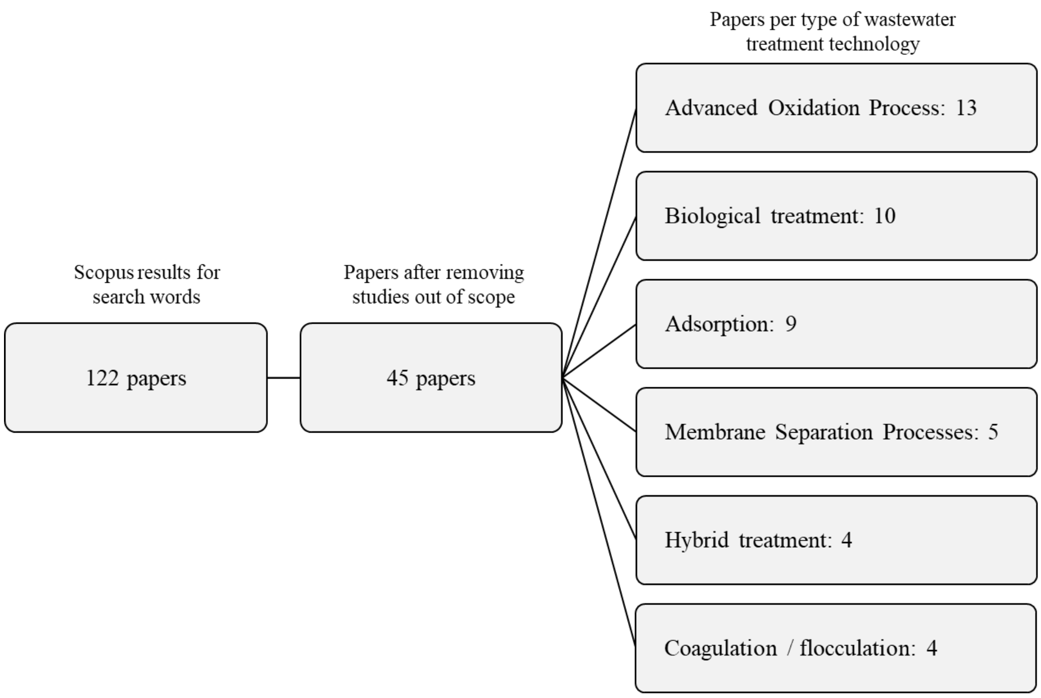
Advanced technologies can overcome conventional treatment drawbacks, including advanced oxidation processes (AOPs), biological treatment, adsorption, membrane separation processes (MSPs), coagulation/flocculation, and hybrid treatments. Literature reviews have already evaluated tannery effluent treatment technologies, focusing on chemical and biological processes (Lofrano et al., 2013) and technologies applied to complete tannery effluents (Zhao and Chen, 2019). However, a broad understanding of the technologies utilized to remove the recalcitrant pollutants present in post-tanning effluents still needs to be assessed. Thus, this paper provides an extensive literature review of the wastewater treatment technologies utilized to manage the leather post-tanning effluents, as well as a discussion of the specific conditions of application, novelty, and challenges of each technique. The effluent characteristics, disposal limits established by regulations, and future perspectives on the treatment of post-tanning effluents are also discussed in this paper.

6.2. Methodology

The survey of post-tanning effluent treatment technologies was carried out on the Scopus database. Scopus is one of the largest databases, including papers from several research fields and high-level consistency in the search (Pagani et al., 2015). For the initial search, the following terms were considered in the title, abstract, and keywords: "post-tanning" OR "wet-end" OR "wet-finishing" OR "dyeing" OR "retanning" OR "fatliquoring" AND "wastewater" OR "effluent" AND "tannery". The search period was from 2000 to 2020 (carried out in October 2020), and only papers using post-tanning effluents were considered in this paper.

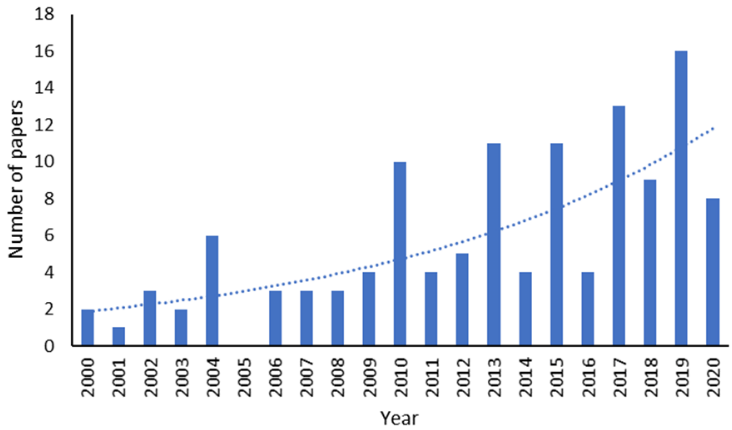
The preliminary results from the Scopus search resulted in 122 papers. These papers were individually analyzed to eliminate overlapping contents and to exclude unsuitable articles. This evaluation resulted in 45 papers, categorized according to the type of treatment applied to the post-tanning effluent: advanced oxidation process, biological treatment, adsorption, membrane separation process, hybrid treatment, and coagulation/flocculation. The results of this search are schematically shown in Figure 6.1.

Figure 6.1: Search results in the Scopus database



According to a bibliometric analysis, it is noticed that the number of publications in the field of post-tanning effluent treatment has grown over the years (Figure 6.2). An exponential trend for the number of publications per year is observed from 2000 to 2020, principally increasing in the last decade (2010 to 2020). Besides, India, Brazil, and China are the countries that most publish in this scientific field.

Figure 6 2: Number of papers per year.



6.3. Post-tanning process: chemicals, wastewater and environmental standards

The post-tanning process provides specific characteristics for each leather application, using tanned leather as the raw material (mainly the chrome-tanned leather wet-blue). This leather production stage promotes features, as appearance, texture, color, and physical-mechanical properties. This process is performed through the chemical steps of deacidulation, retanning, dyeing, fatliquoring, and fixing. The role of each group of chemicals used in post-tanning formulations, as well as their impact on the pollution load of liquid effluents, is described below.

- Deacidulants, such as sodium bicarbonate, sodium carbonate, and ammonium bicarbonate, are used to raise the pH of chromium-tanned leather. Salts, such as sodium and calcium formate and neutralizing syntans, are also applied to the leather in the deacidulation stage (Buljan and Král, 2018; Moreira and Teixeira, 2003). These chemicals agents contribute to the presence of dissolved solids, and neutralizing retanning agents can contribute to the presence of ammoniacal nitrogen in the effluent (Hansen et al., 2020).
- Retanning agents provide complementary characteristics to the chromium-tanned leather according to the leather goods to be produced. Vegetable tannins, synthetic tannins, and resins are among the retanning agents (Auad et al., 2019; Giovando et al., 2009; Saleem et al., 2013). This group of chemicals contributes to a high COD and high

inorganic load, and low biodegradability to the effluent (Buljan and Král, 2018; Hansen et al., 2020; Lofrano et al., 2008; Moreira et al., 2019).

- Fatliquoring agents promote the lubrication of the fibrous structure, increases the softness, impermeability, resistance to light, and flexibility of the leather (Gutterres, 2003; Gutterres and Santos, 2009; Lü et al., 2011). Natural (animal or vegetable) or synthetic oils can be used (Santos et al., 2008; Żarłok et al., 2014). Fatliquoring agents release high COD load and toxicity in wastewater and contribute to low biodegradability (Hansen et al., 2020; Lofrano et al., 2007).
- Dyes used in the leather industry can be classified mainly as acid, basic or direct, according to how they are fixed to the leather (Pandi et al., 2019). Acid dyes are anionic chemicals, with a good diffusion through the wet-blue leather. Azoic acid dyes represent more than 50% of all commercial dyes consumption (Singha et al., 2019). Dyes contribute to the inorganic pollution load, total Kjeldahl nitrogen (TKN) (azoic dyes), and low biodegradability of wastewater (Hansen et al., 2020; Moreira et al., 2019; Ortiz-Monsalve et al., 2020).
- The auxiliary chemicals include fixing agents, fungicides, waterproofing agents, antioxidants, among other chemicals. Some may have toxicity (fungicides) or high inorganic load (fixing agents) (Hansen et al., 2020).

The leather post-tanning produces raw effluents that must undergo decontamination in wastewater treatment plants. Treated effluents must meet environmental standards for final disposal. The discharge concentration standards for pollutants are shown in Table 6.1. This table shows environmental standards from the three countries with the largest number of publications in post-tanning effluent treatment: Brazil, China, and India.

Table 6.1: Environmental standards for effluent discharge in Brazil, China, and India.

Parameter	Brazil (CONAMA, 2011)	China (Ministry of Environmental Protection, 2013)		India (Ministry of Environment, Forest and Climate Change, 2019)
		direct discharge	indirect discharge	
pH	5 to 9	6 to 9	6 to 9	6 to 9
T (ºC)	40			
Chromaticity (°)		30	100	
Settleable solids (mL/L)	1			
Total suspended solids (mg/L)		50	120	50
Total dissolved solids (mg/L)				2100
Oil and Grease (mg/L)	20 (Mineral oil) 50 (Vegetable or animal oil)	10 (Vegetable or animal oil)	30 (Vegetable or animal oil)	10 10
Biochemical Oxygen Demand (BOD) (mg/L)	60% removal*	30*	80*	20**
Chemical Oxygen Demand (mg/L)		100	300	250
Hexavalent chromium (mg/L)	0,1	0,1	0,2	0,1
Trivalent chromium (mg/L)	1,0			
Total chromium (mg/L)		1,5	1,5	
Chloride ion (mg/L)		3000	4000	
Total ammoniacal nitrogen (mg/L)	20	25	70	
Total nitrogen (mg/L)		50	140	
Total phosphorus (mg/L)		1	4	
Sulfide (mg/L)	1,0	0,5	1,0	2,0

*BOD_5; **BOD_3

Brazilian regulation (National Environment Council - CONAMA 430, 2011) establishes discharge standards aimed at all industrial sectors (general industrial standards), whereas the standards of China (Ministry of Environmental Protection, 2013) and India (Ministry of Environment, Forest and Climate Change, 2019) are specific for tannery effluents. The regulations set standards for color, solids, oils and greases, BOD, COD, chromium, chloride, nitrogen, phosphorus, and sulfide, among others.

Indian standards set limits for the release of dissolved solids, and Chinese standards set limits for chlorides, aiming to control the disposal of inorganic pollutants in liquid effluents, preventing salinization of water bodies. On the other hand, Brazilian regulation is more restrictive regarding the emission of ammoniacal nitrogen, an important agent that causes eutrophication (Lei et al., 2020) of water bodies.

An increase in restrictions is observed for effluent discharge standards. India updated its regulation in 2019. The country reduced the permitted concentration levels of BOD and included emission standards for COD and TDS. China has also reduced pollutant concentration limits for the disposal of effluents (Xu et al., 2020). Environmental standards for Chinese tanneries were updated in 2016. Brazilian federal regulation is more general, allowing states to establish more restrictive regulations for industrial effluents. At the state level, the State Environment Council (CONSEMA) Resolution No. 355 (2017) establishes emission standards for liquid effluents discharged into surface waters in the State of Rio Grande do Sul (Brazil). This legislation includes standards that are not defined by the Brazilian federal regulation for total chromium (0.5 mg/L), COD (150 - 330 mg/L), SS (50 - 140 mg/L), and total phosphorus (1 - 4 mg/L). Besides, the emission standard for sulfides (0.2 mg/L) is more restrictive than federal legislation. The State of Rio Grande do Sul also applies toxicity standards for effluents (CONSEMA 129, 2006). The adoption of more restrictive environmental standards should increase the research and development of effluent treatment technologies that reach the limits of regulation.

6.4. Application of technologies for post-tanning wastewater treatment

The technologies applied to the treatment of post-tanning effluents, type of wastewater (synthetic or industrial), main parameters, removal efficiency, and the study details identified in the systematic review are shown in Table 6.2. Data presented in Table 6.2 shows the results from the search carried out in the Scopus database (Figure 6.1). Technologies were grouped into advanced oxidation process, biological treatment, adsorption, membrane separation process, hybrid technologies, and coagulation/flocculation. A discussion of each group of technologies was carried out exploring scientific literature for each technology.

Table 6.2: Technologies applied for treatment of post-tanning effluents.

Treatment technology	Wastewater	Main parameter(s)	Removal efficiency	Study details	Author
			Advanced Oxidation Process		
Electrochemical oxidation	Industrial leather dyeing wastewater	COD	81.2%	Anode: Ti/Pt; J: 18.70 mA/cm²; t: 2.11 h; T: 286.18K; Energy consumption: 3.85 kWh/kg of COD.	(Oukili and Loukili, 2019)
Electrochemical oxidation	Industrial post-tanning wastewater	COD	32%	Anode: Ti/RuO_x-TiO_x-coated; J: 24 mA/cm²; t: 2.15 h; Biodegradability (BOD/COD) raised from 0.3 to 0.67.	(Basha et al., 2009)
Sonoelectrochemical degradation	Simulated wastewater (formic acid - 250 mg/L and NaCl 3 g/L)	Formic acid	97%	1176 kHz ultrasonic irradiation combined with 20 mA electrolysis in 120 min.	(Shestakova et al., 2016)
Photoelectrocatalytic oxidation	Simulated wastewater (acid dye 151, surfactant and CrVI)	TOC, Cr(VI) and discoloration	TOC (95%), Cr(VI) reduction (98-100%) and discoloration (100%)	Anode: nanoporous Ti/TiO_2; pH: 2.0; UV-irradiation	(Paschoal et al., 2009)
Photocatalytic treatment	Simulated wastewater (Rhodamine B - 30 mg/L and Cr(VI) - 20 mg/L)	Cr(VI) and discoloration	Cr(VI) reduction (95.4%) and discoloration (88%)	10 mg of "sandwich" WO_3/rGO/$SnIn_4S_8$(WGS) Z-scheme photocatalysts were added to 100 mL of Rhodamine B or Cr(VI) solution.	(Xu et al., 2019)
Photocatalytic treatment	Simulated wastewater (Methylene blue - 10^{-5}mg/L)	COD, TOC and discoloration	COD (70%), TOC (35%) and discoloration (90%)	50 mg of ZnO@zeolitic Imidazolate Framework (ZIF)-8 was added to 50 mL of dye solution.	(Hongjun et al., 2019)
Photocatalytic treatment	Industrial post-tanning wastewater	COD	35.3%	Wastewater treatment was carried out in a pilot scale solar light reactor with Bentonite-ZnO. Time of treatment: 3 h.	(Deva Kumar et al., 2018)
Photocatalytic treatment	Simulated wastewater (syntans, leather dye (Red2BN) and fatliquor)	COD	64%	Heterostructured mixed oxide $BiVO_4$-ZnO semiconductive photocatalyst in the presence of sun light at neutral pH and 6 h reaction.	(Kumar et al., 2017)
Photocatalytic treatment	Industrial retanning and dyeing wastewater	COD, BOD, TS, TOC and turbidity	COD (97.7%), BOD (99.8%), TS (99.3%). TOC (99.9) and turbidity (99.7%)	Wastewater containing 1 g/L of ZnO and effluent diluted in a 1:200 proportion, irradiated for 4 h at pH 8.0 and 30°C.	(Hasegawa et al., 2014)
Photo-Fenton treatment	Simulated wastewater (syntan)	COD	83%	Ratio 150/500 (w/w) of H_2O_2/$FeSO_4$. Reduction of	(Lofrano et al., 2010)

Treatment technology	Wastewater	Main parameter(s)	Removal efficiency	Study details	Author
				toxicity to *D. magna* could be achieved.	
Fenton oxidation	Industrial leather dyeing wastewater	COD	77%	Heterogeneous catalyst (cobalt oxide doped nanoporous activated carbon - Co-NPAC): 1.0 % (w/w); H_2O_2: 10mM; pH: 3.5 and temperature: 25 °C.	(Karthikeyan et al., 2015)
Ozonation	Industrial post-tanning wastewater	COD and discoloration	COD (70%) and discoloration (90%)	Ozone flow rate: 6×10^{-3} m^3 min^{-1}; pH: 11. Biodegradability of wastewater increased from 0.18 to 0.49 during 30 min of ozonation.	(Preethi et al., 2009)
chlorine dioxide oxidation	Simulated wastewater (benzidine)	COD and Benzidines	COD (65%) and Benzidines (90%)	Molar ratio between chlorine dioxide and benzidines should be 6.5. pH range 7.0-9.0,	(Cao et al., 2007)
			Biological Treatment		
Microalgae	Industrial post-tanning and finishing wastewater	TKN, P, TOC, COD, BOD, N-NH_3.	TKN (71.74%), P (97.64%), TOC (31.35%), COD (56.70%), BOD (20.68%) and N-NH_3 (100%)	Microalgae consortium containing mainly *Tetraselmis sp.* 24 h light period and 75% raw wastewater mixed with 25% secondary wastewater.	(Pena et al., 2020)
Microalgae	Industrial post-tanning wastewater	TKN, TOC, N-NH_3, P-PO_4), COD and BOD.	50%/50% and 75%/25% (raw/ treated effluent): TKN (89.06 and 54.78%), TOC (59.24 and 57.90%), N-NH_3 (99.9 and 89.2%), P-PO_4 (96.59 and 99.81%), COD (40.46 and 43.54%) and BOD (32.70 and 44.73%).	Microalgae *Tetraselmis sp*. Treatment. Tests used 50% raw effluent diluted with 50% treated effluent and 75% raw effluent diluted with 25% treated effluent.	(Pena et al., 2018)
Fungal treatment	Simulated wastewater (Acid Red 357 and Acid Orange 142)	COD, TOC, discoloration and detoxification	COD and TOC (80%), discoloration (90%) and biodetoxification (50-70%)	Fungal treatment using *Trametes villosa* SCS-10. Reduced nutrient supply allowed the highest pollutants reduction	(Ortiz-Monsalve et al., 2019)
Fungal treatment	Simulated wastewater (Acid Red 357, Acid Black 210 and Acid Blue 161)	Discoloration	Acid Red 357 (95.71%), Acid Black 210 (92.76%) and Acid Blue 161 (96.84%)	Fungal treatment with *Trametes villosa* SCS-10. 100mg/L dye concentration; 30°C, pH 5.5; 150 rpm; 168h of treatment.	(Ortiz-Monsalve et al., 2017)
Fungal treatment	Industrial post-tanning wastewater	COD and TOC	COD (91%) and TOC (93%)	Ascomyceteous fungus *Botryosphaeria rhodina* MAMB-05 was able to treat the effluent when diluted 1:10.	(Hasegawa et al., 2011)

Treatment technology	Wastewater	Main parameter(s)	Removal efficiency	Study details	Author
Aerobic biodegradation	Simulated wastewater (1g/L anionic-sulfited vegetable fatliquor)	COD and BOD	COD (89.58%) and BOD (97.24%)	Activated sludge collected from ETE. Food to microbial ratio of 0.15; reaction time of 24 h.	(Kalyanaraman et al., 2013a)
Aerobic biodegradation	Simulated wastewater (1g/L Lecithin-based fatliquor)	COD and BOD	COD (86.21%) and BOD (95.55%)	Activated sludge collected from ETE. Food to microbial ratio of 0.15; reaction time of 48 h.	(Kalyanaraman et al., 2013b)
Aerobic biodegradation	Simulated wastewater (Cr(VI) and acid black dye)	Cr(IV) and discoloration	Cr(VI) reduction (95.8%) and discoloration (92.3%)	Biodegradation by *Lactobacillus paracase* CL110. CrVI and dye inicial concentration of 100 mg/L. In simultaneous treatment, the reduction of CrVI and dye were 58.5% ans 51.9%, respectively.	(Huang et al., 2015)
Aerobic biodegradation	Simulated wastewater (azo dyes)	Acid Blue 113	96%	Biodegradation by bacterial culture mediated with azoreductase enzyme. Initial concentrations of 100 mg/L Acid Blue 113. Treated wastewater could be reused for dyeing operation.	(Senthilvelan et al., 2014)
Enzimatic treatment	Industrial post-tanning wastewater after anaerobic treatment	Sulphide	99.6 %	*Quinone oxidoreductase* immobilized Functionalized Carbon-silica matrix packed bed reactor. pH: 7.0; T: 40°C; 200 mg/L of sulphide inicial concentration.	(Mannacharaju et al., 2020)
			Adsorption		
Hybrid carbon nanochromium composites from chrome-tanned leather shavings	Simulated wastewater (Acid black 210 - 100 mg/L)	Acid black 210	50% of the adsorption capacity of a commercial activated carbon.	q_m: 44.4 mg/g; pH: 8; T: 15–35 °C; Freundlich isotherm.	(Arcibar-Orozco et al., 2019)
Activated carbon from cattle hair activated with H_3PO_4	Pilot-scale post-tanning wastewater	Acid brown 414 and Acid orange 142	Acid Brown 414 (71.06%) Acid Orange 142 (73.05%)	0.1 g of adsorbent in 20 mL of wastewater sample. pH: 3.65, 200 rpm, 24 h at 303 K agitation in a thermostatic shaker.	(Mella et al., 2019)
Modified kaolin	Simulated wastewater (Coriacide Bordeaux 3B, Derma Blue R67, and Coriacide Brown 3J)	Discoloration	>90%	Two commercial clays (DD3 and KT2) were chosen as raw materials. pH 4; T: 20°C; t: 40–80 minutes	(Zen and El Berrichi, 2016)
Chromium-tanned leather shaving waste	Simulated wastewater (Acid Red 357)	Discoloration	58%	q_m: 148.2 mg/g; pH 3.0; T: 35°C	(Piccin et al., 2016)

Treatment technology	Wastewater	Main parameter(s)	Removal efficiency	Study details	Author
Chromium-tanned leather shaving waste	Simulated wastewater (Acid Red 357)	Discoloration	87.37%	q_m: 24.74 mg/g; pH: 2.3; adsorbent conc.: 8.09 g/L; dye conc.: 127.9 mg/L; rotation: 27.5 rpm; pseudo-second order kinetic.	(Gomes et al., 2016)
Cattle hair waste	Simulated wastewater (Acid Blue 161 and Acid Black 210)	Acid blue 161 and Acid black 210	Acid blue 161 (70.82%) Acid black 210 (77.18%)	Acid blue 161: q_m: 104.78 mg/g; pH: 3.0; T: 323K Acid black 210: q_m: 26.29 mg/g; pH: 2.0; T: 303K; Liu isotherm; general order kinetic.	(Mella et al., 2017)
Commercial powdered activated carbon	Industrial post-tanning wastewater	Discoloration	90.2 %	Adsorbent dose: 1.5 g/50 mL; pH: 4.5; T: 35°C.	(Carpenter et al., 2013)
Modified green macro algae: *Caulerpa Scalpelliformis*	Simulated wastewater (phenol) and Industrial post-tanning wastewater (with syntan)	Phenol	87%	q_m: 20 mg/g; pH: 6.0; t: 2h to equilibrium; Langmuir isotherm; pseudo-second order kinetic.	(Aravindhan et al., 2009)
Modified zeolite	Simulated wastewater (Bromocresol purple and chromium)	Bromocresol purple (BCP) and Total cromium (tCr)	Discoloration (90.6%) and tCr (97.6%)	Bromocresol purple: q_m: 175.5 mg/g; pH: 6.5; t: 60 min; T: 303.15 K; initial BCP conc.: 11.7 mg/L. tCr: q_m: 37 mg/g; pH: 8.8; t: 55 min; T: 303.15 K; initial tCr conc.: 16.0 mg/L; Freundlich isotherm.	(Aljerf, 2018)
		Membrane Separation Process			
UF	Industrial dyeing and fatliquoring wastewater	COD, discoloration	COD (91%), discoloration (95%)	Permeate flux: 41.9 L/m².h; T: 25°C; transmembrane pressure: 0.09 Mpa; membrane material: polysulfone; pre-treatment: sieve cloth filtration	(Hongru et al., 2014)
UF	Industrial dyeing wastewater	Discoloration	Discoloration (>70%)	T: 25°C; membrane material: polyethersulphone; pre-treatment: lining filter. Permeation fluxes raised at the highest Reynolds numbers of 9,800 and 13,900.	(Brites Alves and Norberta de Pinho, 2000)
NF	Simulated wastewater (syntans, fatliquor, and azo dye)	COD, BOD and discoloration.	COD (53%), BOD (66%) and discoloration (76%).	Permeate flux: 2000 L/m²h; transmembrane pressure: 30 psi; membrane material: keratin-polysulfone blend (95:5 v/v); pre-treatment: Whatman filter paper and vacuum filter	(Karunanidhi et al., 2020)
NF	Industrial post-tanning and finishing wastewater	Hardness and COD	Hardness (54%) COD (50%)	Permeate flux: aprox. 15 L/m².h; transmembrane pressure of 8 kgf/cm²; T:	(Viero et al., 2002)

Treatment technology	Wastewater	Main parameter(s)	Removal efficiency	Study details	Author
				35.5°C; membrane: MX07 (Osmonics); pre-treatment: wastewater after polishing lagoon and prefilter with pore size of 1 µm.	
NF followed by RO	Industrial post-tanning wastewater	Discoloration, conductivity, TS, TDS, COD, BOD, Cl^-, Cr^{3+}	Discoloration (100%), conductivity (95%), TS (99%), TDS (95%), COD (99%), BOD (99%), Cl^- (96%), Cr^{+3} (100%)	Transmembrane pressure: RO: 1518 kPa; NF membrane material: polyamide skin over a polysulphone support; RO membrane material: thin film composite membrane; no pre-treatment.	(Das et al., 2010)
			Hybrid Process		
Fenton and Biological treatment	Industrial post-tanning wastewater	COD and discoloration	COD (93.7%) and discoloration (89.5%)	Effluent from the dyeing process (acid blue 113 dye). Pre-treatment of dye effluent with Fenton (H_2O_2 & Fe^{2+}) followed by bacterial consortium treatment.	(Shanmugam et al., 2019)
Coagulation/flocculation, Adsorption and Ozonation	Simulated wastewater (Acid Red 357)	TOC, COD, Na^+ and discoloration	Coagulation/flocculation -Adsorption: TOC (50.04%), COD (23.13%), Na^+ (17.05%) and discoloration (61.13%) Coagulation/flocculation -Ozonation: TOC (46.50%), COD (56.25%), Na^+ (11.10%) and discoloration (85.34%)	hair shavings were tested as a low-cost adsorbent	(Mella et al., 2018)
Coagulation/flocculation and Adsorption	Simulated wastewater (acid black-210)	Discoloration	85.2%	Coagulation/flocculation: pH: 10.0; sedimentation time: 60 min.; coagulant (71 mg/L $Al_2(SO_4)_3$) and flocculant (0.090 mg/L polyelectrolyte FX AS1). Adsorption: q_m: 974.7 mg/g; T: 303.15 K; pH: 2.0; activated carbon adsorption best fit to Liu isotherm model.	(Puchana-Rosero et al., 2018)
Gravity settling, Coagulation/flocculation, NF and RO	Industrial post-tanning wastewater (containing fatliquoring)	COD	99%	Coagulation/flocculation: iron sulfate NF: pressure range 828–1242 kPa RO: pressure range 1313-1724 kPa	(Prabhavathy and De, 2010)

Treatment technology	Wastewater	Main parameter(s)	Removal efficiency	Study details	Author
			Coagulation/Flocculation		
Coagulation/flocculation	Simulated post-tanning wastewater	Cr (III) and TOC	Cr (III) (60% to 99%) TOC (~20% to ~60%)	Coagulation using polyaluminum chloride	(Tang et al., 2018)
Coagulation/flocculation	Simulated wastewater (retanning and fatliquoring agents)	Discoloration and COD	Discoloration (90%) COD (90%)	Flocculation using epichlorohydrin-dimethylamine Fast mix: 5 min at 150 rpm Slow mix: 15 min at 50 rpm Settling: 40min Range of pH: 3 to 9	(Niu et al., 2012)
Electrocoagulation	Industrial post-tanning wastewater	COD and TOC	COD (~75%), TOC (~35%)	Electrocoagulation with iron and aluminium electrodes. Current density: 28 mA/cm^2	(de la Luz-Pedro et al., 2019)
Oxidation and Coagulation	Industrial post-tanning wastewater	COD, TOC, SS and discoloration	COD (77.2%), TOC (75.7%), SS (96.9%), and discoloration (98.4%)	1.200 g/L K_2FeO_4; pH: 3; t: 9 min	(Kozik et al., 2019)

6.4.1. Advanced Oxidation Process

Advanced Oxidation Processes (AOPs) are chemical, photochemical, or electrochemical methods that generate hydroxyl radicals (·OH) in situ as the main oxidant. AOPs are known for their high versatility and for helping to the environmental compatibility by degradation of refractory pollutants (Ganiyu et al., 2015). Among the AOPs processes presented in Table 6.2, zinc oxide-assisted photocatalysis (Hasegawa et al., 2014) showed the highest efficiency for the removal of COD (97.7%). The Photo-Fenton process (Lofrano et al., 2010) and the electrochemical oxidation process with Ti/Pt anode (Oukili and Loukili, 2019) also showed high COD removal (83% and 81.2%, respectively). On the other hand, the electrochemical oxidation process proposed by Basha et al. (2009), using Ti/RuOx-TiOx-coated anode obtained the smallest COD removal from the post-tanning effluent (32%). However, this technique was applied as a pre-treatment for biological treatment, with the main objective of increasing the biodegradability of the effluent (BOD/COD ratio increased from 0.3 to 0.67) (Basha et al., 2009). Ozonation also increased the biodegradability of the post-tanning effluent by more than 0.4 after 30 min experiment (Preethi et al., 2009). This delivers a favorable adaptation of electrochemical oxidation and ozonation as pretreatment technologies.

Both techniques have low energy consumption when compared to other AOPs. Electrochemical oxidation had an average energy consumption of 10.88 kWh/kg COD (Basha et al., 2009), and ozonation presented low energy consumption when compared to other AOPs (UV, UV/H_2O_2, H_2O_2/O_3, and O_3/UV) (Venkatesh et al., 2015).

Regarding the discoloration of post-tanning effluents, photoelectrocatalytic oxidation achieved 100% color removal (Paschoal et al., 2009). High discolorations were also achieved by photocatalytic treatment (88 to 90%) (Hongjun et al., 2019; Xu et al., 2019) and ozonation (90%) (Preethi et al., 2009).

To define a proper post-tanning effluent treatment using AOPs it is necessary to consider the oxidation of compounds such as chromium (III) (Lofrano et al., 2013). The oxidation of chromium (III) to chromium (VI) increases the toxicity of wastewater (Fuck et al., 2011; Ritterbusch et al., 2019) and therefore should be avoided. Photolytic, photocatalytic, photoelectrocatalytic, and electro-oxidation treatments have an advantage in this aspect when compared to other AOPs, as they could be used for the reduction of chromium and the oxidation of organic species simultaneously (Xu et al., 2006). Photoelectrocatalytic treatment achieved a greater reduction in chromium (VI) and discoloration when compared to photocatalytic treatment. Similar results were found by Paschoal et al. (2009) in the treatment of wastewater containing both organic and inorganic pollutants using photoelectrocatalytic and photocatalytic treatments.

The high capacity to degrade biorefractory compounds and the non-generation of sludge, except in Fenton-based processes, are relevant characteristics that make this group of technologies promising for the treatment of post-tanning effluents. However, there is high complexity (related to high costs) in the studies evaluated for the construction and operation of wastewater treatment using AOPs. There is also the possibility of releasing intermediate compounds that are more toxic than the original ones. Thus, further studies that include the evaluation of costs and toxicity of by-products are still necessary to develop scientific knowledge in this field.

Although chlorine dioxide oxidation is not classified as an AOP, this technique has been included in this group due to its oxidative characteristic. This technique was applied for benzidines (chemicals used in the production of dyes) removal, obtaining 90% benzidines removal and 65% COD removal.

6.4.2. Biological Treatment

Biological Treatment has a prominent presence in the environmental protection infrastructure. Among the various biological wastewater treatment methods, aerobic processes predominate, especially activated sludge (Xiao et al., 2015). Recently, several techniques have been applied in the treatment of dyes or heavy metals containing wastewater (Huang et al., 2015). Among them are biological processes using microalgae, fungi, activated sludge, bacteria strains, and enzymes.

Through the results compiled in Table 6.2, it is observed that Fungal treatment (Hasegawa et al., 2011; Ortiz-Monsalve, 2019; Ortiz-Monsalve et al., 2017) and aerobic biodegradation (Huang et al., 2015; Kalyanaraman et al., 2013a, 2013b; Senthilvelan et al., 2014) showed substantial removal of COD (above 80%) and color (above 90%) of the post-tanning effluents. All dyes degraded in the compiled studies were azoic. Conventional biological treatment methods are often ineffective for the degradation of azo dyes, due to their complex aromatic structure and the stability or toxicity of the dyes or their by-products (Kertèsz et al., 2014). However, the biological processes tested using the fungal treatment or aerobic biodegradation could degrade the dye structure, transforming azo linkage into N2 or NH3 or incorporated into biomass (Senthilvelan et al., 2014). *Lactobacillus paracase* isolated from deep-sea sediment demonstrated the ability to reduce Chromium (VI), in addition to removing an azo dye (Huang et al., 2015). *Pseudomonas putida* strain KI also demonstrated the potential of azo dyes decolorization and Chromium (VI) removal in packed bed bioreactors (Mahmood et al., 2013).

The fungal treatment also showed high TOC removal (above 80%), and aerobic biodegradation showed BOD removal above 95%. The use of microalgae (Pena et al., 2018, 2020) showed removals always below 60% for COD, TOC, and BOD, revealing less efficiency for these parameters compared to other biological treatments. On the other hand, microalgae treatment achieved high removals of ammoniacal nitrogen and phosphorus from the effluents. Many algal species, such as Chlamydomonas, Chlorella, Scenedesmus, and Nanochloropsis, can assimilate organic or inorganic nutrients such as ammoniacal nitrogen, and phosphates from wastewater results (Saranya and Shanthakumar, 2020). These are important nutrients whose removal prevents water eutrophication (which accelerates the depletion of dissolved oxygen in water) (Al-Najjar et al., 2011; Lei et al., 2020). Therefore, the cultivation of microalgae in wastewater has shown to be a promising path to remove nutrients and generate biomass that can be exploited for different applications, such as biofuels (Pena et al., 2020).

Post-tanning effluents are characterized by high conductivity and the presence of salts, mainly sulfates and chlorides (Hansen et al., 2020; Moreira et al., 2019), and conventional biological treatment is known to be strongly inhibited by salt (Lefebvre and Moletta, 2006). Thus, the results obtained with a salt-tolerant bacterium (Lactobacillus paracase) (Huang et al., 2015) may have useful application in the aerobic treatment of tannery effluent containing moderate salt concentration. The use of salt-tolerant halophytic algae has also been tested to remediate saline effluents (Saranya and Shanthakumar, 2020) and could be a good alternative for post-tanning effluents.

Moving-bed biofilm reactor (MBBR) has been studied as a new technology for the biological treatment of tannery wastewater. MBBR is an immobilized cell system characterized by the use of free-moving carriers (mainly plastics), which are responsible for microbial growth (Swain et al., 2020). A systematic review on the application of MBBR for the treatment of tannery effluents (Rech et al., 2020) found that steady growth of the attached biomass in MBBR achieves a greater organic load reduction and sludge reduction compared to most of the conventional activated sludge treatment. The study also pointed out that MBBR can be used to remove pollutants as phenols and nitrogen.

6.4.3. Adsorption

Adsorption is an advanced method for treating wastewater with heavy metals, aromatic compounds, and dyes (Gomes et al., 2016). The adsorption has stood out among the wastewater treatment techniques due to its low initial investment and operational costs, simplicity of operation, and high efficiency compared to conventional processes (Piccin et al., 2012; Rigueto et al., 2020a).

The results presented in Table 6.2 show that adsorption has been applied for dye removal in 8 of the 9 papers compiled. Only one study evaluated the simultaneous removal of chromium and color, and one paper evaluated exclusively the removal of phenols. Phenols are present in tannin compounds with polyphenolic structures, and these substances contribute to the refractory character of tannery effluent (Benvenuti et al., 2018).

Among the adsorbent materials used in the treatment of post-tanning effluents chrome-tanned leather shavings and cattle hair are used more frequently. However, commercial activated carbon and modified kaolin, green macro-algae, and zeolite were also used as adsorbent materials. Chrome-tanned leather shavings showed removal of acid dyes (anionic) between 58 and 87% (Gomes et al., 2016; Piccin et al., 2016). A study using other leather shavings (Carvalho Pinheiro et al., 2020) showed a great interaction of pickled hide, wet-white leather, and chrome-tanned leather shavings with the anionic dye Acid Brown 414 (removal above 90% at a contact time of 150 min). On the other hand, vegetable-tanned leather shavings were the only efficient to remove the cationic dye Basic Red 2 (96.7% of removal at a contact time of 120 min). Cattle hair waste (Mella et al., 2017) and activated carbon from cattle hair (Mella et al., 2019) showed dye removal between 71 and 77%. The highest pollutant removals were obtained with commercial powdered activated carbon (Carpenter et al., 2013), modified zeolite (Aljerf, 2018), and kaolin (Zen and El Berrichi, 2016), with discoloration greater than 90%.

Many factors affect the adsorption efficiency, including temperature, pH, dye concentration, and adsorbent material (Gomes et al., 2016). The optimal pH values of most studies are in an acidic range, which favors the application in post-tanning effluents, which also have acidic pH (Hansen et al., 2020). Most studies showed optimal temperatures below 35ºC, and all studies showed temperatures below 50ºC. The increase in the operating temperature implies an increase in energy consumption and process costs.

The kinetic and equilibrium information of the studies that modeled the experimental data obtained the best kinetic adjustments of adsorption by pseudo-second order and general order models. The adsorption equilibrium was best described by the Freundlich, Langmuir, and Liu isotherms.

Despite the numerous studies showing adequate removals of pollutants, especially dyes, some challenges need to be overcome for adsorption application on an industrial scale, such as determining the operating lifetime and the possibility of regenerating the adsorbent materials. Although these aspects impact the economic viability of this technology, only one study (Aljerf,

2018) evaluated the regeneration of the adsorbent material, which justifies further studies in this area.

6.4.4. Membrane Separation Process

Membrane Separation Processes (MSPs) can separate dissolved substances from liquid effluents. These processes can be distinguished by driving forces: pressure difference (microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO)), osmosis pressure (forward osmosis), and potential difference (electrodialysis - ED) (Li et al., 2020; Venzke et al., 2018).

Through the results compiled in Table 6.2, it is observed that the use of NF followed by RO (Das et al., 2010) achieved the highest removal of pollutants. This result is consistent with the type of membrane used since RO membranes can separate monovalent ions, NF membrane can separate multivalent ions, and UF membranes remove solutes with a molecular weight higher than 1,000 Da (Galiana-Aleixandre et al., 2013). Thus, RO membranes are expected to show greater pollutant retention compared to NF and UF membranes.

Pore size is not the only factor that defines the removal of pollutants. The pH also influences the charge on the membrane surface (Licona et al., 2018). When the pH is higher than the membrane isoelectric point, the zeta potential is negative, resulting in the deprotonation of functional groups (e.g. carboxyl or sulphone groups). However, when the pH is under the membrane isoelectric point the zeta potential is positive, resulting in a positive surface charge due to the protonation of functional groups (e.g. amine group) (Nicolini et al., 2016). Transmembrane pressure also influences the permeate flux and removal of pollutants. An increase in transmembrane pressure increases the permeate flux and the rejection of pollutants (Das et al., 2010).

Post-tanning effluents present a high concentration of TDS (5,100 to 14,011 mg/L), conductivity (12,290 to 19,400 µS/cm) and COD (2,850 to 10,000 mg/L) (Hansen et al., 2021). These pollutants may cause membrane fouling (Liu et al., 2021) and imply the need for pre-treatment processes. The MSPs applied to the post-tanning effluents used filtration operations as pre-treatment techniques (sieve cloth, lining filter, Whatman filter paper, vacuum filter, and polypropylene filter with a 1 µm pore size). Thus, the higher the quality requirement of the treated effluent (e.g. when removal of monovalent or divalent salts is necessary), the more recommended it is to use membranes with smaller pore sizes (NF or RO). However, higher care should be taken with the pre-treatment of the MSP input stream.

Although widely studied on a laboratory scale, MSPs' industrial application faces membrane fouling, high costs, and waste stream management as the main challenges. Some of these challenges have also been observed while treating effluents from other leather stages of processing, such as unhairing (Galiana-Aleixandre et al., 2013; Tamersit et al., 2018), tanning (Galiana-Aleixandre et al., 2013), and complete tannery effluent (Luján-Facundo et al., 2019), justifying future studies on these drawbacks for the treatment of post-tanning effluents.

6.4.5. Hybrid Process

The presence of recalcitrant compounds in post-tanning effluents can make hybrid processes relevant alternatives for their treatment. The removal of these compounds can be improved by combining two or more processes due to synergistic effects (Grandclément et al., 2017). The association of gravity settling, coagulation/flocculation, NF, and RO (Prabhavathy and De, 2010) achieved the highest COD removal among hybrid treatments. Coagulation/flocculation was responsible for 64% of COD removal, the sequential use of NF reached up to 91% removal, and finally, RO reached 99% of COD removal. Other hybrid processes used coagulation/flocculation as a pretreatment followed by adsorption (Mella et al., 2018; Puchana-Rosero et al., 2018) and ozonation (Mella et al., 2018). The coagulation-flocculation/ozonation combination achieved higher removals of COD and color compared to coagulation-flocculation/adsorption. Both treatments (coagulation-flocculation/ozonation and coagulation-flocculation/adsorption) increased the effluent biodegradability, however coagulation-flocculation/ozonation showed higher BOD/COD ratios, which would facilitate a sequential biological treatment (Mella, 2018).

The Fenton process was also used to increase wastewater biodegradability for biological treatment (Shanmugam et al., 2019). The combined use of these techniques achieved high COD (93.7%) and color (89.5%) removals (Shanmugam et al., 2019). Some AOPs can be applied either as an end treatment, after biological treatment, to remove remaining recalcitrant pollutants, or within biological treatment to increase the effluent's biodegradability. As higher doses of oxidants are usually necessary when applied as a final treatment, the economic prospects of some AOPs can be improved when integrated with the biological process (Di Iaconi, 2012; Ganiyu et al., 2015; Saranya and Shanthakumar, 2020).

6.4.6. Coagulation / Flocculation

Coagulation/Flocculation is usually applied as a primary treatment, as this process helps to remove small particles (diameters from 0.1 to 100 um). The flocculation technique is considered easy to be applied, cost-effective, and highly efficient for removing solids (Tran et al., 2020).

Different coagulants/flocculants have already been studied for the treatment of post-tanning effluents. Polyaluminum chloride was tested to remove chromium (III) and COD (Tang et al., 2018). The formation of chromium (III) complexes with tannins, dyes, and fatliquors favored metal removal due to higher hydrophobicity. However, the chromium complex with acrylic resin was water-soluble, being the major obstacle for chromium (III) removal by coagulation/flocculation. The cationic organic flocculant epichlorohydrin-dimethylamine was also tested (Niu et al., 2012), removing around 90% of COD and color from effluents containing dyes and retanning agents. Besides, for effluents containing a fatliquoring agent, the flocculation performance was poor due to the presence of emulsifiers making the fatliquoring agent water-soluble. $Fe(OH)_3$ and $Al(OH)_3$ produced by electrodes in an electrocoagulation process were also effective for the clarification of post-tanning effluents (de la Luz-Pedro et al., 2019). The neutral pH favored the formation of iron (III) and aluminum hydroxides, increasing treatment efficiency. The total energy consumption of 0.37 and 0.69 kWh / m^3, using Fe and Al electrodes, respectively (de la Luz-Pedro et al., 2019), can be an obstacle to the application of this technique on an industrial scale.

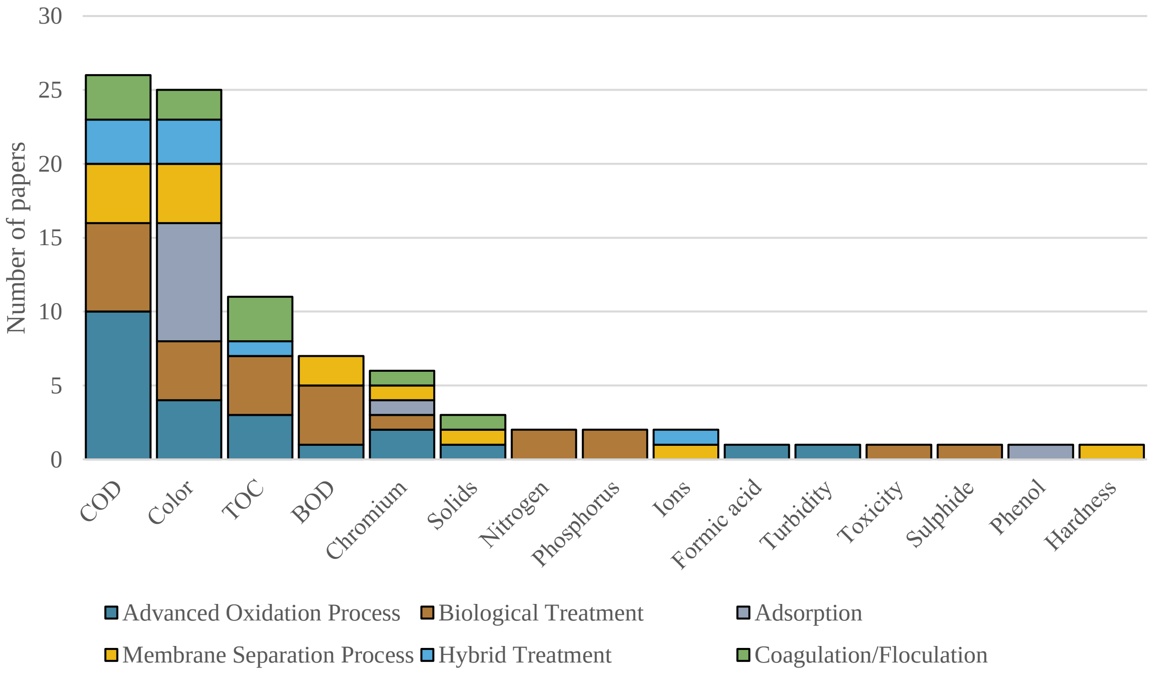
Attention has been paid to highly effective chemicals that do not harm the environment. Potassium ferrate (K_2FeO_4) has been tested to remove COD, TOC, SS, and color. This coagulant has two different removal mechanisms, consisting of the oxidation and the coagulation of impurities present in wastewater (Kozik et al., 2019).

6.5. Discussion and Perspectives

Given the growing concern with environmental protection, tanneries will have to pursue more effective management of process wastewater. The main prospects for the treatment of post-tanning effluents are discussed in this section.

Evaluating the efficiency of the effluent treatment demands the choice of adequate quality parameters. The frequency of each parameter used to evaluate the efficiency of wastewater treatment technologies is shown in Figure 6.3.

Figure 6.3: Parameters evaluated for each treatment technology.



COD is the most frequently monitored parameter for the treatment of post-tanning effluents. BOD is monitored more often in biological treatment, however, its monitoring frequency is, overall, lower than COD. This may be related to the low biodegradability of the post-tanning effluent, with the COD being more relevant than the BOD for measuring the effluent treatment efficiency. AOPs and biological treatment are the most frequently used techniques for the removal of COD and BOD, respectively.

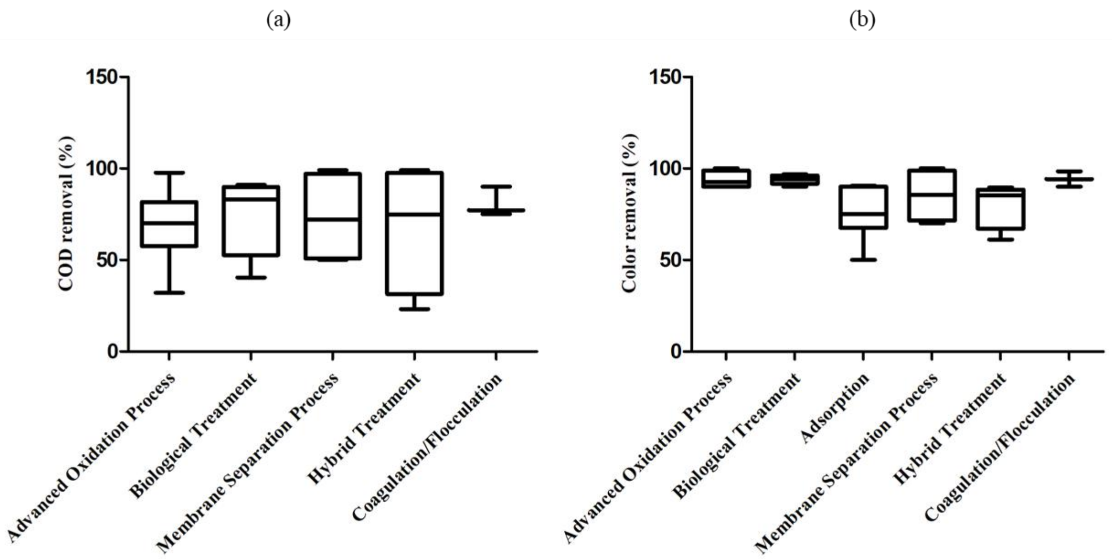
Color is also a parameter of great interest in the treatment of post-tanning effluent, which is colored due to the presence of dyes and can block both sunlight penetration and oxygen dissolution, which are essential for aquatic life (Rauf et al., 2011). Furthermore, dyes have a complex chemical structure and are difficult to treat by conventional methods (Gomes et al., 2016). Thus, there is a considerable need to develop treatment technologies for colored effluents. Adsorption is the most frequent process applied for color removal.

Chromium is also a target in some effluent treatment studies. Chromium may be associated with the use of the rechromming step in post-tanning or leaching of chromium from the main tanning process (Bufalo et al., 2018).

Although nitrogen is one of the most concerned pollutants in tannery wastewater (Wang et al., 2016), this parameter has only been used in two studies. NH_3-N contamination is mainly originated from beamhouse steps (deliming and bating processes) due to the use of ammonium salts, such as $(NH_4)_2SO_4$ and NH_4Cl, to neutralize alkalis that are introduced into the liming process (Lei et al., 2020). Other parameters appear less frequently.

The efficiency of COD and color removals (main parameters evaluated for post-tanning effluent treatment), for each group of technologies, are shown in Figure 6.4. COD and color removal data of each treatment technology group were analyzed by the Kruskal Wallis statistical test followed by Dunns' post-test in the GraphPad Prism software (data were non-parametric). The analysis showed no significant difference for the efficiencies of color and COD removals when comparing the groups of treatment technologies, considering a 95% confidence interval. A discussion of the results for each treatment technology group is presented below.

Figure 6.4: Removal efficiency (%) of COD (a) and color (b) per group of technology.

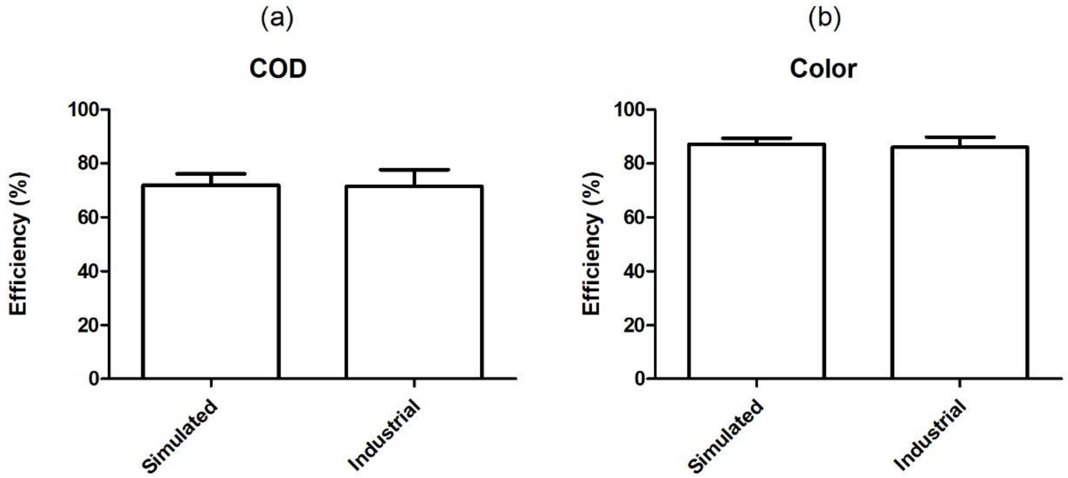


The pollution input of effluents has a significant impact on the efficiency of treatment techniques. In electro-oxidation, complete mineralization of heavily loaded effluents proved to be impractical due to energy costs (Basha et al., 2009). In ozonation, the initial concentration of the effluent also showed a significant depletion on the removal of COD (Preethi et al., 2009). The increase in pollution load also reduced the efficiency of biological treatments tested by several authors (Huang et al., 2015; Mannacharaju et al., 2020; Ortiz-Monsalve et al., 2019, 2017; Senthilvelan et al., 2014), which may have adverse effects on biomass production and/or enzyme activity. The exception was the microalgae study, which concluded that a higher wastewater load of nutrients is more appropriate for the microalgae consortium (Pena et al., 2020). Adsorption is also suitable for the removal of contaminants present in small quantities (Rigueto et al., 2020b). Thus, the reduction of the pollution load of wastewater at the source (implementing cleaner technologies during leather processing) can be an important alternative for the effluent treatment technologies to achieve greater pollutant removal efficiencies.

Some alternatives can be adopted for cleaner leather production and the obtention of less polluted effluents. The reduction in the supply of fatliquoring agents (Gutterres, 2003, 2001; Heidemann, 1993) and retanning agents (Gutterres, 2007; Heidemann, 1993) has been investigated since the chemicals applied to leather are related to the pollution load of effluents (Hansen et al., 2020). Adjustment of leather process operational conditions was also tested, including the study of process parameters (pH, temperature, and process time) in the fatliquoring process (Gutterres and Santos, 2009), an integrated rechroming, neutralization, and post-tanning (Ayyasamy et al., 2005), and a compact dyeing process (Haroun, 2005), aiming to increase process bath exhaustion and reduce the pollution load of effluents. The industrial-scale application of formulations with optimized inputs of leather chemicals and with the adjustment of operational conditions that maximize the exhaustion (absorption of the chemicals from the process baths) seems to be a way to respond to the necessary minimization of effluents pollution. To implement these adjustments, tanneries must apply tests on a pilot and industrial scale, evaluating the quality of the baths and the leather produced. Variations in the formulation or the sort of processed leather can interfere with the quality of the product obtained. The use of natural dyes (Fuck et al., 2018; Sudha et al., 2016) and natural biocides (microencapsulated essential oils) (Kopp et al., 2020) has also been investigated since these products are extracted from sustainable sources and hazardous chemicals are not used during production, reducing the pollution of liquid effluents. Some drawbacks for the application of natural products limit their use on an industrial scale, such as limited availability and instability (e.g. Monascus purpureus dye with low colorfastness to UV light - Fuck et al., 2018). Thus, further research is needed to overcome these drawbacks, given the benefits that the use of natural products would bring to the leather process.

58% of the studies used simulated effluent for the experiments, and 42% used industrial effluent. The efficiency of removing COD and color (parameters used most frequently) for simulated and industrial effluents are shown in Figure 6.5. The average removal efficiency is similar for simulated and industrial effluents, and the standard deviation for industrial effluents is higher compared to simulated effluents. Studies using synthetic effluents are relevant to control process variables and to model and understand the effluent treatment mechanism. However, industrial effluents are more complex. The presence of other substances in industrial effluent can interfere with treatment efficiency, which may justify a higher variability in removal efficiencies. Thus, the use of real industrial effluents needs to be further explored, approaching the industrial-scale conditions and enabling the implementation of post-tanning effluent treatment technologies in tanneries.

Figure 6.5: Removal efficiency (%) of COD (a) and color (b) for simulated and industrial effluents.



Some of the treatment technologies explored in this systematic review can be applied along with conventional tannery wastewater treatment (Figure 6.6). Certain technologies can be applied before biological treatment, to increase the biodegradability of effluents (adsorption, electrochemical oxidation, Fenton, photo-Fenton, ozonation, and photocatalysis) or to remove

SS or chromium (III) (coagulation/flocculation). Other techniques are applied for final polishing of the effluents, aiming to remove pollutants present in low concentrations after the conventional treatment of the effluents (adsorption, chlorine dioxide oxidation, enzymatic treatment, Fenton, MSPs, and photoelectrochemistry) to reach the standards foreseen in regulations for disposal or to enable the reuse of the treated effluent. Some technologies can also be used in a complementary way in biological treatments, such as microalgae, for the removal of nutrients, and enzymatic (azoreductase), isolated bacteria (Lactobacillus paracase), or fungal treatments for the removal of azo dyes. MBBR can be applied to remove organic matter as well as pollutants such as phenols and nitrogen.

Figure 6.6: Technologies that can be applied along with the conventional treatment of tannery effluents.

Treatment technologies applied prior to biological treatment:

- Adsorption
- Coagulation / flocculation
- Electrochemical treatment
- Fenton / Photo-Fenton
- Ozonation
- Photocatalysis

Complimentary/novel biological treatment technologies:

- Biodegradation by *Lactobacillus paracase* CL110 (combined to conventional biological treatment)
- Bacterial culture mediated with azoreductase enzyme
- Fungal treatment
- Microalgae (complimentary to conventional biological treatment)
- Moving-bed biofilm reactor

Effluent polishing treatment technologies:

- Adsorption
- Chlorine dioxide oxidation
- Enzimatic treatment (removal of sulphide from anaerobic treatment)
- Fenton
- Membrane separation processes
- Photoelectrochemistry

Wastewater from beamhouse (Daniels et al., 2017; Gutterres et al., 2010) and tanning (Benhadji et al., 2018; Daniels et al., 2018; de Aquim et al., 2019; Zhang et al., 2017) processes can be recycled. However, the post-tanning stage is very diversified since it must meet the desirable properties of the leather for the final product. The low standardization of the process (compared to beamhouse and tanning) makes effluent reuse less feasible. Only 7 of the 45 articles carried out the treatment of effluents with a focus on their reuse. MSPs stand out among these studies. Effluent reuse after MSP treatment was already applied for dyeing and fatliquoring steps. The permeate was reused in the neutralizing process (Hongru et al., 2014) and as wash water (Das et al., 2010), and the concentrate was recycled in the dyeing and/or fatliquoring process (Das et al., 2010; Hongru et al., 2014), consisting of an adequate alternative to face the management of the MSPs waste stream. Recycling of concentrate streams obtained from MSPs is possible when the same formulation is used repeatedly in the tannery.

6.6. Conclusion

This review addressed the main technologies for the treatment of post-tanning effluents. The evaluated techniques included the advanced oxidation process, biological treatment, adsorption, membrane separation process, coagulation/flocculation, and hybrid treatment. The main operational conditions, novelty, and challenges of the techniques were presented.

Overall, to meet more restrictive criteria of regulation standards, or even to recycle treated effluent, complementary technologies to the conventional treatment of tannery effluents must be adopted. These technologies should be focused on the removal of recalcitrant pollutants and salts from post-tanning effluents. From the studies evaluated in this systematic review, the following treatments can be recommended, according to the objective of the Wastewater Treatment Plant:

- AOPs and adsorption can be implemented before conventional biological treatment to increase biodegradability.
- Conventional biological treatment can be improved by microalgae (removal of nutrients), enzymatic (azoreductase), isolated bacteria (*Lactobacillus paracase*), or fungal treatments (removal of azo dyes);
- AOPs, adsorption, and enzymatic treatment (*Quinone oxidoreductase*) were efficient for the final polishing of the effluents, to reach the regulation standards for disposal;
- Membrane Separation Processes demonstrated good applicability when the reuse of the treated effluent is aimed.

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Capítulo 7

Considerações Finais

7.1. Conclusões

O estudo realizado mostrou que os produtos químicos utilizados nas etapas de acabamento molhado do couro representam uma importante e preocupante contribuição na carga poluente orgânica e inorgânica dos efluentes líquidos gerados. A análise das formulações permitiu mapear a situação atual do consumo de produtos químicos e de água no acabamento molhado e a caracterização dos produtos químicos mostrou como cada classe e variedade de produto químico impacta na qualidade dos efluentes líquidos de processo. A partir desta caracterização, a formulação de acabamento molhado utilizada como estudo de caso foi ajustada, com foco na redução da dosagem de produtos químicos com maior oferta (maior percentual mássico) na formulação (recurtentes e óleos). Por fim, tecnologias aplicadas ao tratamento dos efluentes gerados foram estudadas em uma revisão sistemática. As conclusões das quatro etapas desta pesquisa estão apresentadas a seguir.

A análise de consumo de água e produtos químicos no acabamento molhado foi apresentada no Capítulo 3. Esta avaliação identificou as etapas em que ocorrem os maiores consumos de produtos químicos (recurtimento e engraxe) e de água (lavagens), permitindo futuras proposições de otimizações focadas nestas etapas. A avaliação de 43 formulações indicou um consumo médio de produtos químicos no acabamento molhado de 360,2 kg de produtos por tonelada de couro processado, e um consumo médio de água de 8,6 m^3/t. O estudo também apontou valores máximos indicados para o consumo de produtos químicos e água: 424 kg/t de produtos químicos e 10 m^3/t de água. Estes valores foram indicados com o objetivo de fornecer uma referência de consumo para os curtumes e a indústria de produtos químicos para o couro, e por sua vez contribuem para evidenciar formulações que utilizam quantidades excessivas destes insumos. Com relação às caracterizações de efluentes de acabamento molhado compiladas a partir da literatura, verifica-se que é um efluente pouco biodegradável, com elevada condutividade e presença de sais (especialmente sulfatos e cloretos).

A caracterização físico-química e citotóxica dos produtos químicos de acabamento molhado e dos efluentes brutos gerados neste processo foi apresentada no Capítulo 4. As principais características dos grupos de produtos químicos avaliados neste estudo são:

• Os agentes desacidulantes da formulação conferiram elevada condutividade e teor de sólidos dissolvidos ao efluente bruto. Além disso, o agente recurtente neutralizante é responsável pela maior carga de nitrogênio amoniacal.

• Os taninos vegetais (de acácia) e sintéticos (fenólico, naftalénico e dicianodiamida) são responsáveis pela maior carga de poluição inorgânica (sólidos dissolvidos, cloretos e sulfatos) nos efluentes de acabamento molhado. Os taninos sintéticos possuem maior citotoxicidade em comparação aos taninos vegetais.

• Os óleos contribuem com a maior demanda química de oxigênio nos efluentes e são o grupo químico com a citotoxicidade mais elevada.

• O agente de fixação e o corante possuem elevada condutividade e contribuem com a carga inorgânica dos efluentes líquidos. Além disso, o corante e auxiliar de tingimento possuem elevada carga de nitrogênio total.

O ajuste na oferta de produtos químicos (Capítulo 5) mostrou-se eficiente na redução do impacto ambiental do processo de acabamento molhado. A dosagem de produtos químicos foi reduzida em 26%, com foco em recurtentes e óleos. Os banhos residuais dos testes em escala piloto e industrial mostraram redução na carga poluente dos parâmetros avaliados (condutividade, SDT, sulfato, DBO e DQO). Além disso, as formulações testadas em escala piloto mantiveram as propriedades organolépticas do couro em termos de maciez, enchimento e flor, e melhoram a impregnação de resina no couro. Os testes físico-mecânicos realizados no ensaio em escala industrial mostraram que a redução no fornecimento de produtos químicos produziu um couro com propriedades físico-mecânicas adequadas para a sua aplicação. Além disso, os custos da formulação de acabamento molhado foram reduzidos em 24%. É importante salientar que para implementar a técnica apresentada neste trabalho em outros curtumes é necessário aplicar os testes em escala piloto e industrial, avaliando a qualidade dos banhos e do couro produzidos, como foi realizado. A execução destas etapas é necessária pois variações na formulação ou no tipo de couro processado podem interferir na qualidade do couro obtido. Esta pode ser uma importante alternativa tecnológica para reduzir os impactos ambientais dos curtumes, haja visto que são processadas mais de 360 milhões de peles por ano no mundo, o que corresponde a uma massa superior a 6,5 milhões de toneladas (FAO, 2016). Desta forma, a extrapolação do uso desta técnica em outros curtumes pode reduzir de forma importante a massa de produtos químicos empregados e a carga poluente dos efluentes desta indústria.

As tecnologias aplicadas ao tratamento de efluentes de acabamento molhado foram estudadas no Capítulo 6. O estudo mostrou que tecnologias complementares ao tratamento convencional de efluentes de curtumes podem ser adotadas para atender a padrões de lançamento mais restritivos, ou mesmo para reciclar o efluente tratado no curtume. Essas tecnologias devem estar focadas especialmente na remoção de poluentes recalcitrantes e sais dos efluentes líquidos, podendo ser implementadas (i) antes do tratamento biológico convencional para aumentar a biodegradabilidade e remover sólidos e cromo (III); (ii) de forma complementar ao tratamento biológico (com foco na remoção de nutrientes (nitrogênio e/ou fósforo) ou contaminantes específicos, como corantes e fenóis); e (iii) aplicado no polimento final de efluentes.

Os resultados obtidos neste estudo indicam um caminho a ser seguido para melhorar o gerenciamento dos efluentes líquidos e do consumo de água e de produtos químicos nos curtumes, diminuindo o impacto ambiental da etapa de acabamento molhado do couro. A identificação dos parâmetros poluentes mais importantes para cada grupo de produtos químicos de acabamento molhado permite direcionar estudos de otimizações no processo. Desta forma, é possível reduzir a oferta de produtos químicos com foco naqueles produtos que mais impactam os parâmetros de poluição críticos, para os quais as estações de tratamento de efluentes líquidos não conseguem alcançar a eficiência de remoção necessária para atender à legislação ambiental. A qualidade do couro obtido deve ser levada em consideração, devendo atender às especificações necessárias para o produto final.

7.2. Sugestões para trabalhos futuros

Sugestões para trabalhos futuros são apresentadas:

- Analisar o efeito da quebra da emulsão (presente nos óleos de engraxe) na citotoxicidade dos banhos residuais, e comparar a eficiência do tratamento biológico do curtume antes e após a quebra da emulsão, separando o óleo sobrenadante. Os óleos são aplicados no processo de engraxe na forma de uma emulsão. A sulfatação, a sulfitação e a dosagem de agentes emulsificantes são métodos comuns aplicados para preparar as emulsões de óleo (LYU *et al.*, 2016; SIVAKUMAR *et al*., 2008). No entanto, o tratamento de óleos emulsionados é geralmente oneroso e demorado, devido à sua toxicidade para o tratamento biológico (ZHOU *et al*., 2009). Essas emulsões requerem a quebra da estabilidade, visando tratar efetivamente a água antes do seu lançamento no corpo hídrico receptor. Rotas desmulsificantes podem anular ou minimizar a estabilidade da emulsão, levando à separação de fases imiscíveis (ZOLFAGHARI *et al*., 2016) e são geralmente classificadas em rotas químicas, físicas e biológicas (CAI *et al*., 2019). Nos curtumes, os banhos residuais contendo emulsões oleosas são enviados diretamente ao sistema de tratamento de efluentes. No entanto, as análises realizadas neste trabalho mostraram elevada citotoxicidade destas emulsões, podendo reduzir a eficiência do tratamento biológico de efluentes. Desta forma, justifica-se a condução de estudos que avaliem a influência da quebra da emulsão na eficiência do tratamento de efluentes.

- Otimizar a dosagem dos produtos químicos, individualmente, avaliando sua sorção no couro com a variação de pH e temperatura, e determinar a cinética e isoterma de sorção do produto químico, visando aumentar a exaustão dos banhos. A caracterização dos produtos químicos permitiu identificar quais produtos possuem maior impacto em cada um dos parâmetros avaliados nos efluentes líquidos. Desta forma, a otimização pode ser direcionada aos produtos químicos que contribuem com os parâmetros críticos da estação de tratamento de efluentes, como COD, sais, nitrogênio, entre outros.

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