TATIANA AURORA CONDEZO CASTRO

PRODUÇÃO, CARACTERIZAÇÃO E APLICAÇÃO DE CARVAO ATIVADO PULVERIZADO OBTIDO A PARTIR DE LIGNINA KRAFT

Tese apresentada à Universidade Federal de Viçosa, como parte das exigências do Programa de Pós-Graduação em Ciência Florestal, para obtenção do título de *Doctor Scientiae*.

Orientador: Cláudio Mudadu Silva

Coorientador: Marcelo Cardoso

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RESUMO

CONDEZO CASTRO, Tatiana Aurora, D.Sc., Universidade Federal de Viçosa, maio de 2023. **Produção, caracterização e aplicação de carvão ativado pulverizado obtido a partir de lignina kraft**. Orientador: Cláudio Mudadu Silva. Coorientador: Marcelo Cardoso.

A extração da lignina kraft (LK) do licor preto (LP) gerado no processo de polpação é uma opção atraente devido aos diversos produtos de alto valor agregado que podem ser obtidos deste material. A possível conversão de fábricas de polpa celulósicas em biorrefinarias diversificaria sua linha de produtos e aumentaria a capacidade de produção de polpa, ao diminuir a carga orgânica (lignina) enviada para a queima nas caldeiras de recuperação. A produção de carvão ativado (CA) a partir de LK é uma opção viável devido às boas características físico-químicas, ao alto volume e disponibilidade da matéria prima. O uso do CA no processo de produção de polpa celulósica kraft é amplo, sobretudo para o tratamento de águas e de efluentes. Na presente pesquisa o CA foi utilizado visando o tratamento setorial dos filtrados do branqueamento (remoção de Mn) e no tratamento terciário de efluentes para a remoção de fósforo e matéria orgânica (DQO). O CA produzido foi quimicamente ativado com NaOH e apresentou características físico-químicas e morfológicas adequadas, as quais foram determinadas através de análise elementar e imediata, análise de metais, capacidade de troca catiônica, ponto de carga zero, número de iodo, análise de microscopia eletrônica de varredura, espectroscopia na região infravermelho e difração de raio-X Adicionalmente foram feitos testes de cinética para conhecer o mecanismo de adsorção avaliando modelos de pseudo primeira e segunda ordem, difusão intrapartícula e Elovich. O equilíbrio de adsorção também foi avaliado, aplicando-se modelagem com as equações de isotermas de Langmuir e Freundlich. O adsorvente apresentou uma alta capacidade de remoção de fósforo e de matéria orgânica 88,1% e 52,8% respectivamente. Na remoção de Mn não foi evidenciada nenhuma remoção do elemento, pelo contrário foi liberado Mn na solução. Esta liberação do elemento está associada à alta concentração de metais (Mn) no CA e na LK. No entanto, o uso de CA para a remoção de Mn não deveria ser descartado. O CA a partir de LK foi eficiente no tratamento terciário para a remoção de fósforo e de matéria orgânica recalcitrante, permitindo uma melhora da qualidade do efluente final.

Palavras-chave: Biorrefinaria. Tratamento de Efluentes. Lignina Kraft. Carvão Ativado. Poluição hídrica.

ABSTRACT

CONDEZO CASTRO, Tatiana Aurora, D.Sc., Universidade Federal de Viçosa, May, 2023. **Production, characterization and application of powdered activated carbon from kraft lignin**. Adviser: Cláudio Mudadu Silva. Co-adviser: Marcelo Cardoso.

The possibility of extracting kraft lignin (KL) from the black liquor (BL) generated in the pulping process is an attractive option due to the various high-value-added products that can be obtained from this material. The possible conversion of pulp mills into biorefineries would diversify their product line and would increase the pulp production capacity by decreasing the organic load (lignin) sent for burning in the recovery boilers. The production of activated carbon (AC) from KL is a viable option due to good physicochemical characteristics, high volume, and raw material availability. The use of AC within a kraft pulp mill is broad, mainly for water and effluent treatment. The research aimed at the sectorial treatment of bleaching filtrates (Mn removal) and the tertiary treatment of effluents for phosphorus and organic matter (COD) removal. The produced AC was chemically activated with NaOH and presented adequate physicochemical and morphological characteristics. which were determined through elemental and immediate analysis, metal analysis, cation exchange capacity, point of zero charges, iodine number, scanning electron microscopy, spectral analysis with infrared spectroscopy, and X-ray diffraction. Additionally, kinetic tests were performed to understand the mechanism of adsorption, evaluating models of pseudo first and second order, intraparticle diffusion, and Elovich. The adsorption equilibrium was also evaluated, applying modeling with Langmuir and Freundlich isotherm equations. The adsorbent showed a high capacity of phosphorus and organic matter removal 88.1% and 52.8%, respectively. In the Mn adsorption tests, the removal of the element was not evidenced, on the contrary, Mn was released into the solution. This release of the element is associated with the high concentration of metals (Mn) in the AC and KL. However, the use of AC for Mn removal should not be discarded. The AC from KL was efficient as a tertiary treatment in removing phosphorus and recalcitrant organic matter, allowing the improvement of the final effluent quality.

Keywords: Biorefinery. Effluent Treatment. Kraft Lignin. Activated Carbon. Water Pollution.

LISTA DE SIGLAS E ABREVIATURAS

ANOVA	Análise de Variância.
AOP	Advanced Oxidation Processes.
BET	Brunauer-Emmett-Teller.
CA/AC	Carvão ativado / Activated Carbon.
CAC	Commercial Activated Carbon.
CANaOH/ NaOHAC	Carvão ativado com NaOH / Activated Carbon with NaOH.
CTC/CEC	Capacidade de Troca Catiônica / Cation Exchange Capacity.
DBB	Delineamento Box Behnken.
DBO/ BOD	Demanda Bioquímica de Oxigênio / Biochemical oxygen demand.
DQO/COD	Demanda Química de Oxigênio / Chemical Oxygen Demand.
ECF	Elemental Chlorine Free.
EDS	Energy Dispersive Spectroscopy.
ETE/ETP	Estação de Tratamento de Efluentes / Effluent Treatment Plant.
GAC	Granular Activated Carbon.
IN	Iodine Number.
ICP-OES	Inductively Coupled Plasma Optical Emission Spectroscopy.
IR-ATR	Infrared Spectroscopy with Attenuated Total Reflectance.
KLC	Kraft Lignin Char.
LK/KL	Lignina Kraft / Kraft Lignin.
LP/BL	Licor Preto / Black Liquor.
MEV/SEM	Microscopia Eletrônica de Varredura / Scanning Electron Microscopy.
OL	Organosolv Lignin.
PAC	Powdered Activated Carbon.
pH	Potencial de Hidrogenio.
pH_{PZC}	Point of Zero Charges.
PT	Fósforo Total.
SL	Soda Lignin.
SLRP	Sequential Liquid Lignin Recovery and Purification.
TCF	Totally Chlorine Free.
TSC	Total Sulfur Compounds.
WT	Water Treatment.
XRD	X-Ray Diffraction.

SUMÁRIO

1. INTRODUÇÃO GERAL

A indústria de polpa celulósica kraft gera durante o processo de deslignificação da madeira (etapa de polpação) um resíduo orgânico (lignina) com alto potencial de transformação. A lignina extraída da madeira forma parte do chamado licor preto (LP), o qual é composto por uma fração orgânica e outra inorgânica (CARDOSO, 1998). Normalmente a lignina é queimada nas caldeiras de recuperação para a geração de energia, limitando o seu alto potencial de uso para outros fins. Atualmente existe uma crescente tendência em extrair uma fração da lignina do LP, chamada de lignina kraft (LK), para a sua aplicação em outros setores industriais (CAO *et al.*, 2018; RIDHO *et al.*, 2022). Aproximadamente 70 milhões de toneladas de LK são produzidas anualmente em todo o mundo (LIU *et al.*, 2020), sob processos e/ou tecnologias diversas de extração já patenteadas, entre elas o conhecido processo LignoBoost (TOMANI, 2010).

A disponibilidade e o grande potencial da LK têm chamado a atenção para o desenvolvimento de inúmeras pesquisas na obtenção de produtos com alto valor agregado (CHATTERJEE; SAITO, 2015; DE ASSIS *et al.*, 2018; DESSBESELL *et al.*, 2020). O aproveitamento deste material auxilia na transformação das fábricas de celulose em biorrefinarias. Entre os usos da LK como matéria prima destaca-se a produção de carvão ativado (CA) devido a seu alto teor de carbono, disponibilidade e o alto volume de produção (BRAZIL *et al.*, 2022; FIERRO *et al.*, 2008).

O emprego do CA no processo de produção de polpa celulósica kraft pode incluir o tratamento de águas e efluentes (CONDEZO *et al.*, 2023). Os efluentes gerados nas fábricas possuem uma alta carga orgânica complexa e que pode causar efeitos negativos nos corpos hídricos (MANDEEP *et al.*, 2019). Na etapa de branqueamento da polpa é gerado o efluente com a maior carga orgânica e volume enviado à estação de tratamento de efluentes (ETE) (COLODETTE; GOMES, 2015). O possível uso do CA para o tratamento dos filtrados do branqueamento é uma alternativa atrativa que permite o reuso da água e consequentemente a diminuição do seu consumo. O tratamento com CA pode remover metais que causam, a degradação das cadeias de carboidratos durante o branqueamento da polpa celulósica, o consumo de reagentes de branqueamento e a incrustação e corrosão nos equipamentos (CONDEZO *et al.*, 2023).

Além do uso do CA como tratamento setorial, ele pode ser utilizado para o tratamento terciário dos efluentes antes de serem lançados aos corpos d’água. Os efluentes tratados finais podem conter material recalcitrante que não são removidos durante o tratamento biológico nas ETE (HAQ; MAZUMDER; KALAMDHAD, 2020). O teor de fósforo nos efluentes após tratamento biológico é um aspecto ambiental relevante, já que concentrações de fósforo inadequadas poderiam causar eutrofização das águas (YU *et al.*, 2022). Existem registros que concentrações de 0,5 mg/L de fósforo total em efluentes gerados em fábricas de polpa celulósica branqueada foram capazes de causar eutrofização nos corpos hídricos (BOTHWELL, 1992); no entanto, na legislação ambiental brasileira não existem padrões de lançamento de fósforo total em efluentes industriais.

O presente trabalho objetivou produzir carvão ativado quimicamente usando a lignina como matéria prima, e avaliar seus possíveis usos no tratamento de efluentes de fábricas de polpa celulósica kraft. O estudo foi dividido em quatro artigos que equivalem a cada capítulo da tese.

Capitulo 1 – Este capitulo intitulado "Possible alternatives for using kraft lignin as activated carbon in pulp mills – a review", corresponde ao artigo já publicado da tese na revista Nordic Pulp & Paper Research Journal publicado em 2023. O artigo trata de uma base bibliográfica da pesquisa onde se discute as características, benefícios, viabilidade e tecnologias para a extração da lignina do LP. Apresentou-se os sistemas produtivos, os tipos e formas de ativação e regeneração, as tecnologias empregadas, os desafios ambientais e a viabilidade econômica para a produção de carvão ativado. Foram apresentados e discutidos os possíveis usos do CA para o tratamento de águas e efluentes no processo de produção de polpa celulósica kraft, seus desafios e perspectivas futuras.

Capitulo 2 – No Capitulo 2 foi detalhada a produção do carvão ativado a partir da LK, usando como agente ativante NaOH. Após a obtenção do CA, o adsorvente foi caracterizado e suas propriedades foram analisadas para o seu uso como adsorvente.

Capitulo 3 – Neste capitulo foi avaliada a capacidade de adsorção do CA na remoção de fósforo e de matéria orgânica (DQO recalcitrante) em efluentes após tratamento biológico, como parte de um tratamento terciário. Buscou-se verificar a viabilidade técnica do uso do CA para o eficiente tratamento e melhoria da qualidade final dos efluentes antes de serem descartados nos corpos hídricos. No estudo foram realizadas análises da cinética e do equilíbrio de adsorção.

Capitulo 4 – Avaliou-se o comportamento do carvão ativado para a adsorção de metais, especificamente Mn. O estudo de adsorção foi feito em batelada, utilizando-se uma solução sintética.

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CAPITULO 1

POSSIBLE ALTERNATIVES FOR USING KRAFT LIGNIN AS ACTIVATED CARBON IN PULP MILLS – A REVIEW

ABSTRACT

The uses of kraft lignin (KL), obtained from the black liquor (BL) in the pulping process, allow the production of activated carbon (AC), a product with high added value in the pulp mill. The AC can be used in three different sectors in a cellulose pulp mill: sectorial treatment of the cellulosic pulp bleaching filtrates; wastewater treatment; and in the treatment of water received by the mill. Thus, this article considers the steps in the production of AC, their types, and the advantages and challenges of its use in the kraft cellulose pulp mill as well as in other industries.

Keywords: Activated carbon; Cellulosic pulp mill; Lignin; Wastewater treatment; Water treatment.

1. INTRODUCTION

The pulp and paper industry is one of the industries with the highest generation of pollution (COLODETTE; GOMES, 2015; NETWORK, 2018). These mills produce a large volume of effluents containing both organic and inorganic toxic matter, which makes pollution of freshwater one the biggest environmental concerns for these industries (GAVRILESCU *et al.,* 2012). The industrial stage with the highest contaminant load in the bleached cellulosic pulp production process is bleaching.

Although the vast majority of Brazilian mills already have adequate effluent treatments which comply with local environmental legislation, the large volume destined for effluent treatment plants (ETPs) and the presence of recalcitrant substances in the final treated effluent are aspects that can still be improved. A possible solution for this problem is the treatment of stage effluents, aiming at their reuse in a closed water circuit.

The stage treatment of effluents enables the reuse of water, reduces fresh-water consumption and, consequently, reduces the volume of the organic and volumetric load of the effluents directed to the ETP (QUEZADA *et al.,* 2014).

Several types of effluent treatment can be used in the pulp and paper industry, such as physical, chemical, electrochemical and biological processes (PATEL *et al.,* 2021; WU *et al.,* 2021; SINGH *et al.,* 2022). The water and wastewater treatments using activated carbon have been widely evaluated (SCIBAN; KLASNJA 2004; MOHAN *et al.,* 2006; GUO *et al.,* 2008; LAM *et al.,* 2008; YANG *et al.,* 2010; DJILANI *et al.,* 2015; ALY-ELDEEN *et al.,* 2018). Currently, activated carbon (AC) is used in several industrial sectors because it is able to decolorize, deodorize and purify liquid or gaseous emissions. The wide possibility of application of AC is related to its excellent adsorption capabilities, attributed to its physical-chemical characteristics. Among these characteristics, porosity, pore size and high surface area can be mentioned. The chemical interaction between polar substances and heteroatoms, mainly oxygen and hydrogen, components of the non-polar surface of AC, form structures or functional groups that also benefit the adsorption process. The production of AC can be achieved from several precursor raw materials that depend upon the type of industry and the available feedstock. In the pulp industry, for instance, AC may be produced from lignin contained in black liquor (BL). Modern kraft pulp mills have currently invested in technologies for obtaining lignin from BL, due to its wide range of industrial applications. Thus, the pulp industry can become more diversified and generate additional income through the production of new bioproducts aside from cellulosic pulp. Although the actual tendency is to obtain kraft lignin (KL) through BL precipitation, knowledge about the potential uses of lignin and its commercialization is still lacking.

In this regard, the AC produced from KL can provide an attractive opportunity for the treatment of stage effluents from the pulp industry itself, improving the final effluent quality, mainly in the removal of such recalcitrant compounds as phenols, as well as color.

The objective of this work is to show different alternatives of the use of the AC from KL contained in BL, for the treatment of water and effluents generated in pulp mills. In each alternative, the interest and benefits of extracting many contaminants or impurities from these effluents were explained. In addition, the authors address the extraction process of KL from BL, the production of AC and its possible integration in a kraft pulp mill.

The indexed publications were collected manually by referring to the title, abstract and the keywords from 144 articles obtained by keywords search of “activated carbon” and “kraft lignin”, from february 2023 to 1993. Searches were performed in the Science Direct (https://www.sciencedirect.com/) (43 articles) and Scopus (https://www.scopus.com) (101 articles). However, some identified research articles were not relevant according to the objectives of the review. Other studies relevant to the review were included; which cover obtaining and characteristics of kraft lignin, activated carbon (in general) and operation of the kraft pulp industry and its effluents (157 articles).

2. KRAFT LIGNIN AS A PRECURSOR OF ACTIVATED CARBON

2.1. Why is kraft lignin produced?

KL is obtained from the BL generated after the wood chips are cooked during the kraft pulp manufacturing process, the technology which gives this type of lignin its name. Briefly, the BL consists mainly of lignin and other organic and inorganic components, resulting in the delignification of the wood through the chemical reagents used. This BL is directed towards the evaporators of the chemical recovery circuit, where its solids would be concentrated at around 72% to 81%. Afterward, the concentrated BL is sent for burning in the recovery boiler, where the organic fraction is incinerated, releasing heat for the production of steam and electricity, while the inorganic fraction goes on to other steps in order to obtain the reagents used in the cooking. For each ton of kraft pulp, 10 tons of weak BL and approximately 1.5 tons of dry solids are produced after the chemical recovery process (TRAN; VAKKILAINNEN, 2016), of which 30% to 45% (depending on the wood species) corresponds to the concentration of lignin (CARDOSO, 1998).

Currently, many pulp mills face problems in the recovery boiler with so-called production “bottlenecks” due to the high organic load being sent to the boiler. In order to correct this, one possible solution could be the diversion of a fraction of the concentrated BL to obtain KL. This alternative, in addition to producing high value-added products such as activated carbon, reduces the organic matter to be incinerated in the boiler and increases the pulp production capacity without disturbing the plant's operation (BENALI *et al.,* 2014). The amount of lignin available for precipitation can vary from 5% to 20%, depending on the needs of the facility (DESSBESELL *et al.,* 2020).

It is common for many kraft pulp mills to have a surplus of energy, and approximately 20% of the recovered KL can be withdrawn and used for other applications without disrupting the mill's operation (VAKKILAINEN; VÄLIMÄKI, 2009; GOUVÊA, 2012; JIN *et al.,* 2012; GUSTAFSSON *et al.,* 2017; ABDEL-AZIZ *et al.,* 2019).

KL is obtained by acidifying the BL, lowering the pH. As the pH decreases, hydrogen ions interact with the negatively charged lignin due to the presence of weakly dissociated acid groups (e.g., phenolic and carboxylic groups). Then, the lignin loses stability, beginning to aggregate into larger particles and precipitates. Several technologies on the market that precipitate BL lignin follow this principle.

2.2. Technologies used to obtain kraft lignin

The lignin contained in the BL from the kraft process can be isolated through chemical, physical, physical-chemical and biological treatments (KAZZAZ; FATEHI, 2020). The criteria for selecting the most adequate lignin isolation treatment can be divided as follows: i) lignin must be isolated quantitatively; ii) it must be free of contaminants; and iii) the procedure must be simple and easy to perform. These criteria are mainly satisfied when KL is isolated by acidification. Precipitation can be achieved using different types of acidifying reagents such as sulfuric acid, hydrochloric acid and carbon dioxide, among others (GAO *et al.,* 2020). Thus, the quality of the precipitated lignin and its characteristics will be directly related to the type of reagent used.

Commercial processes for extracting and purifying KL by precipitation are already available on the market, such as the LignoBoost process, owned by Valmet (a Metso company) since 2008 (TOMANI, 2010). In this process, CO_2 and H_2SO_4 are used as acidifying agents in BL and allow separation of ~98% pure KL with low carbohydrate content and 1% to 3% w w^{-1} ash (BENALI *et al.,* 2014). The estimate of the total investment costs and the production capacity for a LignoBoost plant is detailed by both Dessbesell *et al.* (2020) and Tomani (2010).

Other technologies are also available on the market, such as LignoForce, developed by FPInnovations (KOUISNI *et al.,* 2012), the TMP-Bio process developed by FPInnovations and Noram Engineering (BARBIER; HAMEL, 2018) and Sequential Liquid Lignin Recovery and Purification (SLRP), a process developed by Lignin Enterprises LLC (BERLIN; BALAKSHIN, 2014; LAKE; BLACKBURN, 2014). In the LignoForce process, BL is oxidized using O_2 under controlled conditions before the CO_2 acidification step. This technology minimizes or eliminates total sulfur compounds (TSC), which consequently reduces the consumption of carbon dioxide and sulfuric acid during acidification (KOUISNI *et al.*, 2012). In the TMP-Bio process, hydrolyzed lignin and sugar are produced through the enzymatic hydrolysis of noble wood with a capacity of 1 t $week^{-1}$ (BARBIER; HAMEL, 2018). It presents lighter-colored lignin, free from odors and sulfur, with a structure similar to native lignin (KAZZAZ; FATEHI, 2020). In SLRP, the BL lignin is precipitated using column reactors with countercurrent flow. The BL, introduced at the top, comes into contact with CO_2 that flows up from the bottom under high temperature and pressure to form dense drops of liquid lignin (LAKE; BLACKBURN, 2014). Subsequently, the liquid lignin is separated by gravity and acidified with H_2SO_4 to a pH of 2-3. This process differs from more traditional methods where lignin precipitates as small solid particles and needs further filtration. Whatever technology for precipitating KL is used, the water and/or energy consumption must not be increased. Moreover, the Na/S balance must not be altered in the white liquor chemical recovery cycle, as this can affect the quality of the kraft pulp (BENALI *et al.*, 2014).

2.3. Characteristics of kraft lignin

Lignin is a complex irregular three-dimensional macromolecule of aromatic nature that has been extensively evaluated and characterized (CHEN *et al.,* 2017; SHAO *et al.*, 2017; JARDIM *et al.,* 2020; KAZZAZ; FATEHI, 2020;). Due to its complex chemical structure, isolation is difficult, and when it can separate, the original molecular structure is compromised. Usually, the lignin extracted from BL has a molar mass in the range of ~1,000 g mol^{-1} to 20,000 g mol^{-1} (the non-uniformity of lignin prevents the characterization of a specific weight), is insoluble in water and has a dark color and an unpleasant odor (JUNIOR *et al.*, 2020). Lignin is stable in mineral acid solutions and soluble in hot aqueous bases (NORGREN *et al.*, 2001). The solubility of KL in water is low due to the deficiency of hydrophilic groups in its chemical structure (KAZZAZ; FATEHI, 2020).

The characteristics of KL, in terms of elemental composition and ash content, depend on the type of methodology employed for its extraction and purification, precursor (coniferous, hardwood or other types of biomass) and the conditions for cooking the chips. Thus, a rigorous selection of the precursor and an efficient extraction of lignin that aims mainly at a minimum ash content in both cases is convenient since these compounds can obstruct the pores of the adsorbent and consequently reduce its adsorption capacity. Ash contents of 0.8% for KL obtained by the LignoBoost method were reported by Tomani (2010), although ranges between 0.5% and 3.0% are known (KAZZAZ; FATEHI, 2020). Another important aspect is the lignin yield, which progressively decreases as the pH is lowered (GARCÍA *et al.,* 2009). However, the best quality KL is obtained at low pH (SANTOS *et al.,* 2014).

Other sources of technical lignin (extracted lignin) can be obtained depending on the method of lignocellulosic biomass processing to obtain the pulp. In addition to the kraft process, we can find the sulfite process and sulfur-free processes such as organosolv and soda. Sulfite pulp technical lignin can have medium to high molecular weights, higher than KL, because of the addition of sulfonate groups (RIDHO *et al.*, 2022). The sulfite process is responsible for the generation of lignosulfonates. The production of lignosulfonates requires several purification steps, as the liquor resulting from the sulfite process contains a high level of sugar. The main reactions that cause lignin solubilization in this process are sulfonation and acid hydrolysis (DEMUNER *et al.*, 2019). These reactions are caused by SO_2 and HSO_3^- (acid sulfite), HSO_3^- (bisulfite), or HSO_3^- and SO_3^{2-} (neutral sulfite) in the presence of a cation (such as sodium, calcium, magnesium or ammonium). The organosolv process uses organic solvents with or without catalysts, and is considered one of the smoothest delignification processes, as it obtains a lignin with a structure close to the original one. Organosolv lignin (OL) contains few carbohydrates, ash and other non-lignin impurities (ZENG *et al.*, 2023). The process can produce pure lignin, with high yield and homogeneity (RABELO *et al.*, 2023). Soda lignin (SL) uses NaOH as the chemical active to solubilize most of the lignin. SL presents higher purity than lignosulfonate lignin, although it has a lower molecular weight.

The use of any type of technical lignin for the production of AC can be possible, although the lignin of kraft process is more important as it can be used on a commercial scale (SUHAS; CARROTT; CARROTT, 2007). Lignin such as organosolv have already been evaluated as adsorbents for metals such as copper (ACEMIOGLU *et al.*, 2003). Others such as lignosulfonates have been evaluated for the removal of copper and cobalt ions (JIANG *et al.*, 2020). Lignosulfonates, for having many active functional groups on the vertices and edges of carbon, allow chemical reactions (esterification, oxidation and sulfonation) that provide better adsorption; as the case of heavy metals (ZHANG *et al.*, 2023).

In addition to AC production, kraft lignin can be used as a component for the production of other products, such as solid fuels such as pellets or briquettes, where KL seeks to improve physical-mechanical properties such as mechanical durability. Other uses of LK are its application in the production of chemical products such as polymers to improve thermal stability and flexural strength; in the production of adhesives using biophenols as a substitute for phenols derived from petroleum; in the production of liquid fuels through LK gasification; for the production of carbon fibers and among others (DEMUNER *et al.*, 2019).

3. ACTIVATED CARBON PRODUCTION

3.1. Types and ways of obtaining the activated carbon

Numerous raw materials can be used to manufacture AC, which must have high carbon content and, especially, a low ash content (MENÉNDEZ-DÍAZ; MARTÍN-GULLÓN, 2006; CARROTT *et al.,* 2008a; FENG *et al.,* 2021). Lignocellulosic biomasses and some industrial residues are examples of precursors that are widely used to produce AC (GAO; YUE; GAO, 2016).

The production of AC must be carried out in two stages: carbonization and activation. In carbonization, the precursor material develops an incipient pore structure due to partial combustion and thermal decomposition. Char is the residue formed during the pyrolysis of biomass, with carbon content in the range of 25% to 50% on a dry basis (BERGNA *et al.,* 2018). From lignin, during pyrolysis, solid char, liquid oil, aromatic products, gases (carbon monoxide and carbon dioxide) and volatile liquids (methanol, acetone and acetaldehyde) are formed (PANDEY; KIM, 2011). Other volatile products that we can find during lignin pyrolysis are vanillin and guaiacol at 400 ºC, catechol of 600 ºC to 800 ºC and aromatic hydrocarbons and phenols at 1000 ºC (SHARMA *et al.*, 2004). Pyrolysis breaks the lignin β-O-4 bonds, which subsequently form free radical species at temperatures above 350 °C (CHU *et al.,* 2013). During lignin pyrolysis, reactions of dehydration, decarboxylation and decarbonylation occur. They may also show lignin dehydrogenation at high temperatures.

Yields from pyrolysis of lignin during carbonization in the Pyroprobe® pyrolizer can decrease by 62% with increasing temperature at 400°C, and a gradual decrease of 40% at 750°C (SHARMA *et al.*, 2004). However, char yields increase with decreasing heating rate. Low heating rates favor the production of carbon with a more orderly structural arrangement and surface areas increase in shorter carbonization times (BRAZIL *et al.*, 2017). Among the parameters that affect the carbonization process are: temperature, residence time, heating rate and type of precursor material. These parameters directly affect the physical and chemical characteristics of the adsorbents. For example, the application of excessive temperatures during the pyrolysis process can increase the ash content contained in the precursor material by triggering the formation of metallic oxides (MAULINA; IRIANSYAH, 2018). Consequently, the increase in ash impairs the adsorption process, blocking the entrance of the adsorbate into the CA pores. Additionally, the extreme conditions in the parameters during the carbonization process can affect the carbon content and the fixed carbon content. The carbon atoms during carbonization are responsible for creating the irregular microcrystalline structures that form the initial porosity of the material.

In the activation, the porous matter formed in the previous stage is activated, through physical or chemical processes, or a combination of both. It is important to point out that AC production can also be performed in a single phase (BERGNA *et al.,* 2018).

AC can be classified according to particle size into powdered activated carbon (PAC), with particles of 15-25.10^{-3} mm, or granular activated carbon (GAC), with particles between 1-5 mm. PAC is normally used for liquid phases, in systems with batch agitation and when the solute has difficulties in diffusing into the pores. Also, it is used in gaseous flows, because that PAC can have a bimodal distribution of pores, high surface area and a low bulk density generally, achieving a higher adsorption of the odors compounds (HUANG *et al.*, 2019). Among some industrial applications of the PAC that can be indicated the discoloration of sugar, food industry, pharmaceutical and cosmetic uses, and in the treatment of waste and municipal waters (MENÉNDEZ-DÍAZ; MARTÍN-GULLÓN, 2006a). The use of PAC in the cosmetic industry has gained a great deal of attention in facial cleansers, facial masks, soaps and in products to treat acne and dermatitis (SAJJAD *et al.*, 2021). GAC is normally used in fixed beds in continuous processes and with low pressure drops. There are two types of GAC formats, broken (having irregular particles) and molded (cylindrical in shape, obtained by pelleting) (MENÉNDEZ-DÍAZ; MARTÍN-GULLÓN, 2006). More uses of PAC and GAC can be seen in Figure 3.

AC production is usually done in pyrolysis reactors that can be divided into fixed-bed and movable-bed reactors. Among those with movable-bed we can find three groups, mechanical reactors (the most common rotary kiln), reactors where the raw material moves under gravity and pneumatic ones (bubbling, spouted and fluidized beds) (MOPOUNG; DEJANG, 2021). Rotary kilns are the most popular among all, they have a longer residence time than other types of kilns due to their wide length. The kiln contains a mixer along the inside of the kiln to provide a more homogeneous gassing of the raw material. This produce activated carbons with a more controlled pore structure, more microporosity and a lower proportion of mesopores (MARSH; RODRÍGUEZ-REINOSO, 2006a). The microporosity of AC gives it a high surface area and retention capacity, while the mesopores and macropores allow it to retain large molecules. The characteristics of the reactor allow the use of raw materials of different shapes, sizes and calorific values, producing uniform pyrolite products with possible continuous operation (MOPOUNG; DEJANG, 2021). Multiple hearth kilns, consisting of a rotating central vertical axis that allows the material to be transported through each of the stationary floors (stages) that the kiln has internally. Thus, the material is transported by gravity, alternately falling from one stage to the nearest one. In the kiln, there are several supplies of heat and steam in different stages and temperature regulation is relatively simple. The quality of the AC produced can be slightly lower than the rotary kilns, due to the low residence time, developing more mesoporous carbons (MARSH; RODRÍGUEZ-REINOSO, 2006a). In the case of fluidized bed kilns, they are characterized by good heat and mass transfer, with excellent contact of the carbon particles with the activating gases. It has a shorter residence time than other activation kilns. The main problem with this type of kiln is the extensive reaction of the carbon causing a lot of burning of the outer part of the particles. The activated carbons of this type of kiln are of relatively low quality and are mainly used in powdered form for decolorizing purposes.

The indicated kilns types are designed for the physical activation of the raw material. However, the production of chemically activated carbon is possible if a previous step of impregnation of the raw material, with the activating agent, is carried out before activation and with a subsequent step of washing the AC (KANG; PARK; RIM, 2006).

The choice of any of the reactors for the production of AC from KL must consider the characteristics of the KL, mainly its thermoplastic nature, which could complicate its processing. The format of the AC for its production in reactors must also be evaluated. Production of GAC from KL may not be advisable on an industrial scale. The low density and hardness of lignin char may not withstand the mechanical friction that occurs inside reactors such as rotary kilns (RAGAN *et al.*, 2011).

3.2. Activation

There are two ways to activate char, physical or thermal activation and chemical activation, both with an expected yield of activation of approximately 15% to 25% (KIM *et al.,* 2019).

3.2.1. Physical activation: characteristics, applicability and environmental aspects

In physical activation, the char produced in carbonization is partially gasified through the use of an oxidizing agent, water vapor and mainly CO_2. These activators react with the carbon atoms and remove part of the mass from the internal surface of the solid in the initial micropores created in the previous step and the development new pores (AHMIDA *et al.,* 2015). The development of char porosity during activation consists of three mechanisms: i) the opening of inaccessible pores formed in previous stages; ii) the creation of new pores; and iii) the enlargement of existing pores (MARSH; RODRÍGUEZ-REINOSO, 2006).

Among some physical activators of kraft lignin we can mention CO_2, tested for the first time by Rodriguez-Mirasol *et al.* (1993). The author, during the carbonization of KL, as a step prior to activation, observes the constriction of micropores with increasing temperature, reducing the accessibility of N_2 molecules during experimental conditions and consequently decreasing the surface area.

In the literature, physical activations record BET surface areas of the AC that can vary from 1343 $m^2\ g^{-1}$ at 850 ºC, during 40 h under CO_2 flow (RODRÍGUEZ-MIRASOL; CORDERO; RODRÍGUEZ, 1993), to 1853 $m^2\ g^{-1}$ at the same temperature at decrease reaction time to 20 h under CO_2 flow. Activated carbons had ash contents of between 10% to 11%, although they could be removed through acid washes. Microporous ACs and widening of the micropore size distribution as activation proceeds was also observed. Carrot *et al.* (2008) verified that inorganic impurities, such as Na_2CO_3 and Na_2SO_4, in KL influence the behavior during pyrolysis under N_2 flow and activation in CO_2 or steam. The inorganics contained in KL undergo a rapid decrease in weight during pyrolysis at temperatures above 750 °C, due to the catalytic reaction promoted by the ash. This reaction causes a collapse or blockage of the micropore structure initially created during pyrolysis. However, the activated carbon produced had BET surface areas of up to 1600 m^2 g^{-1}, micropore volumes of 0.5-0.6 cm^3 g^{-1}, and average widths between 1.2-1.4 nm.

Other more current works employ ultrasonic (KIM *et al.*, 2021) and plasma physical treatments. Plasma treatments with oxygen or argon flow showed more significant changes in carbon morphology when compared to chemically activated carbons with 5 M sulfuric acid. A greater amount of micrometric pores, a rougher surface, a larger BET surface area (up to 63% increment) and a higher carbon content were found (BRAZIL *et al.*, 2018). The use of plasma favored a higher carbon yield due to a lower proportion of oxygen (~ 6% to 10 %) in the atmosphere, creating chars with more hydrophobic characteristics. Physical activations in an oxidizing atmosphere such as air was reported by Suhas (2017) in demineralized KL, obtaining microporous carbons with BET surfaces of up to 1305 m^2 g^{-1}.

The physical activation process is widely applied by industries (YANG *et al.,* 2010). From an economic and environmental point of view, its simplicity, low production cost (employing unused chemical reagents) and lack of a washing step to further remove reagents all represent advantages (BERGNA *et al.,* 2018). However, low yields, as a consequence of high temperatures and longer activation times (BERGNA *et al.,* 2018), and low pore development, represent disadvantages (GUO; ROCKSTRAW, 2006; GAO *et al.,* 2020). The characteristics of AC depend on the activating agent, precursor material type, manufacturing methodology, activation parameters and particle size (MENÉNDEZ-DÍAZ; MARTÍN-GULLÓN, 2006; GAO *et al.,* 2020). Thus, each type of AC produced has a specific application. Accordingly, characterization and proof tests are always needed to assess their adsorption capacity for certain specific contaminants.

In the literature, physically activated carbon can be used for the adsorption of aromatic compounds (ROSAS *et al.,* 2014), phenol and p-nitrophenol (COTORUELO *et al.,* 2012; CHAUDHARY *et al.,* 2022), organic compounds like toluene and benzene (RODRÍGUEZ-MIRASOL *et al.,* 2005; COTORUELO *et al.,* 2007c; a), surfactants (COTORUELO *et al.*, 2009), pharmaceutical products (COTORUELO *et al.*, 2011; MIRZAEE *et al.*, 2021), dyes (COTORUELO *et al.,* 2011a; c; CHAUDHARY *et al.,* 2021b) such as congo red (COTORUELO *et al.*, 2010; MA *et al.*, 2020), methylene blue (BRAZIL *et al.*, 2020; ZHU *et al.*, 2021) and anthraquinone acid dyes (CHAUDHARY *et al.*, 2021), gases such as sulfur dioxide (SUMATHI *et al.,* 2009), steam (BEDIA; RODRÍGUEZ-MIRASOL; CORDERO,

2007) and heavy metals (AKIBA; OMORI; GAUBEUR, 2022) such as Cu and Pb (ZAINI *et al.,* 2021).

3.2.2. Chemical activation: characteristics, applicability and environmental aspects

Chemical activation employs several types of reagents, which can be grouped into alkaline, acidic, neutral and self-activating. During this activation, four pore formation pathways can be developed: pore creation, expansion, combination and collapse (GAO *et al.*, 2020). There are two chemical activation manufacturing methodologies. The first consists of preliminary pyrolysis of the biomass, followed by impregnation of the char with the activator, drying and heat treatment. The second consists of direct impregnating of the biomass with the activator, drying and heat treatment without any preliminary pyrolysis (FIERRO; TORNE-FERNÁNDEZ; CELZARD, 2007). The carbonization process before activation can enrich the carbon content, along with the removal of some gases such as CO, CO_2, H_2 and CH_4, responsible for creating the initial porosity in the char (YANG *et al.*, 2010).

AC quality depends on the chemical agent and the precursor material proportions. The activation temperature and the residence time also affect this quality. Activation temperature is related to the type of activating agent, precursor and heating source. In chemical activation, it is also common to use inert gases to protect the precursor from excessive degradation during burning (GAO *et al.*, 2020). But, in this type of activation, recovery of the chemical reagent is labored, which can increase production costs as well as lead to corrosion and environmental problems due to the inevitable washing step (GAO *et al.*, 2020; RAMIREZ-GUTIERREZ *et al.*, 2020).

The washing step removes the chemical reagent located in the spaces of the porous structure of the char, and the inorganic residues present in the precursor material (YANG *et al.,* 2010; KWIATKOWSKI *et al.,* 2017; RAMIREZ-GUTIERREZ *et al.,* 2020). However, the washing step of the AC is often insufficient to remove these residues, releasing potential contaminants by leaching, which can restrict its application (BERNARDO *et al.*, 2016; RAMIREZ-GUTIERREZ *et al.*, 2020). Studies indicate that between 7 to 40 liters of water can be used to wash AC in order to generate 1 kg of AC at neutral pH (NG *et al.,* 2003; GABARRELL *et al.,* 2012; HJAILA *et al.,* 2013). However, on an industrial scale, the volume of water may be lower due to more sophisticated infrastructure and facilities (SUGANYA; KUMAR, 2018).

The environmental impact caused by the application of chemical reagents can be reduced by the use of reagents which cause lower levels of contamination and corrosion, such as sulfuric acid (H_2SO_4) (SIVARAJ *et al.,* 2010; ADEMILUYI; DAVID-WEST, 2012; OLIVARES-MARÍN *et al.,* 2012; RAHMAN *et al.,* 2019) and sodium hydroxide (NaOH) (FIERRO *et al.,* 2007b; BLANCO *et al.,* 2008; CAZETTA *et al.,* 2011). It must be noted that H_2SO_4 and NaOH rarely provide the best results when compared to other reagents (HAYASHI *et al.,* 2000; LI; LUO, 2013). Nevertheless, these reagents can produce AC with high quality when the activation parameters are optimized (TORNÉ-FERNÁNDEZ *et al.,* 2009; KWIATKOWSKI *et al.,* 2017; RAHMAN *et al.,* 2019). Therefore, careful selection of the activating reagent will be decisive in order to develop good absorptive characteristics, as well as contributing toward higher efficiency and lower costs and environmental impact. Among other activating agents that we can find in the literature is zinc chloride ($ZnCl_2$), one of the first reagents used in the activation of charcoal obtained from kraft lignin (GONZALEZ-SERRANO *et al.,* 1997; HAYASHI *et al.,* 2000; MALDHURE; EKHE, 2011). Its use has been decreasing over time mainly due to the high environmental impact and corrosion problems (MENÉNDEZ-DÍAZ; MARTÍN-GULLÓN, 2006). Reactive such as phosphoric acid (H_3PO_4), nowadays widely used as an activating agent for lignin, obtaining high surface areas (BRAZIL *et al.,* 2022b; GUO; ROCKSTRAW, 2006). Phosphoric acid reacts with lignin through the cleavage of aryl-ether bonds, forming ketone groups and causing condensation and dehydration, in addition to generating CO and CO_2 at temperatures from 100 ºC (MONTANÉ; TORNÉ-FERNÁNDEZ; FIERRO, 2005). Impregnation rates 2:1 (H_3PO_4/lignin) at 425 ºC originated chars with larger pore structures, mesopores and a BET surface of 1459 m^2g^{-1}, good characteristics in the removal of toxic pollutants such as phenol and chromium (GONZALEZ-SERRANO *et al.*, 2004).

Very high rates of H_3PO_4 in the impregnation of the material, contrariwise, can block pores. In the study by Brazil *et al.* (2022) activated carbon with H_3PO_4, and microwave pyrolysis, also showed good adsorption capacity, in this case for methylene blue and amoxicillin, with 140 mg g^{-1} and 220 mg g^{-1} respectively. The authors demonstrated that at temperatures between 25 ºC and 100 ºC, the volatilization of water and low molar mass components of lignin begins. Between 500 ºC and 700 °C, almost all mass loss of volatile materials occurs under an oxidizing atmosphere. At temperatures between 750 ºC to 1000 ºC, the AC of lignin presents the greatest mass loss, as the phenol and hydroxyl groups are decomposed.

In the case of potassium hydroxide (KOH) in the study by Gao *et al.* (2013), demonstrated that impregnation rates 3:1 (KOH:KL) at temperatures of 750 ºC for 1 h, generated BET surface areas greater than 2,900 m^2 g^{-1}, decreasing when impregnation rates, temperatures and time increased to 4:1, 800 °C and 1.5 h respectively. The produced activated carbon showed a rapid adsorption of Ni (II), increasing with the pH rise of the solution during the adsorption process.

On the other hand, Li *et al.* (2014) found maximum surface areas of 2762.5 m^2 g^{-1} at temperatures of 750 ºC for 2 h, KOH:LK ratio 4:1 and N_2 flow rate of 160 cm^3 min^{-1}. A decrease in BET surface area of 1912 m^2 g^{-1} at the same 4:1 ratio (KOH:KL) and flow rate of 13 l min^{-1} over 2 h were found at 600 °C (CORREA; OTTO; KRUSE, 2017). Recent studies using KOH as a kraft lignin activator for CO_2 removal achieved adsorptions of 2.01 mmol g^{-1} at 25 ºC, partial pressure of 15 kPa, up to 5.20 mmol g^{-1} at 0 ºC and partial pressure of 100 kPa in CO_2 atmosphere (LI *et al.*, 2022; ZHAO *et al.*, 2023). In addition to the reagents mentioned, other activating agents such as orthophosphoric acid (FIERRO *et al.*, 2005, 2007; FIERRO; TORNÉ-FERNÁNDEZ; CELZARD, 2006; HERNÁNDEZ-ABREU *et al.*, 2020), sodium carbonate (HAYASHI *et al.*, 2000), potassium carbonate (JIN; YU; WU, 2012; LI *et al.*, 2016) among others (FIERRO *et al.*, 2013), have been widely evaluated as AC activating agents from KL, showing good results in the physical-chemical characterization of AC and in the removal of several adsorbates. Chemically activated carbons are mostly used for metal removal (KRIAA *et al.,* 2010; ADEMILUYI; DAVID-WEST, 2012; THENMOZHI; SANTHI, 2014; YANG *et al.,* 2015; ASIMAKOPOULOS *et al.,* 2021; SHAHROKHI-SHAHRAKI *et al.,* 2021), even with the environmental challenges they pose. They have also been used to remove hydrogen sulfide (GUO *et al.,* 2007), dyes (CAZETTA *et al.,* 2011; WANG *et al.,* 2021; BRAZIL *et al.,* 2022a; DE MORAES *et al.,* 2023), phenols (FIERRO *et al.,* 2008), bisphenol A (HERNÁNDEZ-ABREU *et al.*, 2020, 2021), ammonia (GUO *et al.,* 2005), SO_2 (ROSAS *et al.*, 2017) and pharmaceuticals (diclofenac and nimesulide) (SELLAOUI *et al.,* 2017b), among other compounds (FIERRO; SCHUURMAN; MIRODATOS, 2007).

3.2.3. Economic and environmental viability of activated carbon manufacturing

AC has a wide commercial demand for air and water treatment, which has recently increased, due to the creation of new legislation around the world, seeking to stop and/or reduce the growing air and water pollution. Other uses include soil remediation, pharmaceutical and food industry applications, the hybrid car market, adsorption of impurities (H_2S, siloxanes and VOCs) in biogas plants, and so on (U . S . INTERNATIONAL TRADE COMMISSION, 2018). Although this is a growing market, the main factor that restricts the manufacture of AC is the scarcity of raw materials. However, the use of agricultural by-products is a good and environmentally correct alternative to reduce production costs.

Costs for AC production using agro-industrial by-products have been studied by several authors (LAI; NGU, 2020; LEÓN *et al.*, 2020; MUKHERJEE *et al.*, 2022; NG *et al.*, 2003;

STAVROPOULOS; ZABANIOTOU, 2009). Ng evaluated the production of granular activated carbon for a plant that processes 10,000 kg/day of pecan shells, and estimated a production of 1,370 kg/day of AC physically activated with steam and 2,964 kg/day when chemically activated with phosphoric acid, with a yield of 13.7% and 29.6% respectively. The annual production cost in the study was 1.22 U.S $ million and an annual production of 448 tons of AC with a price of 2.72 U.S $ per kg for AC with steam. In the case of AC with phosphoric acid, annual production costs were estimated at 2.78 U.S $ million for an annual production of 960 tons and an estimated AC cost of 2.89 U.S $ per kg. The production of AC physically required less use of equipment and a smaller number of operating processes, in contrast to chemical activation, which requires a greater number of steps and equipment. Additional steps such as preparation of the activating agent, impregnation of the precursor material with the reagent, drying of the impregnated material and washing of the AC are necessary for chemically activated carbons. Among some of the costs that lead to these additional steps can be mentioned glass-lined acid soak tanks 40,000 U.S $, glass-lined acid wash tanks, 40,000 U.S $, glass-lined acid recovery tank 40,000 U.S $, glass-lined acid storage tanks 35,000 U.S $ and rotary dryer 150,000 U.S $. However, chemically activated carbon only slightly increases its value when compared to AC physically, this is due to the greater yield of AC with acid. Lai and Ngu (2020) studied AC production using waste palm oil as a precursor material which required a total fixed capital investment of 6.31 million U.S $ when chemically activated, while the physical activation process required only 2.12 million U.S $, varying according to the different activating agents. The estimates were made for a AC plant that processes 10,000 kg/day of palm oil, with a final AC production of 3,000 kg/day. The estimated cost of AC per kg will depend on the activating agent, which for NaOH it has an estimated cost of 3.04 U.S $ and an annual production of 960 tons of AC (assuming 320 operational days). In the case of AC obtained from KL, the cost that represents its production of lignin, around 260 and 500 US $/MT (BAJWA *et al.*, 2019), has to be considered in the calculation of total costs.

The growing demand for AC meant that in 2002 the estimated world production of AC was 750,000 t year^{-1}, with the Asian continent being the leader in its production, followed by the Americas and Europe (MENÉNDEZ-DÍAZ; MARTÍN-GULLÓN, 2006). China, in 2019, was the largest exporter of AC with a value of US$ 435 million (OEC, 2021). That same year, in South America, Brazil was the largest exporter, with exports of US$1.38 million (OEC, 2021). Thus, the global AC market is expected to reach US$ 4,064.7 million by 2027 (GLOBENEWSWIRE, 2021). In 2020, the main AC producers were Mainland China, the United States of America, Western Europe and Northeast Asia (MARKIT, 2020).

The production costs of other products with high added value obtained from KL, such as carbon fibers, may have higher cost estimates than AC, 6.27 US$ per kg for a carbon fiber yield of 35%. The cost of manufacturing carbon fiber is highly dependent on the precursor to be used (it represents 51% of the total cost) (BAKER; RIALS, 2013). Thus, the authors indicate that more than US$100 million over the last 10 years has been invested to examine possible routes for the supply of low-cost carbon fiber. The production of micro and nanoparticles of lignin for the production of solid foams, emulsion stabilizers, UV protection agents or chelating agents, are another type of products with high value and costs are estimated between 0.87 and 1.17 US% per kg with a selling price between 1.24 to 1.56 US$ per kg (DE ASSIS *et al.*, 2018).

In addition to the economic challenges posed by AC production, another important factor is the environmental aspect. Restrictions or challenges are related to the final disposal of the AC after use, which can be solved by reactivating it or reusing it to manufacture other products. Reusing or reactivating AC avoids disposal issues and reduces the carbon dioxide footprint by up to five times when compared to virgin AC (MARKETS; MARKETS, 2021).The reuse of saturated CA for brick making is a sustainable alternative that could be implemented due to its elemental composition. Components such as ash (contained in CA) can react and combine with calcium hydroxide, forming stable compounds with agglomerating power for the production of bricks (SILVA, 2011). Residual materials such as recycled cigarette butts (MOHAJERANI; KADIR; LAROBINA, 2016), tannery sludge (JUEL; MIZAN; AHMED, 2017), clay-fly ash (SUKMAK; HORPIBULSUK; SHEN, 2013) and residual coal (ABDRAKHIMOV; ABDRAKHIMOVA, 2017) have been shown to be viable as part of the components in the manufacture of ecological bricks. However, before brick production, pre-treatments will be necessary to remove the water contained in the CA.

Additionally, another challenge is related to the effluents generated during the washing of chemically activated carbon, which can pose a high environmental and operational risk depending on the type of reagent used. A possible disposal alternative is sending it to the evaporators of the chemical recovery circuit (Figure 2), although the operational part must be rigorously evaluated due to the high volume that the effluent may have and the possible problems of incrustations and corrosion caused by chemical reagents.

3.3. Activated carbon regeneration

The adsorption capacity of AC is limited. When the AC reaches its maximum adsorption capacity (full saturation), it is called “exhausted AC”. There are two options for discarding or regenerating. Disposal in landfills or incineration are alternatives that make it impossible to reuse AC, thus being unsustainable as well as generating economic and environmental costs. On the contrary, regeneration makes it possible to reduce consumption and the possibility of recovering adsorbed products that may have some economic value, although the high cost can be an impediment. It is noteworthy that, after each regeneration, the AC decreases its adsorption capacity to the point where it can no longer be regenerated. Thus, the regeneration of AC is only viable if there is a clear economic advantage in relation to the purchase or manufacture of new AC.

Regeneration consists of the desorption or release of the retained adsorbate, leaving the carbon surface free. The types of regeneration can be divided into thermal, chemical, biological and vacuum processes. The most outstanding regeneration techniques are presented in Table 1.

Table 1. Summary of types of methods used for activated carbon regeneration.

Regeneration Type		Description	Disadvantages	Benefits	References
Thermal	Thermal	High temperatures between 600-1200 ˚C in the presence of O_2, air, CO_2	It is not produced in situ, requires furnaces or ovens. Needs washing to remove residue. 5-15% AC loss per regeneration cycle	Eliminates organic and some inorganic contaminants. Viability in quantities >200.000 t of AC	(ROMÁN *et al.*, 2013; SALVADOR *et al.,* 2015a)
	Microwave	Microwave irradiation, heats up at the molecular level. Fast thermal reactions	The by-products generated can be more dangerous than the initial pollutants. Limited in industrial applications	Short treatment times, reduces energy and cost. Greater control over heating. Internal heating. Requires small spaces	(FOO; HAMEED, 2012; SUN *et al.*, 2017; FOO, 2018; GAGLIANO *et al.*, 2021)
Biological		Microorganisms use the contaminants to generate energy. Protons and electrons generated are transferred to the substrate until they are degraded into simple molecules	Temperature, pH and concentration of the solution need strict control. Slow bioregeneration rate. Combination of difficult-to-treat organic compounds	It consumes less energy by operating at low temperatures. Environmentally friendly	(MENÉNDEZ-DÍAZ; MARTÍN-GULLÓN, 2006; GAMAL *et al.*, 2018)
Chemistry	Solvents	Chemical solvents remove solute from saturated activated carbon	AC with up to 50% less adsorbing power. Efficiency mainly depends on the solubility of the adsorbed substances. Requires further purification of the solvent	Complete mineralization of the adsorbed species. Possible recovery of adsorbed compounds	(MEZZARI, 2002; FOO; HAMEED, 2012; FOO, 2018)
	Wet Oxidation	Pressures between 20-200 bar, temperature between 150 to 300 ˚C, requires O_2 to oxidize the material, as well as pumps	Long residence times, high implementation cost. High energy demand for compressing air and pumping liquids. High temperatures, pressures and oxidizing atmospheres can degrade AC	Fast reaction rate allows easy decomposition of contaminating molecules to less toxic ones	(LEDESMA *et al.*, 2015; SALVADOR *et al.*, 2015b; GAMAL *et al.*, 2018)
	Supercritical Fluid	Supercritical fluids such as CO_2, water, propane, butane, hexane and methanol are used as solvents for extracting solutes	Requires very corrosion-resistant equipment capable of operating under extreme conditions	High dissolving power. Transport and penetration properties of these flows provide high diffusivity	(MANJARE; DHINGRA, 2019; USHIKI *et al.*, 2020)

Table 1. (*continued*).

Regeneration Type		**Description**	**Disadvantages**	**Benefits**	**References**
Chemistry	Electrochemistry	It consists of the oxidation of matter through the electrical passage between two electrodes. Mineralizes the contaminant using the electron as a reagent	High implementation cost and high energy consumption in the operating system. Corrosion of electrodes may occur	No washing or chemicals required. Low temperatures, no damage to pores, low CO_2 emission and high efficiency. Requires small to medium spaces	(FERRÁNDEZ-GÓMEZ *et al.*, 2021; MCQUILLAN *et al.*, 2018; ZHOU *et al.*, 2019)
	Fenton	Uses $Fe^{2+} + H_2O_2$	H_2O_2 is toxic at high concentrations, low ferrous ion regeneration rate, sludge generation. Increase in pH during the process	Occurs at ambient temperature and pressure, process simplicity	(HULING *et al.*, 2009; SRUTHI *et al.*, 2018)
	Photocatalytic	Combines photochemistry with catalysis to speed up the chemical reaction	In general, it has a removal efficiency of less than 80% and progressively decreases with each regenerative cycle	No chemical agents needed	(SALVADOR *et al.*, 2015b; SHANG *et al.*, 2020)
Vacuum		Desorption occurs by exposing the adsorbent to a vacuum source. Oriented to separate gas mixture streams to obtain pure gas streams	Reduction in atmospheric pressure during adsorbent and adsorbate interactions leads to desorption	It has not yet been investigated for liquid phase adsorption-desorption processes. Saves costs and reduces cooling time	(LARASATI *et al.*, 2021; SALVADOR *et al.*, 2015b)

4. USES OF ACTIVATED CARBON IN KRAFT PULP MILLS

Kraft pulp mills are good candidates for the manufacture of AC, mainly because they have the raw material (such as KL) in large volumes throughout the year and the necessary infrastructure for its production. In addition, the chemical characteristics of KL, such as its high carbon content, make it a viable option for this transformation. Once the AC is produced, it can be used within the mills themselves in several sectors that can bring benefits in the operational, productive, economic and environmental spheres, as shown in Figure 1 and 2.

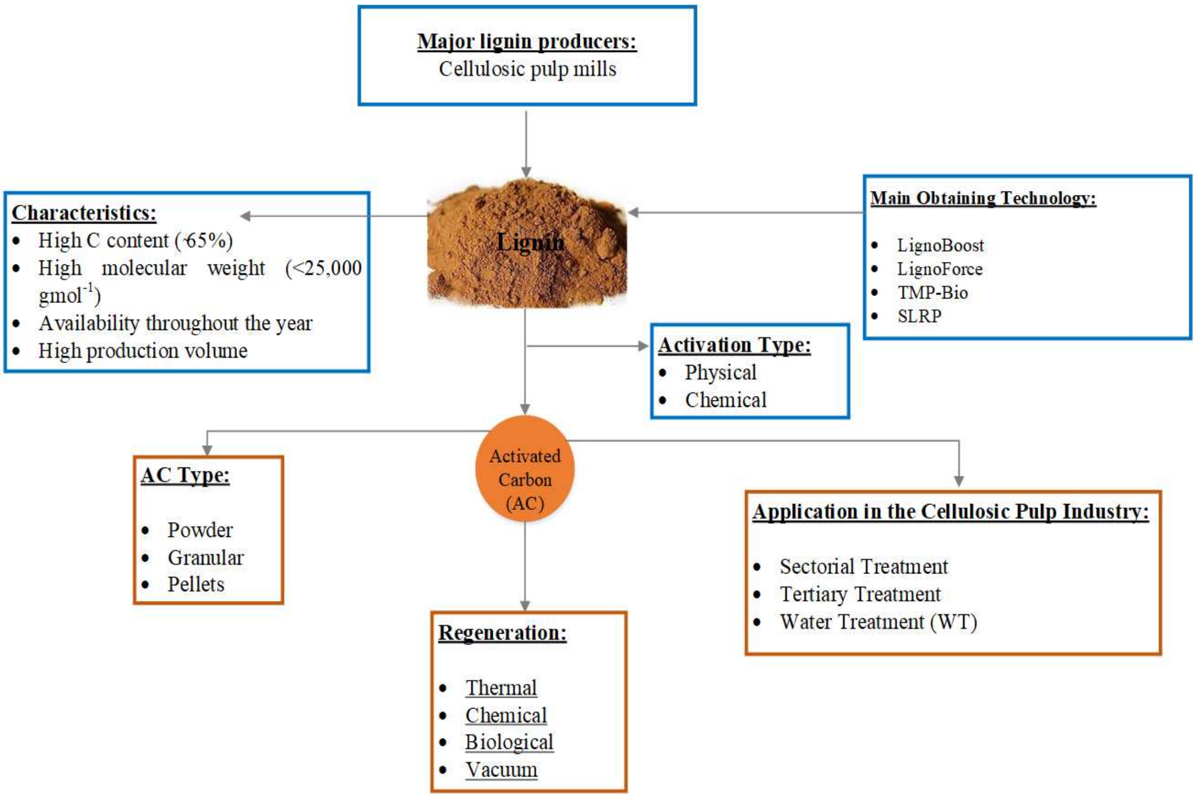


Figure 1. Kraft lignin as biomass for the production of activated carbon.

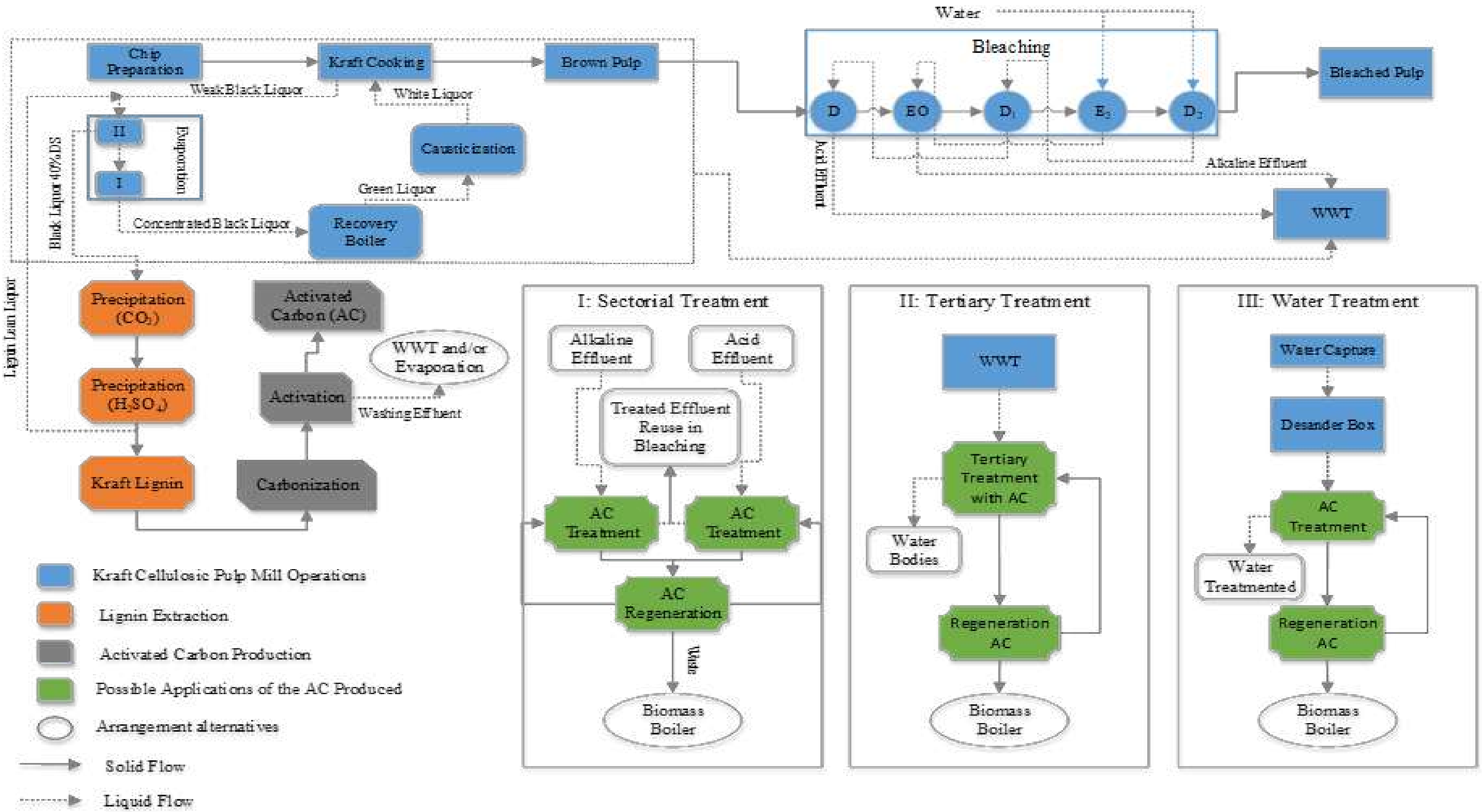


Figure 2. Flowchart of an integral kraft pulp mill designed for the production of activated carbon and possible applications.

4.1. Treatment of filtrates in bleaching (metal removal)

AC can be used for the treatment of filtrates generated in the bleaching of cellulosic pulp. Bleaching is the manufacturing step in a kraft pulp mill which generates the highest net load of contaminating effluents (85% of the total volume), approximately between 12 m^3 tsa^{-1} to 25 m^3 tsa^{-1} (SUHR *et al.,* 2015). After each stage of bleaching, it is normally necessary to wash the pulp before it can be directed to a new stage. The filtrates generated in bleaching washers are generally used in a countercurrent washing system, to save energy, water and reagents. There are several types of countercurrent washing systems, such as split-flow, direct and jump-stage, the latter being adopted in the flowchart in Figure 2, which represents a bleaching sequence with alternating acid and alkaline stages.

The bleaching filtrate consists of suspended and dissolved organic and inorganic materials. They contain elements such as calcium, magnesium, potassium and silicon, and in lower concentrations, manganese, iron, aluminum, copper and barium from wood. Additionally, some cations and anions of chloride, sulfide, carbonate, nitrate, phosphate, acetate and oxalate can be found. These compounds are responsible for possible deposits and incrustations in equipment. Transition metal ions are retained in the pulp due to their complexation with carboxyl groups, including Fe^{2+}, Fe^{3+}, Cu^{2+} and Mn^{2+}, which are associated with the reversion of brightness. However, some of the metals are removed during the acid stages of bleaching (COLODETTE; GOMES, 2015). The transition metals manganese, iron and copper interfere with the catalytic decomposition of oxygen-based chemicals during the ECF (elemental chlorine free) and TCF (totally chlorine free) bleaching processes of cellulose, causing an increase in the consumption of these agents. Hydrogen peroxide is the pulp bleaching reagent most influenced by the action of transition metals. Iron and manganese also increase the breakdown of carbohydrate chains. For this reason, these metals catalyze the formation of the hydroxyl radical (OH^-) which attacks the cellulose and lignin chains (JEMAA *et al.,* 1999; COLODETTE; GOMES, 2015). The removal of metals in a jump-stage washing system, which starts washing at the last stage, allows for sectorial treatment of the filtrate at each bleaching stage. This can prevent or minimize some problems in pulp quality, in addition to providing greater savings in the production of kraft pulp, by avoiding problems of corrosion, incrustations, clogging, consumption of reagents and possible environmental problems in the ETP. The sectorial treatment of filtrates using AC provides the possibility of reusing water, reducing and/or canceling the consumption of fresh water and the load and volume of effluents for the ETP (QUEZADA *et al.,* 2014).

Although no studies have been found in the literature using AC produced from KL or any other precursor for the adsorption of metals in bleaching filtrates, good results can be expected, since it has already been shown in several studies that KL is capable of adsorbing metals in general (SCIBAN; KLASNJA, 2004; MOHAN *et al.,* 2006; GUO *et al.,* 2008; ŠĆIBAN *et al.,* 2011). Maldhure and Ekhe (2011) was the only work found using AC from KL, activated with $ZnCl_2$ under microwave treatment at 500 ºC-800 ºC. The authors reported that the adsorption of Cu (II) ions, in synthetic solution, it had a removal of almost 75% at pH 5.5. The use of AC chemically develops ideal characteristics for the adsorption of metals, such as the enrichment of functional groups. Functional groups present on carbon improve surface chemistry in the adsorption process (SAJJADI *et al.*, 2019). Thus, the selection of the chemical reagent will determine the reactivity with the carbon surface. Metal adsorption has a strong dependence on the AC surface chemistry and not on the surface area (carbon texture) (YOUSSEF; EL-NABARAWY; SAMRA, 2004). Thus, this type of AC would be recommended for the adsorption of metals in the filtrates generated in pulp bleaching.

The use of GAC-type carbons has been used in the adsorption of metals such as cadmium and lead in fixed-bed column tests, obtaining removal rates from 72% to 99.5% and from 71% to 100%, respectively (JUSOH; SHIUNG; NOOR, 2007). Another study by Wasewar *et al.* (2009), evaluated the removal of selenium using PAC and GAC in optimal dosages of 10 g l^{-1} and 8 g l^{-1} respectively, for the removal of 100 g l^{-1} of Se (VI) . Other metals such as copper, nickel, zinc and chromium have also been evaluated in PAC adsorption treatments (ONG *et al.*, 2010). The use of PAC or GAC represents an alternative in the adsorption of metals.

Finally, AC produced from KL must be given special care when the objective is to remove metals. As KL has a high content of inorganic material (RIDHO *et al.*, 2022), this must be removed in pre-treatments such as demineralization (FIERRO *et al.*, 2007), to avoid a possible release of unwanted elements that impair the quality of the final effluent.

4.2. Use of activated carbon in tertiary treatment

The filtrate obtained after washing the bleached pulp contains compounds that can increase the chemical and biological oxygen demand (COD and BOD), phosphor, the color and the toxicity of the final effluent sent to the ETP (LINDHOLM-LEHTO *et al.,* 2015; CABRERA, 2017; MANDEEP *et al., 2019).*

The use of AC in a tertiary effluent treatment plant is intended to reduce the color, COD and other compounds that may not have been removed in previous stages of the effluent treatment sequence. Although color is not a parameter evaluated in the conditions of discharge of effluents into bodies of water in Brazil, according to the National Council for the Environment (CONAMA, 357/05), it can cause problems related to aesthetics and difficulties in light penetration. Recalcitrant compounds (among them residual lignin) are primarily responsible for the brown color of effluents, because it is difficult to aerobically or anaerobically degrade them using microorganisms (HAQ *et al.,* 2020). Organochlorines, compounds that originated in the bleaching of pulp, resulting from the reaction of residual lignin in the pulp, after pulping, with chlorine or chlorine dioxide, are responsible for the color, residual COD and toxicity of the treated effluent (LINDHOLM-LEHTO *et al.,* 2015). Thus, chlorinated compounds are an important source of water pollution, producing oxygen depletion and bioaccumulation of toxic compounds. This can cause the death, and even genotoxicity, of aquatic animals (SPONZA, 2003; LINDHOLM-LEHTO *et al.,* 2015; MANDEEP *et al.,* 2020).

The use of AC for the treatment of this type of effluent becomes an interesting option for the removal of color and organic compounds (SHAWWA *et al.,* 2001; MUHAMAD *et al.,* 2011; HAQ *et al.,* 2020). The physical and chemical properties of AC are crucial to determine its best application in the removal of target adsorbates. For example, when the interest is color removal in liquid phase systems, a porosity with radii in the range of 20-500 Å is recommended (YAHYA; AL-QODAH; NGAH, 2015).

The use of AC as a tertiary treatment in pulp mills could be by PAC. After the adsorption process, PAC recovery can occur via sedimentation and sand filtration or membrane filtration (CECEN; AKTAS, 2011). Another alternative for use consists of its arrangement in compact beds of granular material, such as GAC, arranged in ascending and descending flows or in moving beds (MARSH; RODRÍGUEZ-REINOSO, 2006c). GAC is mainly used for the adsorption of organic molecules, which were not removed in the biological treatment in ETP (CECEN; AKTAS, 2011). The implementation of a tertiary treatment station in kraft cellulosic pulp mills would result in a high quality effluent; although separating AC from treated effluent poses a challenge in the case of PAC.

4.3. Industrial water treatment

In addition to the treatment of effluents, AC can be used in the water treatment (WT) of a pulp mill. Currently, the most commonly used treatment is conventional treatment. The WT consists of a step of a grit removal, coagulation, flocculation, decantation and filtration. AC can be introduced after decanting the coarse material, where an improvement of the water quality in the system is needed. Normally AC layers are placed in sand filters or used before disinfection in the drinking water treatment, although this depends on the characteristics of the water and its final use.

GAC is commonly used as a filter medium in tanks or filters, for the treatment of natural organic material. There are three options for locating GAC in conventional water treatment: a) before the rapid mixing unit (pre-adsorption); b) combined during the filtration step; and c) after the rapid filtration. In the case of PAC, it can be implemented at four points (see Figure 3), although the choice must be evaluated according to criteria such as: mixing efficiency, optimal contact time, minimal interference within the process and final water quality (PÁDUA, 2006). The selection between GAC or PAC for any of the alternatives for use in water treatment is possible. However, the use of PAC in water catchment or before the quick mixing unit can lead to a higher consumption of AC, as it could remove some impurities instead of being removed during coagulation, flocculation and sedimentation. In general, it can be said that the PAC offers a relatively low initial investment and flexibility in changing the applied dosage depending on variations in water quality, when compared with the GAC, although the difficulty of regeneration, sludge disposal and the removal itself of PAC particles are its main disadvantages (PÁDUA, 2006). Physically active carbons may be a better choice for water treatment, rather than chemically activated carbons, due to possible leaching of chemical agents used during chemical activation (BERNARDO *et al.*, 2016). Activated carbons for water treatment need to have a large surface area, fast adsorption rate and large and stable pores (TOBI *et al.*, 2019). These characteristics can be found in physically activated carbons, when the activation conditions are improved.

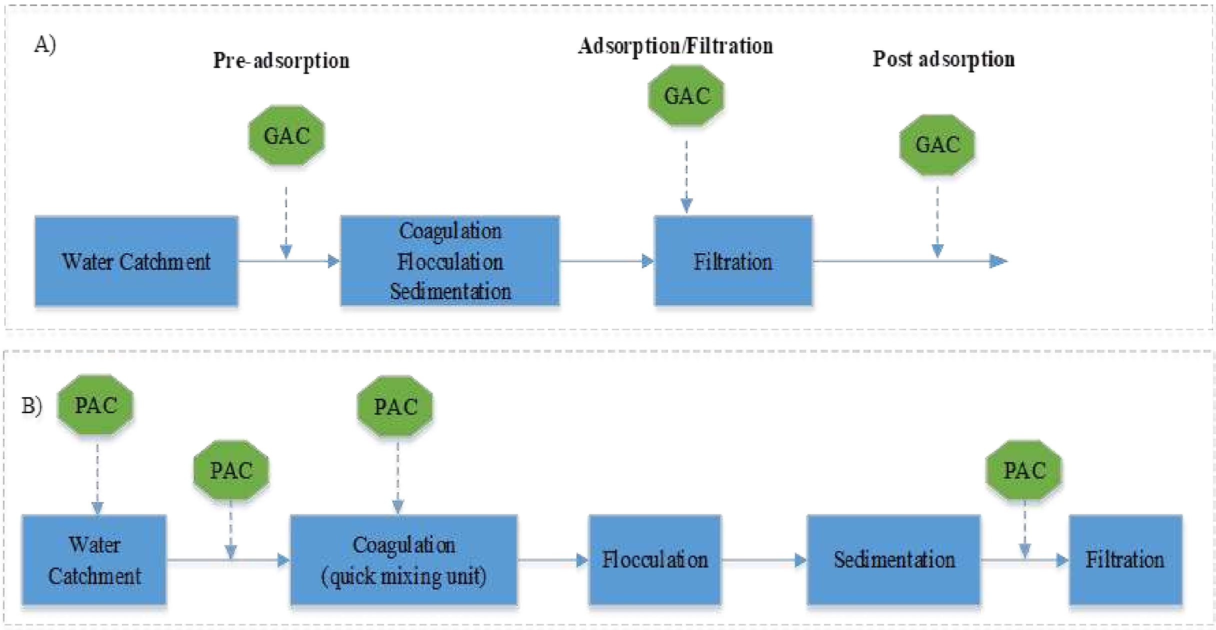
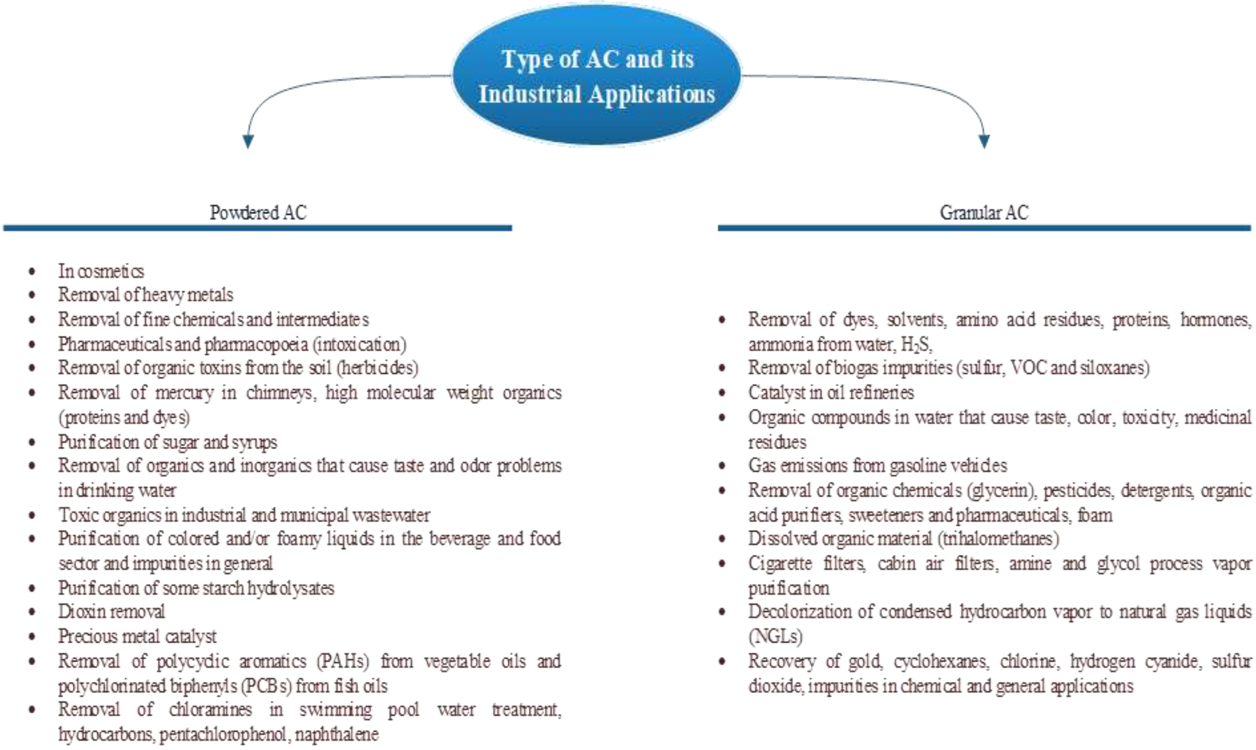


Figure 3. Possible points of application of GAC (A) and PAC (B) for water treatment (WT) (PÁDUA, 2006).

During the treatment of drinking water, substances responsible for taste and odor in the water, in addition to organic and inorganic compounds that may be present, must be eliminated. Some causes of these parameters can be the chlorophenols and bromates generated during disinfection with compounds that contain chlorine and the treatment of water with ozone, respectively (CECEN; AKTAS, 2011).

5. USE OF ACTIVATED CARBON IN OTHER MARKETS

AC is used by many industrial sectors, as shown in Figure 4, and another which presents itself as a great candidate is in the removal of phenols from wastewater (SELLAOUI *et al.,* 2019). Phenol is a highly toxic aromatic organic compound, with a production of approximately 6 million tons per year worldwide. These can be found in industrial effluents from ceramics, textiles, fungicides and herbicides, plastics production, paints, refineries, petrochemicals and the pharmaceutical industry. Some polyphenols are used in medicines, while others are employed in the manufacture of personal care products (salicylic acid) or perfumery. Currently, effluents frequently show the presence of phenols that are treated with chlorine, forming chlorophenols, corrosive components that affect the skin and mucous membranes, harmful to health (FIERRO *et al.,* 2008).



Powdered AC

- In cosmetics
- Removal of heavy metals
- Removal of fine chemicals and intermediates
- Pharmaceuticals and pharmacopoeia (intoxication)
- Removal of organic toxins from the soil (herbicides)
- Removal of mercury in chimneys, high molecular weight organics (proteins and dyes)
- Purification of sugar and syrups
- Removal of organics and inorganics that cause taste and odor problems in drinking water
- Toxic organics in industrial and municipal wastewater
- Purification of colored and/or foamy liquids in the beverage and food sector and impurities in general
- Purification of some starch hydrolysates
- Dioxin removal
- Precious metal catalyst
- Removal of polycyclic aromatics (PAHs) from vegetable oils and polychlorinated biphenyls (PCBs) from fish oils
- Removal of chloramines in swimming pool water treatment, hydrocarbons, pentachlorophenol, naphthalene

Granular AC

- Removal of dyes, solvents, amino acid residues, proteins, hormones, ammonia from water, H_2S,
- Removal of biogas impurities (sulfur, VOC and siloxanes)
- Catalyst in oil refineries
- Organic compounds in water that cause taste, color, toxicity, medicinal residues
- Gas emissions from gasoline vehicles
- Removal of organic chemicals (glycerin), pesticides, detergents, organic acid purifiers, sweeteners and pharmaceuticals, foam
- Dissolved organic material (trihalomethanes)
- Cigarette filters, cabin air filters, amine and glycol process vapor purification
- Decolorization of condensed hydrocarbon vapor to natural gas liquids (NGLs)
- Recovery of gold, cyclohexanes, chlorine, hydrogen cyanide, sulfur dioxide, impurities in chemical and general applications

Figure 4. Industrial applications of powdered and granular activated carbon (CABOT, 2021).

In addition to phenols, there are other types of pharmaceutical products with polluting potential, such as paracetamol, amoxicillin, diclofenac, among a wide range of products called “emerging contaminants of concern” (IOVINO *et al.,* 2015; SELLAOUI *et al.,* 2017a; GOMEZ-CEBALLOS *et al.,* 2021). These types of components reach wastewater through industry, urine and excreta from medicated humans and animals. Low concentrations of these compounds are associated with chronic toxicity and may be bioaccumulative (SELLAOUI *et al.,* 2019). The treatment of these components by conventional processes is often inefficient (SOTELO *et al.,* 2012). Technologies such as advanced oxidation processes (AOP) are a good alternative, although they are expensive and complex to handle (IRANI *et al.,* 2015). Treatment with AC represents another widely evaluated possibility for this purpose (GONZALEZ-SERRANO *et al.,* 2004; IOVINO *et al.,* 2015; SELLAOUI *et al.,* 2017b; YAZIDI *et al.,* 2019; SPESSATO *et al.,* 2020), as it is a versatile and low-cost process in terms of energy.

AC can also be used in the textile industry to remove dyes (COTORUELO *et al.*, 2007). There are over 10,000 commercial dyes available worldwide, with over 700,000 tons of dyes produced annually (PATHANIA; SHARMA; SINGH, 2017). Inadequate disposal of this effluent represents a relevant problem in ecosystems. Wastewater that contains dyes prevents light penetration, reduces the photosynthetic activity of aquatic plants and inhibits the growth of biota. These effluents are difficult to treat biologically and chemically, due to their complex molecular structure (SIDIQUA; PRIYA, 2021). Therefore, AC represents an alternative with good results in removing different types of dyes (EL QADA *et al.,* 2006; MALIK *et al.,* 2007; YAO *et al.,* 2013; DJILANI *et al.,* 2015; PATHANIA *et al.,* 2017; EGBOSIUBA *et al.,* 2020; BALOO *et al.,* 2021; MUNIYANDI *et al.,* 2021).

An industry that has been using AC for many decades is the gold industry for the adsorption process of gold and other precious metals. In this process, the metal is solubilized during leaching, and AC is used for the adsorption of the cyano complex Au(CN)-2, followed by processes such as elution and electrolysis until the precious metal is extracted (LAM *et al.,* 2008; ARAUJO *et al.,* 2009).

Currently, the main world producers of AC use coconut husk, peat, coal and wood as precursor material. AC is mainly used in water treatment (38%), air and gas purification (24%) and food processing (19%) (MARKIT, 2020).

KL represents another possible precursor of AC at an industrial level, due to the large volume in which it can be produced and its availability throughout the year in kraft pulp mills. Among some of the most important producers of AC we can mention the Calgon Carbon Corporation (USA), Osaka Gas Chemicals Co. Ltd. (Japan), Cabot Corporation (USA), Donau Carbon GmbH (Germany), Haycarb Plc. (Sri Lanka), Kuraray Chemical Co. Ltd. (Japan), Kureha Corporation (Japan), Oxbow Systems Inc. (USA), Puragen Activated Carbons (USA), Silcarbon Aktivkohle GmbH (Germany), Activated Carbon Technologies (Australia).

6. CHALLENGES AND FUTURE PROSPECT

Current biological (aerobic) treatment processes in ETP in the pulp mills generally meet environmental requirements, although they have some restrictions. The cellulosic pulp effluent faces several difficulties due to the variation of the characteristics that the generated effluents can have. These effluent variations are associated with the configuration of the industrial process itself, the type and quality of the processed wood and possible operational problems. Problems like recalcitrant organic material, heavy metals and color are some of them. The activated sludge process is one of the most used conventional treatments in the cellulosic pulp mills (DA MATA; MORAIS; SILVA, 2020). This type of treatment presents some operational challenges such as the sedimentability of the sludge. The sedimentability of the sludge can be low and sensitive to the variations of compounds that present a certain toxicity. The implementation of AC in the biological treatment of ETPs combines the adsorption capacity of activated carbon, and the biodegradation of organic matter by biological treatment. Some works have already evaluated the use of AC within biological treatment to improve and/or enhance its efficiency (KARGI; PAMUKOGLU, 2004; HU *et al.,* 2015). Kargi and Pamukoglu (2004) demonstrated that the combination of AC with biological treatment improved the removal of COD (94%), N-ammonia (30%) and toxic compounds in leachate from landfills. Hu *et al.* (2015) in the treatment of municipal wastewater, showed an efficiency in COD removal of 39%, increased sludge sedimentability, among other benefits. Removal (>90%) of recalcitrant compounds such as antibiotics has also been observed in systems composed of AC and biological treatment (ALVARINO *et al.*, 2016). In pulp mills there are recalcitrant organic compounds (such as residual lignin) that cannot be degraded by bacteria in the biological system (LINDHOLM-LEHTO *et al.,* 2015; HAQ *et al.,* 2020; ADESIDA *et al.,* 2022). Thus, the use of AC in the activated sludge system could help in the removal of recalcitrant material and the sedimentability of the sludge in kraft pulp mills.

The use of AC within any of the alternatives indicated in the work requires an exhaustive study starting with the raw material. KL is a material with excellent characteristics for its use as a precursor to AC. However, AC is a complex material, with high heterogeneity and low reactivity due to its reticulated nature (LI; MCDONALD, 2014; RIDHO *et al.,* 2022); which can affect the yield and textural properties of AC. Another factor to consider is the high content of inorganic material that contains KL (RIDHO *et al.*, 2022), which can affect the specific surface area, the porosity of the carbon and consequently its adsorption capacity (FIERRO *et al.*, 2007). The selection of the type of activation along with the AC production parameters should also be evaluated, as it directly influences the quality of the produced AC. The choice of some of the alternative uses of AC (exposed in the work) in pulp mills will depend on its operational viability, efficiency, costs and the environmental scope.

7. CONCLUSIONS

The possibility of kraft pulp mills adopting a technology, in the market, to precipitate a fraction of the lignin contained in BL presents a wide range of alternatives for the manufacture of high added-value products such as AC. This adsorbent can be used in the treatment of water and effluents in several sectors within the very mills where it is produced, allowing in some cases for the closing of circuits, lower consumption of freshwater, minimization of the volume and load of effluent destined in the ETP, minimization and/or elimination of pulp quality problems, reduced consumption of bleaching reagents and reduction of corrosion problems. Thus, the manufacture of AC within a kraft pulp mill expands the number of products that can be obtained from wood, converting the mill into a true biorefinery.

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CAPITULO 2

PRODUCTION, CHARACTERIZATION, AND POSSIBLE USE OF ACTIVATED CARBON DERIVED FROM LIGNIN IN KRAFT PULP MILLS

ABSTRACT

The production of activated carbon (AC) from kraft lignin (KL) from pulp mills represents an option for diversifying their product portfolio and increase their business opportunities. The objective of the present work was to produce AC using kraft lignin and evaluate its characteristics for possible uses in the treatment of water and effluents of those same mills. The AC was produced in two stages: carbonization at 450 °C for 1 h, and activation at 700 °C for 1 h using sodium hydroxide (NaOH) as an activator. The AC obtained in this fashion, named "NaOHAC", was washed until a neutral pH was reached, then dried and stored. The NaOHAC produced showed characteristics similar to those of other efficient adsorbents, and its elemental and immediate analysis was within the range of typical charcoal, with a carbon content of 76.6%, ash 32.5%, fixed C 48.8%, iodine number 1538 mg g^{-1}, and point of zero charges 7.0. In scanning electron microscopy (SEM), the formation of porosity in NaOHAC was evidenced. In the electronic spectroscopy in the infrared region, during the production of the AC, the reduction and/or degradation of some of the functional groups of the kraft lignin such as OH was verified. During the evaluation of inorganic material from KL and NaOHAC, elements such as Ca, Na, P, K, S, Fe, Cu, Mn, Cr, Ni, and Zn were found. The presence of heavy metals was also detected in X-ray analysis, showing crystalline structures of γ-Fe and α-Fe.

Keywords: Kraft Lignin, Powdered Activated Carbon, Chemical Activation, Sodium Hydroxide

1. INTRODUCTION

Lignin is a complex three-dimensional macromolecule, aromatic in nature and of high molar mass, formed by the disordered polymerization of phenylpropane monomers with hydroxyl or methoxyl substituents (CAO *et al.*, 2018; CHEN *et al.*, 2017; GARCÍA *et al.*, 2009), joined through various bonds such as ether (C-O-C) or carbon-carbon (C-C) bonds, β-O-4, α-O-4, β-5, β-β, 5-5, and 4-O-5. The kraft lignin (KL) obtained from the black liquor (BL) generated after the cooking stage of the chips during the kraft pulp manufacturing process is one of several types of lignin that can be found on the market.

The production of activated carbon (AC) from kraft lignin has been evaluated (BRAZIL *et al.*, 2022; FIERRO; TORNE-FERNÁNDEZ; CELZARD, 2007; LIU *et al.*, 2020). The choice of KL as a precursor for AC is relevant because of its good chemical characteristics, high carbon content, and structure similar to bituminous coal (BRAZIL *et al.*, 2018). Other determining factors in this choice are its year-round availability and the increased production volume that can be had in a kraft pulp mill. About 70 million tons of lignin are generated annually during kraft pulp production, of which only 2% is used for the manufacture of products with higher added value, and the rest is used as fuel in boilers (LIU *et al.*, 2020). The high complexity and heterogeneity of lignin is one of the main challenges for its industrial use. Additionally, the deviation of a fraction of the BL (partially-concentrated black liquor in the evaporators of the chemical recovery circuit) for the precipitation of lignin reduces the calorific value or the liquor, therefore a greater amount of BL can be burned in the recovery boilers, without exceeding its limit, for generation of heat.

The production of AC consists of two steps: carbonization and activation. Carbonization occurs by partial combustion and thermal decomposition of the precursor material, forming char as the main product, with carbon content in the range of 25 to 50% on a dry basis (BERGNA *et al.*, 2018). During pyrolysis, in the case of lignin, products such as solid char, liquid oil gases, and volatile liquids are formed, whose proportion mainly depends on the temperature and heating rate (PANDEY; KIM, 2011). In the second step, the porous matter (char) is activated through physical or chemical processes or a combination of the two, although carbonization and activation can also be performed in one step.

Chemical activation of carbon, even with the possible environmental risks this poses, is widely used for metal removal purposes (ASIMAKOPOULOS *et al.*, 2021; SHAHROKHI-SHAHRAKI *et al.*, 2021; TOUNSADI *et al.*, 2016; YANG; YU; CHEN, 2015), water treatment (VALDÉS-RODRÍGUEZ *et al.*, 2022), removal of dyes (JAWAD *et al.*, 2022), and removal of organic material (ODA *et al.*, 2021). Carbon activation using NaOH has shown good results, as reported by several authors, employing various lignocellulosic raw materials (CAZETTA *et al.*, 2011; FIERRO; TORNE-FERNÁNDEZ; CELZARD, 2007; HAYASHI *et al.*, 2000; LINARES-SOLANO *et al.*, 2012). NaOH, as a chemical activator, presents the lowest costs (LINARES-SOLANO *et al.*, 2012) and the lowest environmental impact risks when compared to other activating agents such as $ZnCl_2$ and H_3PO_4. The decrease in the costs of the AC production process is convenient, since one of the major challenges of AC production is its high costs (SAMRANE; BOUHAOUSS, 2022). In a kraft pulp mill, the use of NaOH as an activator becomes interesting due to the availability of the reagent in the mill (used in the cooking and bleaching of the pulp) and the possible disposal of the filtrates generated in the washing of the existing black liquor evaporators. The possible sending of the filtrates generated in the AC washing in the chemical recovery circuit could limit the use of KOH and H_3PO_4 as an activating agent for charcoal, since potassium can cause problems such as a reduction in the melting point and solidification of the ashes, which causes its fouling inside the recovery boiler. Therefore, it causes the formation of deposits that hinder the transit of gases inside the recovery boiler, in addition to impairing thermal exchange (CARDOSO, 1998). In addition, the fact that NaOH is less corrosive than other reagents allows for a longer equipment life (ISLAM *et al.*, 2017). NaOH reacts strongly with most raw materials which contain carbon, resulting in the oxidation of the carbon precursor, alkali carbonates (such as Na_2CO_3), alkali metals, and hydrogen. When employing sodium hydroxide as an activator to produce AC, the best results were obtained in materials with a disordered or amorphous structure (LINARES-SOLANO *et al.*, 2012), similar to those of KL.

Several scientific studies have been conducted using KL as a raw material for the production of chemically activated carbon, as listed in Table 1. In this Table, we can observe that only seven articles were found in which NaOH was used as an activating agent. In the seven studies found, the authors did not perform a broad characterization that included, for example, morphological analysis, and only did adsorption tests of nitrogen, methylene blue, and phenol. The aforementioned advantages of NaOH as an activating agent and the scarce characterization of AC led to its selection as an activator in this study. In addition, the use of AC with NaOH was selected considering the adsorption of organic material and metals (not yet studied in the literature), which will be evaluated in future publications.

Table 1. Research conducted using kraft lignin (KL) as a raw material for the production of chemically activated carbons.

Activating agent	Origin of KL	Adsorbate	Reference
$ZnCl_2$	*Eucalyptus grandis*	-	(GONZALEZ-SERRANO *et al.*, 1997)
	-	Cu	(MALDHURE; EKHE, 2011)
	Eucalyptus	SO_2	(ROSAS *et al.*, 2017)
$ZnCl_2$, H_3PO_4, K_2CO_3, Na_2CO_3, KOH, NaOH	Spruce wood	-	(HAYASHI *et al.*, 2000)
$ZnCl_2$, KOH	-	CO_2	(ZHAO *et al.*, 2023)
H_3PO_4	*Eucalyptus grandis*	Phenol, Cr	(GONZALEZ-SERRANO *et al.*, 2004)
	-	Methylene blue, Amoxicillin	(BRAZIL *et al.*, 2020; BRAZIL *et al.*, 2022)
	Eucalyptus	-	(BRAZIL *et al.*, 2018)
	-	-	(GUO; ROCKSTRAW, 2006)
	-	-	(MONTANÉ; TORNÉ-FERNÁNDEZ; FIERRO, 2005)
	-	N_2	(FIERRO *et al.*, 2005; FIERRO; TORNÉ-FERNÁNDEZ; CELZARD, 2006)
	Pine	Methylene blue	(FENG *et al.*, 2021)
	Softwood	Methylene blue	(FIERRO *et al.*, 2007)
	-	Methylene blue	(DE MORAES *et al.*, 2023)
	-	N-butanol	(FIERRO; SCHUURMAN; MIRODATOS, 2007)
	Eucalyptus	Bisphenol A	(HERNÁNDEZ-ABREU *et al.*, 2020)
	-	Au (III), Pd (II), Cr (III), Co (II), Cu (II), Ni (II), Pb (II), Zn (II), Pt (IV) e Ru (III)	(AKIBA; OMORI; GAUBEUR, 2022)
KOH	-	Ni (II)	(GAO *et al.*, 2013)
	-	N_2	(LI *et al.*, 2014)
	-	Methylene blue, Amoxicillin	(CORREA; OTTO; KRUSE, 2017)
	-	CO_2	(LI *et al.*, 2022)
	Hardwood	Methylene blue	(LIU *et al.*, 2020)
K_2CO_3, KOH	Straw	Iodine	(JIN; YU; WU, 2012)
K_2CO_3	-	N_2	(LI *et al.*, 2016)
NaOH	-	Methylene blue	(TORNÉ-FERNÁNDEZ *et al.*, 2009)
NaOH, KOH	-	-	(FIERRO; TORNE-FERNÁNDEZ; CELZARD, 2007)
	-	N_2	(KWIATKOWSKI; FIERRO; CELZARD, 2017)
	-	N_2	(BLANCO *et al.*, 2008)
		N_2	(CARROTT; RIBEIRO; SUHAS, 2010)
NaOH, H_3PO_4	-	Phenol	(FIERRO *et al.*, 2008)
H_2SO_4	-	-	(LI; LUO, 2013)

Thus, the objective of the present work was to produce KL-activated carbon, using NaOH as an activating agent, and to characterize it by elemental analysis, ash content, fixed carbon, point of zero charges (pH_{PZC}), iodine number (IN), cation exchange capacity (CEC), scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS), electronic spectroscopy in the infrared region, and x-ray diffraction (XRD).

2. MATERIAL AND METHODS

2.1. Carbonization of kraft lignin

The kraft lignin (KL) was obtained from a cellulosic pulp mill in the southeast region of Brazil and characterized in terms of elemental and metals analysis, immediate analysis, point of zero charges, cation exchange capacity, iodine number, scanning electron microscopy, spectral analysis with infrared spectroscopy and X-ray diffraction. One step of pre-carbonization was made using 50 g of dry KL, called KL char (KLC), in a 304 stainless steel reactor, under an inert atmosphere comprised of off-gases generated by pyrolysis. The temperature increase was gradual, 25 °C every 15 minutes until reaching the final temperature of 450 °C, where after reaching the final temperature, it remained for one hour in an electric muffle. The reactor had an adaptation to a condenser for the recollection of the condensable gases.

2.2. Char Ativation

The char obtained was ground and sifted through a 100-mesh sieve. Afterward, it was dried in an oven at 105 °C for 24 h and stored in a hermetically sealed plastic bag. The activating agent used was NaOH in microbeads (97-98%) and mixed with char in a 3:1 ratio, placed in an oven at 105 °C for 15 h. The activations were done in the same stainless-steel reactor in an electric muffle under oxygen-free conditions. No inert gas was used. The impregnated char was heated on a temperature ramp from 5 to 10 °C min^{-1} to a final temperature of 700 ºC, where after reaching the final temperature, it remained for 1h. The final temperature and time conditions and the NaOH/char ratio were chosen based on the best results found in the literature recording BET surface areas >2000 m^2 g^{-1} and micropore volume >0.79 cm^3 g^{-1} for lignocellulosic material and kraft lignin (CARROTT; RIBEIRO; SUHAS, 2010; CAZETTA *et al.*, 2011; FIERRO; TORNE-FERNÁNDEZ; CELZARD, 2007; KWIATKOWSKI; FIERRO; CELZARD, 2017; LINARES-SOLANO *et al.*, 2012).

The main reaction that occurs between hydroxide and carbon during activation, over a range of 700 °C to 900 °C, was demonstrated by Linares-Solano *et al.* (2012):

According to Lillo-Rodenas *et al.* (2003), the development of micropores can be obtained by equations (1) and (2).

$$6NaOH + 2\,C \leftrightarrow 2\,Na + 3\,H_2 + 2\,Na_2CO_3 \tag{1}$$

$$4\,NaOH + C \rightarrow 4\,Na + CO_2 + 2\,H_2O \tag{2}$$

After activation, the AC was washed with a dilute acid solution of 0.1 M HCI and subsequently with distilled water to reach a pH of approximately 7. The washed AC was oven-dried for 24 h at 105 °C, ground, sifted (fraction below 0.15 mm), and stored until its characterization. The yield (Y) of the materials was calculated by the weight difference of the precursor material before ($W_{initial}$) and after (W_{final}) carbonization and activation, using equation (3).

$$Y(\%) = \frac{W_{final}}{W_{initial}} 100 \tag{3}$$

2.3. Characterization of activated carbon

Characterization of both the final AC produced, called NaOHAC, and the precursor material, KL, was performed. Also, the characterization of a commercial coconut shell activated carbon, called in the text CAC, was done for comparison purposes.

The characterization of volatile content, ash, and fixed carbon was determined by Brazilian standard NBR 8112 (1986), in the Wood Panels and Energy Laboratory (LAPEM). The elemental analysis was performed in the Pulp and Paper Laboratory (LCP), using the Elemental Analyzer, model TruSpec CHN Micro and TruSpec S (LECO) according to TAPPI 1266 om-02 (2006). Metal concentration determination was performed by inductively coupled plasma optical emission spectroscopy (ICP-OES) in the Spectroscopy Laboratory. The point of zero charges was done according to Regalbuto and Robles (2004). Routine cation exchange capacity (CEC) was performed using 10 cm^3 of TFSA + 25 mL of distilled water, and the analysis of microelements Fe, Mn, and Cu was performed using 10 cm^3 of TFSA + 100 mL of Mehlich-1 extractant performed by the Soil, Plant Tissue, and Fertilizer Analysis Laboratory. The CEC was done to determine the exchange capacity between the anionic and/or cationic charges on the NaOHAC surface. Iodine number was performed according to the Brazilian ABNT-NBR MB-3410 standard (1991), to predict the capacity of the AC to adsorb micropollutants with average diameters smaller than 2 nm. All the analyses detailed above were done in triplicate in different laboratories of the Federal University of Viçosa (UFV).

The morphology of the AC was analyzed using Leo 1430 VP scanning electron microscopy (SEM) equipment (Carl Zeiss Jena, Thuringia, Germany), operating at 15 KV, and SEM-EDS analysis in the Microscopy and Microanalysis Laboratory of UFV. The SEM-EDS was done in order to find the distribution of the chemical elements (O, Na, Si, P, S, K, Ca, Cr, Mn, Fe, Cu, Zn) present in KL, KLC, and NaOHAC, which were expressed in terms of concentration (%). The elements were selected based on the chemical composition of eucalyptus wood (BORLINI *et al.*, 2005; DE ANDRADE *et al.*, 2011) and on the result of the elements registered in the NaOHAC during the analysis in ICP-OES. The data generated was analyzed using Minitab® version 18 software, making a comparison of means by analysis of variance (ANOVA) followed by the Tukey test. The significance level used was $p \leq 0.05$ in all cases.

The characterization of the chemical structures (functional groups) present on the surface of the AC was determined by infrared spectroscopy with attenuated total reflectance (IR-ATR), using a Varian 660-IR, USA instrument fitted with a GladiATR attenuated reflectance accessory (PIKE Technologies, USA). The spectra were recorded in the region from 4000 to 400 cm^{-1} with 16 scans and a spectral resolution of 4 cm^{-1}. The crystal structure of the samples was characterized by Bruker model D8-Discover X-ray diffraction equipped with a copper tube (λ = 15418 Å), Goebel mirror, and LinxEye detector. Scans θ-2θ were made between 5° and 90° with a step of 0.05° and 1 second per step at room temperature. The analysis was performed in the laboratory of X-ray Diffraction and Scattering at UFV.

3. RESULTS AND DISCUSSION

The yield found in the production of NaOHAC was 23%, higher than those found by Jin *et al.* (2012), who used straw lignin activated with K_2CO_3 and KOH as the activated carbon precursor, which produced 19.8% and 18.7%, respectively.

The elemental and immediate analyses, iodine number, and point of zero charges of kraft lignin (KL), NaOH-activated carbon (NaOHAC), and commercial activated carbon (CAC) are listed in Table 2.

Table 2. Elemental analysis, volatile, ash, and fixed carbon content, iodine number, and point of zero charges analysis of kraft lignin (KL) NaOH activated carbon (NaOHAC) and commercial activated carbon (CAC).

Sample	Elemental Analysis					Immediate Analysis			Iodine Number (mg g^{-1})	pH_{PZC}
	C (%)	H (%)	O * (%)	N (%)	S (%)	Volatiles (%)	Ashes (%)	Fixed C (%)		
KL	62.8	5.6	28.5	0.2	2.9	70.3	1.5	28.3	-	-
NaOHAC	76.6	1.0	21.1	0.1	1.2	18.7	32.6	48.8	1,538	7.0
CAC	84.7	1.0	14.1	0.2	0.03	7.7	10.4	81.9	727	7.5

*Values obtained by difference

The result of the carbon content (C) found in KL is within the range of values usually observed in the literature of 41% to 65%, depending on its origin (hardwoods or softwoods) and the type of methodology used for the precipitation of lignin (FIERRO; TORNÉ-FERNÁNDEZ; CELZARD, 2006; MONTANÉ; TORNÉ-FERNÁNDEZ; FIERRO, 2005; WALTERSSON, 2009; WIKBERG *et al.*, 2015). In the production of NaOHAC, there was an increase in C content and a decrease in H and O contents compared to the original KL contents. The increment of the C content in NaOHAC is due to the volatilization of various types of oxygenated compounds (NOBRE *et al.*, 2015) and the increase in the degree of aromaticity (FIERRO; TORNÉ-FERNÁNDEZ; CELZARD, 2006). This volatilization of oxygenated compounds occurs during the heat treatment of LK through depolymerization, decarboxylation, dehydroxylation, and decarbonylation reactions (JIMÉNEZ; BAQUERO; DÍAZ, 2006). The decrease in H and O contents can be attributed to the generation of water vapor, carbon dioxide, and carbon monoxide during carbonization (HAMAD, 1981).

Values higher than the C content in NaOHAC (76.6%) were found by Brazil *et al.* (2018) using KL without the use of an activating agent (80%). The authors, however, observed a reduction to 75% after activation with H_2SO_4 and a subsequent reduction to 71% when varying the interaction time with the activating agent. The variations of the treatments in the study influenced the chemical composition of the charcoal.

Carbon, hydrogen, and oxygen are components of a part of the chemical structures (such as carboxylic groups and phenols, among other functional groups) of the AC. These components remain in the AC structure as a consequence of incomplete carbonization, allowing the functional groups and/or their derivatives to make chemical bonds with the adsorbate.

KL had a sulfur content equal to 2.9%, similar to that found by Fierro *et al.* (2006) of 2.15%. This high content when compared to the CAC (0.03%) is due to the presence of Na_2S, used as an auxiliary agent for cooking the wood in the kraft process to separate the cellulosic pulp from the other constituents of the wood. A reduction in sulfur content from 2.9% in KL to 1.2% in NaOHAC is observed. Such a reduction can be explained by the solubility of Na_2SO_4 (LAPPALAINEN *et al.*, 2020) during charcoal washing. The Na_2SO_4 is found within the components of kraft lignin when obtained from black liquor under precipitation with sulfonic acid (SANTOS *et al.*, 2014). It can also be generated in the activation of AC with NaOH under heat treatment (SCHETTINO *et al.*, 2007). Immediate analysis shows that the lignin fixed carbon content increased from 28.3% to 48.8% in NaOHAC, possibly due to the degradation of the volatile carbonaceous material contained in the kraft lignin (NOBRE *et al.*, 2015).

Regarding the ash content, an evident increase from 1.5% in lignin to 32.6% in NaOHAC was observed. The ash found in NaOHAC is composed mainly of silicates and Fe, Cr, Mn, Na, Ni, and S. The silicates may have their origin in the wood from which the lignin was extracted (BORLINI *et al.*, 2005; LOPES *et al.*, 2013), as well as during the delignification process. A possible explanation for the increase in the ash can be the formation of sodium silicates (Na_2SiO_3) that occurred due to the reaction between the NaOH, the char activating agent, and possible silicates contained in KL (JENDOUBI; MGAIDI; EL MAAOUI, 1997). The presence of Si in NaOHAC was verified in SEM-EDS analysis. Ash can reduce the adsorption potential by modifying the interaction between the carbon surface and the adsorbed species, and/or blocking the porosity of the carbon matrix, thus impairing the adsorption process (LOPES *et al.*, 2013). NaOHAC obtained an IN of 1,538 mg g^{-1}. Activated carbons with an iodine number higher than 600 mg I_2 g^{-1} are considered acceptable for adsorption use. IN values of 1,310 mg I_2 g^{-1} and 1,180 mg I_2 g^{-1} when activated with K_2CO_3 and KOH, respectively, have been reported in the literature (JIN; YU; WU, 2012). Thus, it can be considered that although the ash content in NaOHAC is high, it still exhibits an acceptable adsorption capacity.

The results obtained from the metal concentration and the CEC of the samples are presented in Table 3.

Table 3. Metal concentration (mg kg^{-1}) and cation exchange capacity (CEC) of kraft lignin (KL) activated carbon with NaOH (NAOHAC) and commercial activated carbon (CAC).

Sample	Concentration (mg kg^{-1})							
	S	Na	Zn	Ni	Cu	Fe	Mn	Cr
KL	13,948	2,054	4.0	nd	0.7	144	65	5.9
NaOHAC	2,488	5,760	84	5,587	101	26,451	1,159	9,688
CAC	-	-	-	-	-	-	-	-

Sample	CEC, T (cmol$_c$kg^{-1})	Cations for Exchange (mg kg^{-1})						
		Na	K	P	Zn	Cu	Fe	Mn
KL	-	-	-	-	-	-	-	-
NaOHAC	52.4	3,320	15.3	2.0	57	8.6	18,720	327
CAC	22.6	96	7,260	1,250	35.7	4.6	210	260

The CEC of the NaOHAC was 52.4 cmol$_c$kg^{-1}, and the CAC was 22.6 cmol$_c$kg^{-1}. Comparing the two activated carbons, the NaOHAC had the highest CEC value and the highest ash content. This is possibly due to the alkaline metals (such as Na) contained in the raw material. The CEC is a physical-chemical property intrinsic to the mineral and organic constituents of the soil. Its use can give a diagnosis of the retention and exchange of cations in different soil materials. The negative electric charges that can be found in the material (AC) arise from the dissociation of protons from functional groups. Among the main dissociated groups, we can mention the carboxylic and phenolic groups, dependent on the pH of the medium (solution). The CEC could help to estimate the ability of the AC to adsorb heavy metals (cations) on its surface. Additionally, Table 2 shows the elements available for cation exchange between the charges on the surface of the AC. It can be observed that NaOHAC has a higher concentration of Fe and Na, 18,720 mg kg^{-1} and 3,320 mg kg^{-1}, respectively, while the lowest values were for P, 2 mg kg^{-1}, and Cu, 8.6 mg kg^{-1}. The use of NaOHAC for the adsorption of metals such as Fe should take into consideration their initial concentration in the AC. The adsorption of a given adsorbate by the AC should present a reduction of its concentration in the aqueous solution. In this way, the concentration of the adsorbate should be higher than that found in NaOHAC, to enable its quantification.

Due to the high content of inorganic materials in the kraft lignin, it is advisable to demineralize it before producing the AC or to perform a washing step after carbonization.

3.1. Point of zero charges

The electrical charges on the surface of an adsorbent depend on its composition and the characteristics of the adsorbent's surface. The degree of distribution of chemical species that can be found on the surface of activated carbons is affected by the pH of the solution. The pH_{PZC} found for NaOHAC was neutral (7.0), indicating that for a solution with pH greater than pH_{PZC}, the surface charge will be negative, with better adsorbtion of cations (ideal for metal adsorption). Conversely, when the pH of the solution is lower than pH_{PZC}, the charge will be positive, favoring the adsorption of anions. If the use of NaOHAC is for metal removal, one should remember that some metals precipitate at alkaline pH levels. Thus, the surface charge of the adsorbent and the electrostatic interactions between the adsorbent and the adsorbate will depend on the pH during the adsorption process in the solution (NASCIMENTO *et al.*, 2014). A neutral pH_{PZC} facilitates its employment in various application scenarios by being easier to modify its value to more suitable levels for the adsorption of certain adsorbates (FONTES; CAMARGO; SPOSITO, 2001).

3.2. Scanning Electron Microscopy (SEM)

In Figure 1, the three-dimensional morphology and microstructural features of KL and NaOHAC can be observed. Morphological differences between KL and NaOHAC are easily noticed.

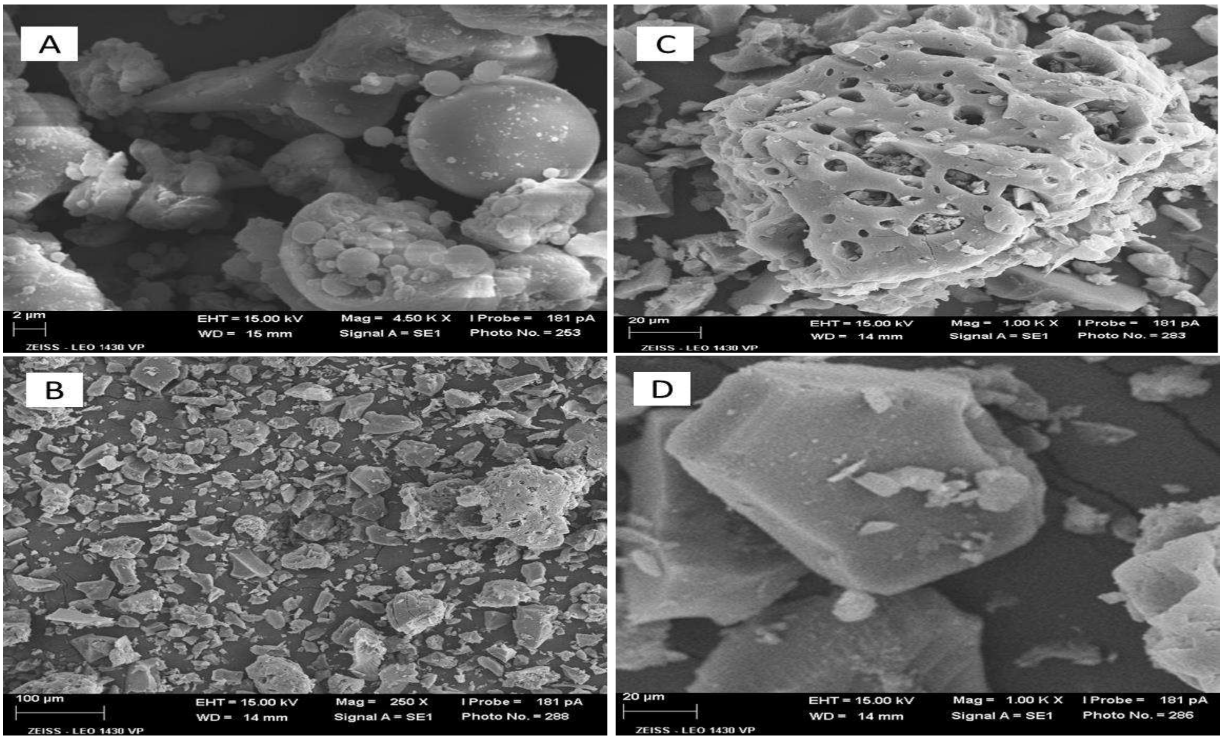

Figure 1. (A) Kraft lignin; (B, C, and D) NaOH-activated carbon.

KL (Figure 1A) has clustered structures of spherical shape, smooth and with few pores, characteristic of lignin obtained by acid precipitation of black liquor (WIKBERG *et al.*, 2015). The spherical shape of KL, thermodynamically more stable, is probably due to the surface tension between the particles (BRAZIL *et al.*, 2022). This surface tension occurs during the evaporation of black liquor in the chemical liquor recovery circuit of the kraft pulp process (FIERRO; TORNÉ-FERNÁNDEZ; CELZARD, 2006). Figure 1B presents a broad view of the irregular fragments of NaOHAC, and the disruption of the original structures due to the thermal and chemical treatment adopted. In Figure 1C, it is possible to observe the amplification of NaOHAC fragments when the porosity was developed after chemical treatment occurred. The morphological difference between KL and NaOHAC demonstrates that NaOH was an effective activating agent in producing pores in KL char (GAO *et al.*, 2013). Figure 1D shows plaque-like structures as found by Brazil *et al.* (2022) in the production of AC with H_3PO_4.

The previous step of carbonization of KL also showed an incipient development of pores in the lignin, shown in Figure 2. The carbonization of the raw material as a step before activation allows the enrichment of both the carbon content and the aromaticity, promoting an increase in the incipient microporosity of the char (MENÉNDEZ-DÍAZ; MARTÍN-GULLÓN, 2006a). This fact occurs since the functional groups during the heat treatment are modified, producing voids.

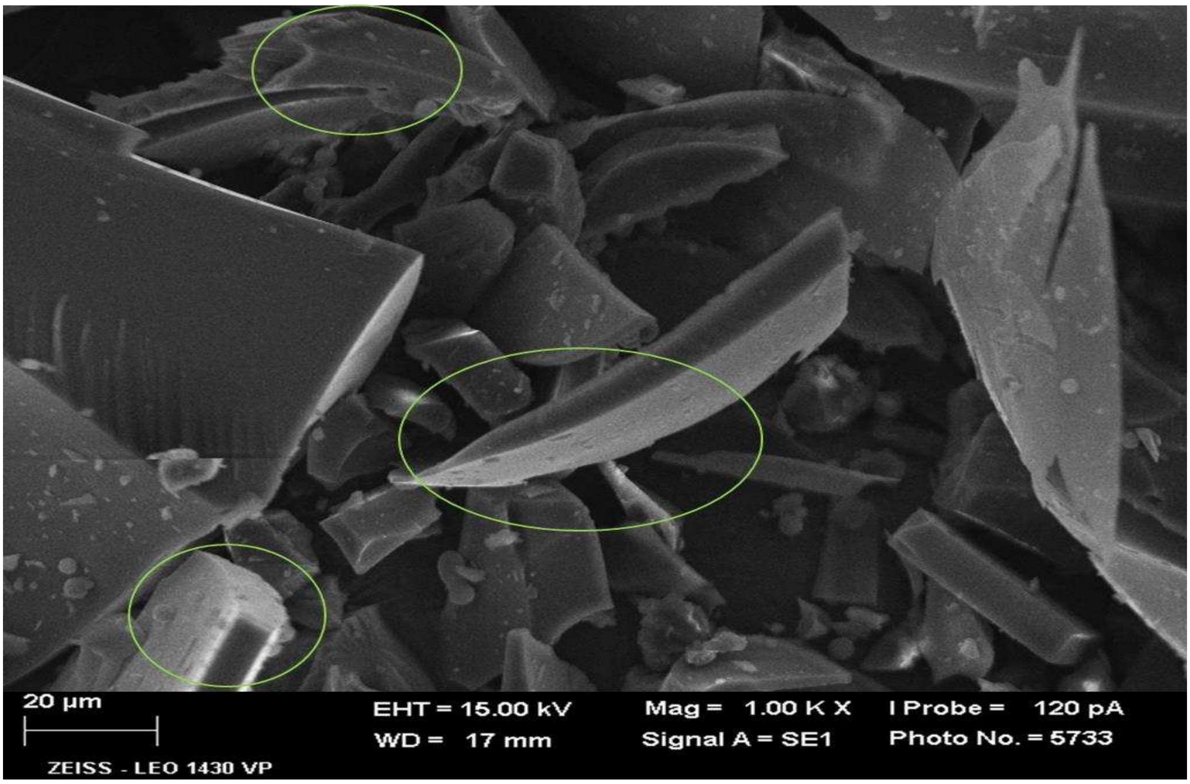

Figure 2. Pores developed after the pre-carbonization of kraft lignin (KL).

The dehydrating and oxidizing character of NaOH allowed the opening of the pores usually formed during carbonization. The high temperature applied during the activation promoted the volatilization of the material and the formation of micropores (BRASIL *et al.,* 2020) as well as the widening of the pores as observed by Xu *et al.* (2014) at temperatures above 500 °C. Along with the micropores, meso- and macropores were formed, which facilitate access to the micropores. The porosity developed in NaOHAC suggests that the activated carbon has a high adsorption capacity, as evidenced in the analysis of iodine number equal to 1,538 mg I_2 g^{-1}. The results of the distribution of the selected elements (O, Na, Si, P, S, K, Ca, Cr, Mn, Fe, Cu, and Zn) in the SEM-EDS have been provided in Table 4. Additional statistics material can be viewed in Annex 1.

Table 4. Concentrations of elements evaluated in kraft lignin (KL), KL char (KLC), and NaOH-activated carbon (NaOHAC) during SEM-EDS analysis.

Chemical element	KL		KLC		NaOHAC	
	Concentration (%)	Standart deviation	Concentration (%)	Standart deviation	Concentration (%)	Standart deviation
O	72.50 a	0.58	66.25 a	4.39	35.86 a	2.63
Fe	0.44 fg	0.07	1.76 d	0.58	31.82 b	2.93
Cr	0.27 g	0.07	0.38 d	0.15	10.37 c	1.07
S	16.78 b	0.38	15.09 b	1.41	10.24 c	0.72
Na	4.79 c	0.24	6.17 c	0.99	5.49 d	0.45
Si	1.65 d	0.19	2.17 d	0.54	2.12 e	0.30
Ca	0.94 e	0.17	2.21 d	0.38	1.39 e	0.16
Mn	0.37 fg	0.14	0.46 d	0.22	0.91 e	0.09
P	0.70 ef	0.19	0.35 d	0.17	0.68 e	0.17
Zn	0.40 fg	0.13	0.73 d	0.16	0.51 e	0.12
Cu	0.37 fg	0.05	0.57 d	0.16	0.30 e	0.07
K	0.60 efg	0.10	1.32 d	0.17	0.16 e	0.05

Concentrations followed by the same letter, in the column, do not differ from each other at 5% probability by Tukey's test.

In the distribution of the elements evaluated, a higher concentration of oxygen and sulfur was evident in KL, with a tendency to decrease at each stage of production of AC, unlike iron, manganese, and chromium, where the concentration was increased. The decrease of oxygen may have occurred during the thermal treatment, causing the volatilization of oxygenated compounds (FIERRO; TORNÉ-FERNÁNDEZ; CELZARD, 2006). Regarding sulfur, its reduction can be elucidated by considering the solubility of Na_2SO_4 (LAPPALAINEN *et al.*, 2020), as explained above. In the case of the elements that have increased their concentration, this may have happened because of oxidation reactions between metals and oxygen, forming oxides such as ferrous oxide, chromium oxide, and manganese oxide. These oxides have a very high melting point (>1000 °C) and are insoluble in water. When the activation temperature of NaOHAC was 700 °C, the compounds did not melt and were retained in the charcoal after the washing step, in contrast to calcium, which had a certain solubility in water and showed a decrease in concentration.

In Table 4, we can also observe that there was no statistical difference between the distribution of the concentration of Si, Ca, Mn, P, Zn, Cu, and K. The highest concentrations in the distribution of the elements in NaOHAC were for oxygen, iron, chromium, sulfur, and sodium, presenting a statistical difference, except for chromium and sulfur. The high concentration in the distribution of chemical elements agrees with the results obtained in the analysis of metals in the ICP-OES.

3.3. Spectral Analysis (IR-ATR)

Figure 3 shows the infrared spectrum of the kraft lignin, the produced activated carbon, and the commercial activated carbon.

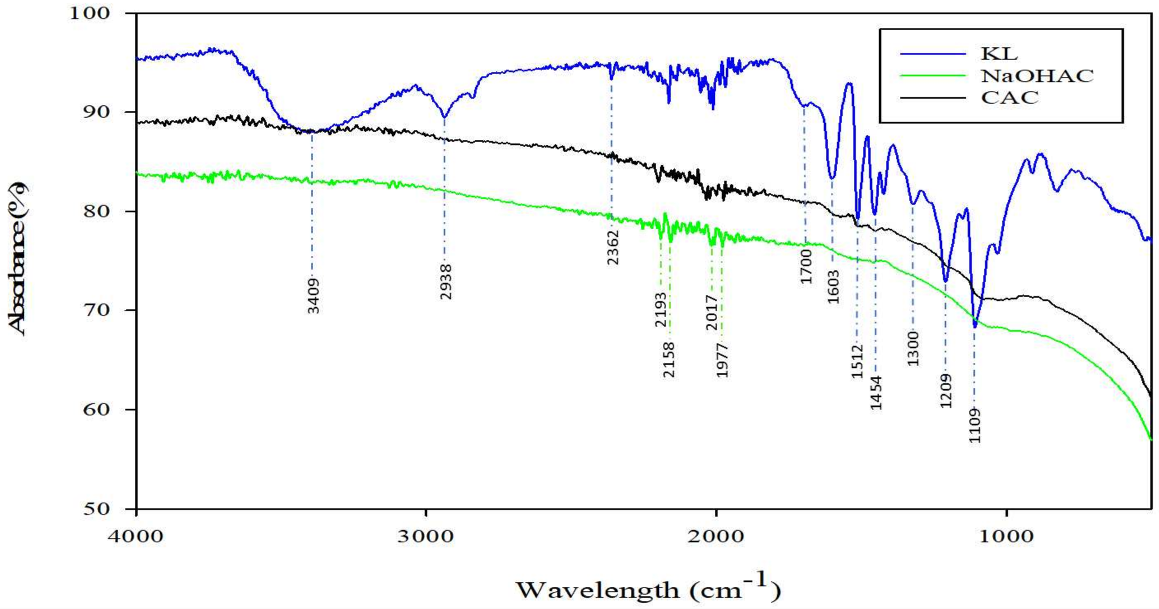

Figure 3. Spectra of kraft lignin (KL), NaOH-activated carbon (NaOHAC), and commercial activated carbon (CAC).

In Figure 3, spectral differences were observed between KL and NaOHAC, but no significant differences were observed between NaOHAC and CAC. The functional groups found in the samples were detailed in Table 5.

Table 5. Functional groups found in the spectra for kraft lignin (KL) and NaOH-activated carbon (NaOHAC).

Sample	Spectral Band (cm^{-1})	Functional Grups	Reference
KL	3409	OH bonds, referring to alcohol, phenols, and carboxylic acid	(LIU *et al.*, 2020)
	2938	Associated with the stretching of C-H bonds of aliphatic molecules, alkanes, alkene, and alkyl	
	2362	Corresponds to C-O bonds	(MISRA *et al.*, 2006)
	1700	Associated with C=O bonds (carboxylic acid, ketone)	(BRAZIL *et al.*, 2022)
	1603	C=C bonds in aromatic rings (aromatic alkene), carbonyl groups	
	1512	Referring to methoxyl groups	(ESTEVES *et al.*, 2013)
	1454	Methylene and methyl groups	
	1300-1000	Stretching of C-O bonds present in fatty acids, alcohols, phenols, esters, and ethers	(BRAZIL *et al.*, 2022)
NaOHAC	2193	Typical triple bonds C≡N	(DOS SANTOS *et al.*, 2019)
	2158	Associated with C=O and/or CO that bind to Na^{+2}	(ALSHUIAEL; AL-GHOUTI, 2020; NACHTIGALL *et al.*, 2007)
	2017	Associated with dicarbonyl	(MIESSNER, 2003)
	1977	Fe-CO	(LIU *et al.*, 2012)

In the spectra, peaks of functional groups characteristic of kraft lignin were found (BRAZIL *et al.*, 2022; LIU *et al.*, 2020). Regarding the changes observed in the supramolecular structure of KL in the production of NaOHAC, they may have occurred as a result of the breaking of chemical bonds during the carbonization and activation processes (ODA *et al.*, 2021). The reduction of the peaks of the initial feedstock (KL) may have been caused by the dehydrating character of NaOH (FIERRO; TORNE-FERNÁNDEZ; CELZARD, 2007; LIU *et al.*, 2020). NaOH acts as a catalyst in the presence of high temperatures. This type of dehydration reaction is also called elimination, and can occur in compounds that have the OH group attached to a saturated open-chain carbon. The hydroxyl groups are generally known as substituent groups that reduce the adsorption capacity. The breaking of the OH bonds on the NaOHAC surface may have influenced the non-acidic character of the charcoal (MENÉNDEZ-DÍAZ; MARTÍN-GULLÓN, 2006b). The presence of heterogeneous oxygen groups (even in small amounts) reduces the adsorption capacity. Oxygen-containing groups cause the water molecule to block the micropores to the pollutant, and the interaction energy between the pollutant and the carbon surface is reduced (CECEN; AKTAS, 2011).

The carbonyl group found in KL consists of acidic groups, which influence the adsorption of organic compounds (CECEN; AKTAS, 2011), although the removal efficiency will depend on the type of adsorbent and the pH of the solution. Generally, the adsorption of organic compounds increases with decreasing pH, while sulfonic groups commonly reduce adsorption. The functional groups found on NaOHAC can modify the polarity of the surface, as well as make the carbon acidic or basic, due to its amphoteric character. The acidic groups usually release protons in basic media, while the basic groups sequester them in acidic media.

In NaOHAC, the 2017 cm^{-1} peak referring to dicarbonyl was formed by the decarbonylation process, generating products such as CO and CO_2 (MIESSNER, 2003), whereas in the case of the 1977 cm^{-1} peak, it is associated with the elongation of the C-O of the Fe-CO (LIU *et al.*, 2012).

Since the ACs are non-polar in nature, they preferentially adsorb non-polar molecules, although some polar substances can be slightly adsorbed on the surface of the AC. The possible affinity of polar substances on the surface of the adsorbent is due to the presence of heteroatoms. Heteroatoms are those that have neither carbon nor hydrogen. Among the most common are nitrogen, oxygen, sulfur, phosphorus, and boron. Thus, the functional groups and heteroatoms confer to the AC an affinity for a certain adsorbate. The acidic or basic character of these components determines properties such as surface charge, hydrophobicity, and electronic density (GUERRA *et al.*, 2015).

3.4. X-Ray Diffraction

The XRD analysis, shown in Figure 4, comprises the diffractogram of KL, NaOHAC, and CAC, where the amorphous and or crystalline structure of the samples can be observed.

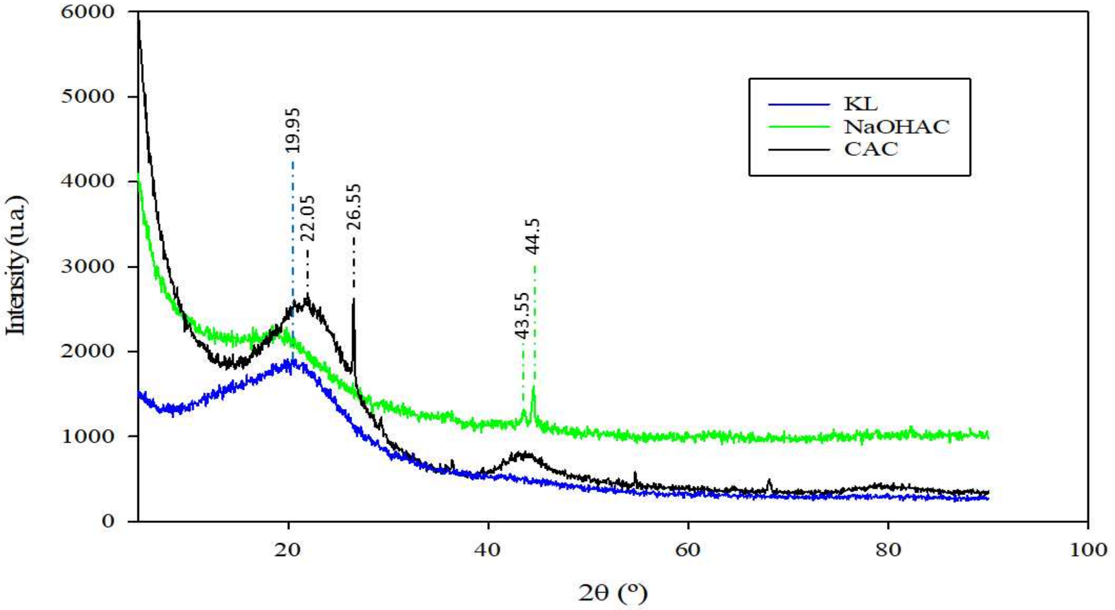

Figure 4. X-Ray diffraction of kraft lignin (KL), NaOH-activated carbon (NaOHAC), and commercial activated carbon (CAC).

NaOHAC mostly exhibits broad undefined regions characteristic of amorphous materials (KETCHA *et al.*, 2012; LOPES *et al.*, 2013; LU *et al.*, 2001), ideal for adsorption (DA SILVA, 2018). The undefined or disordered fractions of the sample bands do not contribute to the peak intensity, so it is reflected only at the bottom of the intensity curve (LU *et al.*, 2001). The amorphous character of NaOHAC can be explained by the breaking of C-C bonds, especially the aromatic rings of lignin during its transformation into activated carbon (KETCHA *et al.*, 2012), although a few peaks were found, at 43.55° (0.208 Å) and 44.5° (0.204 Å), similar to those found by Yan and Cai (2020), indicative of γ-Fe and α–Fe, respectively. The presence of iron in the XRD of NaOHAC agrees with the records of the element in the chemical analysis (26,451 mg kg^{-1}) and the SEM-EDS.

The most abundant heavy metal in KL and NaOHAC was iron, with 144 mg kg^{-1} and 26,451 mg kg^{-1}, respectively. The increase in iron content from KL to NaOHAC may have happened during the heat treatment and in the activation of AC. The interaction of the inorganic material and carbon with NaOH may have caused reactions that contributed to the formation of crystalline structures, as found in the case of Fe. Sodium hydroxide, being a strong and stable base, can react with inert materials at temperatures above 318 °C by melting without decomposition (LINARES-SOLANO *et al.*, 2012). Then, the molten hydroxide can easily react with carbon, mainly forming products such as hydrogen, alkali metals, and alkali carbonates as a result of carbon oxidation (LINARES-SOLANO *et al.*, 2012).

In general, NaOHAC, having an amorphous shape, can present voids between the molecules of the material (FERREIRA; ROCHA; SILVA, 2009), or irregularities in the packing of the aromatic structures (BRAZIL *et al.*, 2022) which could favor adsorption (DA SILVA, 2018).

The peaks of 22.05º and 26.55° found in the CAC sample are characteristic of cellulose, indicative of crystalline regions (RAMBO; SCHMIDT; FERREIRA, 2015) and graphite (CORDERO; RODRÍGUEZ-MIRASOL; BEDIA, 2007) or of quartz (LOPES *et al.*, 2013) respectively. The crystalline structures indicative of cellulose are to be expected, since the CAC is of lignocellulosic origin.

4. CONCLUSION

The production of chemically-activated carbon using NaOH for its possible implementation in pulp mills, represents a good alternative for new business opportunities. This is due to the low cost of the activating agent, the lower impact on equipment (when compared to other activating agents), and the good physical-chemical characteristics obtained from the charcoal produced. In the different analyses performed, it was possible to visualize the morphology of NaOHAC and to determine its chemical composition through analyses such as SEM-EDS, elemental analysis, and spectra analysis, as well as its crystallinity through X-Ray analysis. The NaOHAC presented a high content of organic matter, visualized especially in the chemical analysis, CEC, and SEM-EDS. The inorganic matter, coming from the KL, could be reduced with a washing step prior to the lignin. Despite the presence of inorganic material, it did not affect the good adsorption performance of NaOHAC in the iodine analysis, having registered values above those which were considered acceptable.

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CAPITULO 3

REMOÇÃO DE FÓSFORO E MATÉRIA ORGÂNICA ATRAVÉS DE TRATAMENTO TERCIÁRIO DE EFLUENTES DA INDÚSTRIA DE POLPA CELULÓSICA KRAFT COM CARVÃO ATIVADO

RESUMO

Teores de fósforo inadequados em efluentes tratados finais podem causar a eutrofização das águas, enquanto materiais recalcitrantes (lignina e compostos organoclorados) prejudicam a sua biotratabilidade. Ambos os componentes podem comprometer a qualidade dos corpos de água se não forem removidos dos efluentes. O objetivo da pesquisa foi verificar a viabilidade de remoção de fósforo e matéria orgânica (DQO - recalcitrante) dos efluentes utilizando carvão ativado (CA) produzido a partir da lignina kraft (componente residual do licor negro) no tratamento terciário de efluentes de polpa celulósica. O carvão ativado com NaOH (CANaOH) mostrou ser um eficiente adsorvente de fósforo e de DQO obtendo remoções máximas de 88,1% e 52,8%, respectivamente, para uma massa de CANaOH de 15 g L^{-1}. O modelo de pseudo-segunda ordem e modelo de Freundlich foram os melhores ajustados para o mecanismo de cinética e equilíbrio de adsorção respectivamente, tanto para a adsorção de fósforo como de matéria orgânica. A utilização de CANaOH demostrou ser um eficiente tratamento terciário para o aprimoramento dos efluentes de fábricas de polpa celulósica kraft.

Palavras-chave: Tratamento de efluentes, Demanda química de oxigênio, Eutrofização, Carvão ativado, Lignina Kraft

1. INTRODUÇÃO

O crescimento excessivo de plantas aquáticas pelo incremento de nutrientes, denominada eutrofização, compromete o uso normal do corpo d'água. O aumento de fósforo, nutriente essencial para o crescimento de bactérias e plantas aquáticas, esgota o oxigênio dissolvido na água (YU *et al.*, 2022). A eutrofização pode abranger problemas desde estéticos e recreacionais até geração de maus odores, mortandade de peixes e toxicidade. Segundo Yao *et al.* (2013) a concentração mínima de fosfato para induzir a eutrofização é de ~0,02 mg L^{-1}.

Os efluentes das fábricas de polpa celulósica são geralmente deficientes em nutrientes, portanto a eutrofização não tem sido um tema relevante, embora tenha sido reportados alguns casos onde foram causadores de eutrofização (BOTHWELL, 1992). No estudo de Bothwell (1992) a concentração de fósforo encontrado (aproximadamente 0,5 mg L^{-1}), mesmo inferior ao limite de detecção em uma fábrica de polpa branqueada em Kamloops, British Columbia, foi o suficiente para estimular a produção de algas no rio Thompson, Canada. A madeira, matéria prima para a obtenção de celulose, pode ser a responsável por parte do conteúdo de fósforo no efluente. Espécies como o Eucalyptus possuem um maior teor de fósforo em relação a outros tipos de madeiras (BENTANCUR *et al.*, 2021). Outra forma na qual o fósforo incorpora-se nos efluentes é através da sua dosagem como nutriente no tratamento de efluentes por processos biológicos. No Brasil não existem padrões de lançamento de efluentes para fósforo total (PT). No entanto, há uma crescente preocupação pela qualidade do efluente final lançado aos corpos de água. As grandes pressões internacionais de instituições ambientais e o evidente problema a nível mundial pela escassez de água potável, faz valer o interesse em diminuir as concentrações de fósforo nos efluentes.

Além do fósforo total, existem outros parâmetros importantes que caracterizam os efluentes provenientes de fabricas de polpa celulósica, sobretudo referentes à matéria orgânica, relacionadas à demanda bioquímica de oxigênio (DBO) e a demanda química de oxigênio (DQO). A primeira é indicativa do material biodegradável e a segunda da matéria orgânica total (biodegradável e recalcitrante). O tratamento de efluentes por processos biológicos são os mais utilizados na indústria de polpa kraft. Estes tipos de tratamento são responsáveis por remover concentrações de DBO superiores a 90%, e de 60% a 70% a eficiência na remoção de matéria orgânica (DQO) (MOUNTEER *et al.*, 2007). Os índices de biotratabilidade do efluente (DBO_5/DQO) podem variar de 0,3 a 0,45, o que limita a tratabilidade dos efluentes processos biológicos (COLODETTE; GOMES, 2015). A matéria recalcitrante na estação de tratamento de efluentes, geralmente está associada à lignina residual e à presença de organoclorados.

Tratamentos como a precipitação química (BENTANCUR *et al.*, 2020), a troca iônica, o tratamento biológico e a adsorção (YANG *et al.*, 2020) têm sido utilizados para a remoção de fósforo; enquanto que o processo Fenton (BRINK; SHERIDAN; HARDING, 2017), a eletrocoagulação (COIMBRA *et al.*, 2021), o carvão ativado (CA) (ODA *et al.*, 2021) para a remoção de matéria orgânica. Alguns dos tratamentos mencionados possuem algumas limitantes, como a necessidade de se empregar reagentes químicos, de demandar um controle rigoroso do pH, da temperatura, da taxa de mistura e das concentrações de íons para se obter resultados satisfatórios. A utilização de CA para a remoção de fósforo e de matéria orgânica representa uma alternativa atraente devido à facilidade de operação, baixo custo e à possibilidade de recuperação do adsorbato (LI *et al.*, 2020). O uso de lignina kraft (LK) como matéria prima para a produção de CA é possível devido à boas características físico-químicas do material (BRAZIL *et al.*, 2018). Adicionalmente, o emprego da lignina para produção de CA representa uma alternativa de alto valor agregado, em vez de seu normal envio para queima na caldeira de recuperação (LIU *et al.*, 2020). O CA pode ser utilizado como tratamento de água e/ou efluentes em diferentes setores dentro de uma fábrica de polpa celulósica kraft (CONDEZO *et al.*, 2023). O objetivo do presente trabalho foi estudar a viabilidade técnica da utilização de carvão ativado produzido a partir de lignina, no tratamento terciário, para a remoção de fósforo e de matéria orgânica (DQO) em efluentes gerados da indústria de polpa celulósica kraft.

2. MATERIAS E MÉTODOS

2.1. Materiais

Tanto a matéria prima utilizada na produção de CA, lignina kraft de eucalipto, como o efluente utilizado para os testes de adsorção de fósforo e de matéria orgânica (DQO) foram obtidos de uma fábrica de polpa celulósica kraft branqueada de eucalipto da região Sudeste do Brasil. A solução padrão de fósforo empregado nos testes de adsorção foi o fosfato de potássio monobásico (KH_2PO_4). Todos os produtos químicos utilizados nas diferentes análises no estudo possuem o grau de reagente de laboratório.

2.2. Caracterização

A produção do CANaOH e sua caracterização físico-química e morfológica foi detalhada no Capitulo 2. O efluente tratado foi caracterizado em termos de matéria orgânica (DQO), fósforo, e pH, Tabela 1, segundo as normas de Standard Methods for Examination of Water and Wastewater (2017).

Tabela 1. Caracterização do efluente em termos de pH, DQO e fósforo.

Amostra	pH	DQO (mg L^{-1})	Fósforo Total (mg L^{-1})
Efluente	7,6	429	0,27

2.3. Teste de adsorção de fósforo

No teste de adsorção, uma solução estoque de fosfato de 200 mg L^{-1}, usando KH_2PO_4 e água destilada, foi preparada. A partir da solução estoque foram preparadas concentrações de 2, 4, 6, 8 mg L^{-1} de fosfato. Os testes de adsorção foram realizados em batelada, usando Erlenmeyer de 250 mL, em mesa agitadora (150 rpm) e realizados a uma temperatura de 25 ºC durante 24 horas. Diferentes massas de CANaOH foram pesadas, 0,1, 0,5, 1 e 1,5 g, e colocadas nos

Erlenmeyer com 100 mL de efluente tratado. Os testes de adsorção foram feitos por delineamento fatorial completo (5x5) com um total de 25 tratamentos e em triplicata, Figura 1 (Anexo 2 Tabela S1).

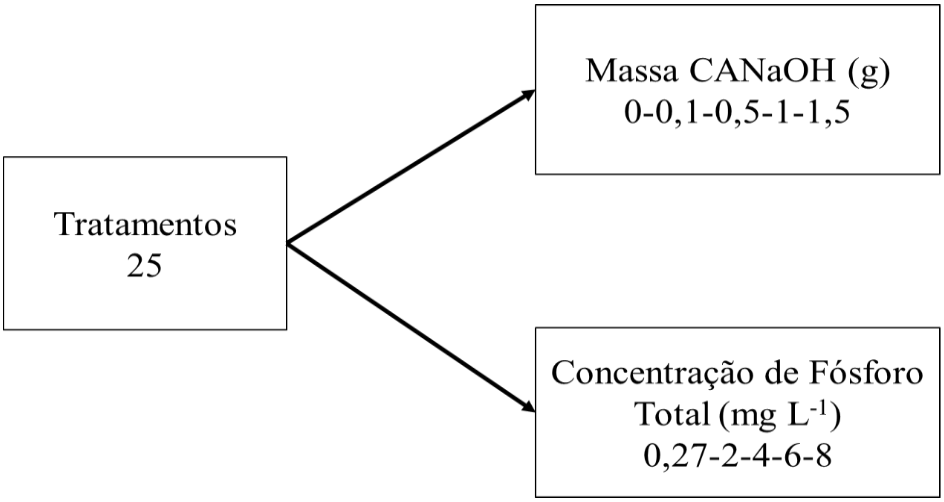

Figura 1. Delineamento experimental para os testes de adsorção de fósforo total.

As diferentes concentrações de fósforo total, avaliadas para cada tratamento, foram dosadas considerando um volume total de 100 mL de efluente e uma solução estoque de 200 mg L^{-1} de fósforo. A adição de diferentes concentrações de fósforo no efluente foi feita para saber a eficiência do CANaOH em cenários com concentrações de fósforo maiores. Após 24 h de agitação, as amostras foram filtradas através de uma membra de fibra de vidro de 0,45 µm, para remover o carvão ativado e determinar posteriormente a concentração de fósforo total.

2.4. Teste de adsorção de matéria orgânica (avaliada pela DQO)

Os testes de adsorção de matéria orgânica (DQO) foram desenvolvidos com a mesma metodologia no item anterior. A remoção de matéria orgânica foi avaliada testando as mesmas massas de CANaOH, 0,1, 0,5, 1, 1,5 g em 100 mL de efluente. A eficiência de remoção de DQO e do fósforo foram determinadas de acordo com a equação (1):

$$Removal\ efficiency\ (\%) = \frac{(C_o - C_e)100}{C_e} \tag{1}$$

Onde: C_o é a concentração inicial de DQO ou fósforo em mg L^{-1}; C_e é a concentração de DQO ou fósforo no equilíbrio em mg L^{-1}.

A eficiência de remoção de fósforo e de DQO foi analisado estatisticamente usando o software SigmaPlot® 14.0, avaliando como fatores as “massas de CANaOH”, “concentrações de fósforo” e “DQO” Tabela 2.

Tabela 2. ANOVA dos fatores “massa de CANaOH”, “concentração de fósforo” e “concentração de DQO” para a resposta “Eficiência de remoção de fósforo” e “Eficiência de remoção de DQO”.

Resposta	Fonte de Variação	DF	SS	MS	Valor F	Valor-P*
Eficiência de Remoção de fósforo	Massa de CANaOH	4	81.041	20.260	4.725	<0,001
	Concentração de fósforo	4	7.852	1.963	457	<0,001
	Massa de CANaOH x Concentração de fósforo	16	16.887	1.055	246	<0,001
	Residual	50	214	4,29		
	Total	74	105.996	1.432		
Eficiência de remoção de DQO	Massa de CANaOHxDQO	4	5.807,02	1.451	2.582	<0,001
	Residual	10	562	0,56		
	Total	14	5.812			

*Fatores e suas interações com valor de P<0,05 são diferentes estatisticamente.

2.5. Cinética de adsorção

A massa de carvão ativado utilizada para os testes de cinética foi de 0,5 g em 100 mL de efluente, a uma concentração de 4 mg L^{-1} de fósforo. A massa de 0,5 g de CA foi escolhida para a realização dos testes de cinética, por atingir valores superiores a 50 % de remoção de fósforo e superiores a 40% na remoção de DQO. Mesmo que os resultados com 0,5 g de CA não representem as maiores remoções atingidas, uma menor quantidade de massa de CA se traduz em menos resíduos e menores custos, quando aplicado a nível industrial. O teste foi feito em duplicata avaliando intervalos de tempo de 1, 2, 6, 30, 60, 120, 180, 240, 300 e 360 min. Os resultados foram plotados em Microsoft Office Excel 16, com ajuste dos modelos linearizados de pseudo-primeira ordem (2), pseudo-segunda ordem (3) (KRIAA; HAMDI; SRASRA, 2011); também foi ajustado outros modelos como a difusão intrapartícula (4) de acordo com Weber e Morris (1963) e Elovich (5) (NASCIMENTO *et al.*, 2014), apresentados a continuação:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1 t}{2,303} \qquad (2)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (3)$$

$$q_t = k_d t^{0.5} + C \quad (4)$$

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t) \quad (5)$$

Onde: q_e e q_t é a quantidade de adsorbato adsorvida na fase sólida no equilíbrio e em um tempo qualquer t (min) respectivamente (mg g^{-1}); k_1 e k_2 são as constantes de taxas de equilíbrio para a pseudo-primeira ordem (min^{-1}) e pseudo-segunda ordem (g mg^{-1} min^{-1}) respectivamente; k_d é a constante de velocidade de difusão intraparticula (mg g^{-1} $min^{-0.5}$) e C é a constante relacionada com a resistência à difusão (mg g^{-1}); α é a taxa de adsorção inicial (mg g^{-1} min^{-1}) e β é a constante de dessorção (mg g^{-1}).

2.6. Equilíbrio de Adsorção

O tempo de equilíbrio (15 h) foi determinado de acordo com as curvas de cinética e na disponibilidade laboratorial. As massas empregadas foram de 0,1 até 4,0 g de CANaOH para os 100 mL de efluente, a uma temperatura de 25 ºC. Os testes foram feitos em duplicata e os resultados foram ajustados aos modelos de Langmuir e Freundlich usando o software SigmaPlot® 14.0. A quantidade adsorvida por grama de adsorvente (q_e) foi calculada de acordo à Equação (6) e a equação dos modelos de Langmuir, Equação (7), e Freundlich, Equação (8):

$$q_e = \frac{(C_o - C_e)V}{m} \quad (6)$$

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \quad (7)$$

$$q_e = K_F C_e^{1/n} \quad (8)$$

Onde: C_o é a concentração inicial de DQO ou fósforo (mg L^{-1}); C_e é a concentração de DQO ou fósforo no equilíbrio (mg L^{-1}); q_e é a quantidade adsorvida de matéria orgânica (DQO) ou fósforo em equilíbrio por grama de adsorvente (mg g^{-1}); V é o volume do efluente (L); m é a massa de CA (g); q_{max} é a capacidade máxima de adsorção (mg g^{-1}); K_L é a constante de Langmuir relacionada com a energia de adsorção (L mg^{-1}); 1/n é a constante relacionada com a heterogeneidade da superfície; e K_F é a constante experimental da capacidade do adsorvente ((mg g^{-1} (L mg^{-1}))$^{1/n}$).

3. RESULTADOS E DISCUSSÕES

3.1. Remoção de fósforo e de matéria orgânica (DQO)

Os resultados dos testes de adsorção demostraram que o CANaOH tem uma alta eficiência de remoção de fósforo (88,6%) e de matéria orgânica (DQO) (52,8%) conforme mostra a Figura 2.

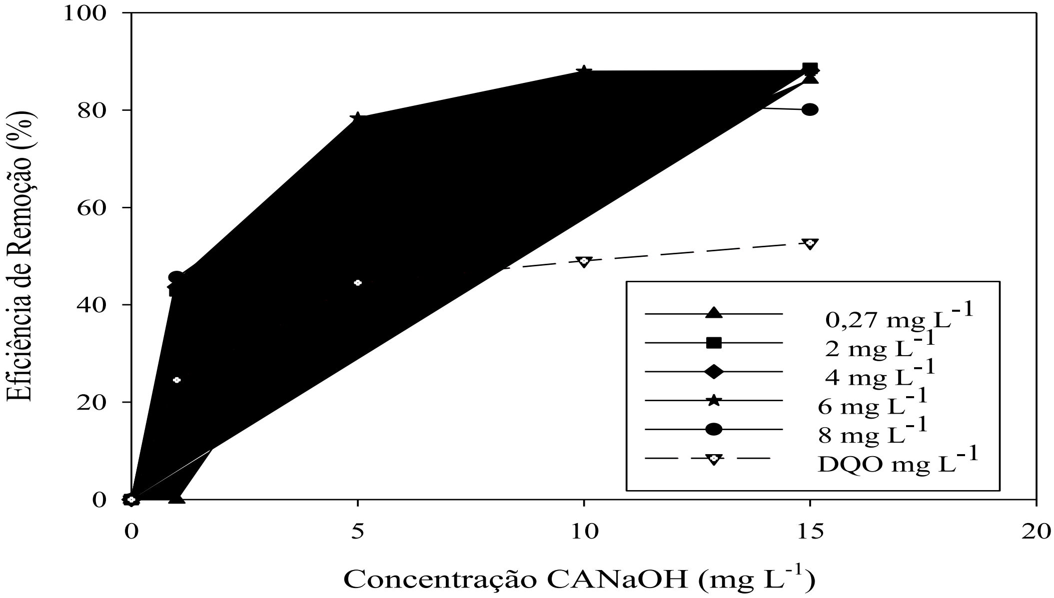

Figura 2. Eficiência de remoção de fósforo para diferentes concentrações iniciais do elemento, e eficiência de remoção de matéria orgânica (DQO) para uma única concentração inicial usando como agente adsorvente carvão ativado com NaOH (CANaOH).

Com cada incremento na massa de CANaOH a tendência da eficiência de remoção foi aumentar até um máximo de 88,1% para concentrações iniciais de 4 e 6 mg L^{-1} de fósforo empregando 15 g de CANaOH; e uma remoção de 52,8% de matéria orgânica (DQO) para a mesma massa de CA. A maior remoção de fósforo do que a matéria orgânica, pode estar associada ao alto número de iodo (1.538 mg I_2 g^{-1}) encontrado no CANaOH. O número de iodo está relacionado à adsorção de micropoluentes (JIN; YU; WU, 2012) com diâmetros menores a <2 nm. Por possuir uma superfície microporosa, o CANaOH beneficia a adsorção de adsorbatos de menor tamanho como o fósforo. No caso da eficiência de remoção de DQO, estudos reportaram remoções máximas de matéria orgânica de 55,85% para uma massa de CA de 1,0 g (ODA *et al.*, 2021). Os autores indicam que a alta remoção de matéria orgânica pelo adsorvente está associada a uma maior mesoporosidade do CA, uma vez que a matéria orgânica pode apresentar compostos orgânicos de grande tamanho molecular. Assim, a remoção máxima de 52,8% de matéria orgânica, encontrada neste estudo, foi devido ao fato do CANaOH apresentar um alto grau de microporosidade.

Segundo a análise estatística ANOVA, Tabela 2, o fator "massa de CANaOH", o fator "concentração de fósforo" e a interação entre eles tiveram um efeito significativo na resposta eficiência de remoção fósforo a um nível de significativa de $P<0,05$. Como a interação entre os fatores foi significativa, pode-se inferir que a eficiência de remoção depende da combinação entre massa de CANaOH e a concentração de fósforo. No caso da remoção de matéria orgânica a eficiência de remoção depende da interação da massa de CANaOH e a concentração de DQO. Para analisar os contrastes entre as eficiências de remoção de fósforo e matéria orgânica (DQO) foi realizado o teste Holm-Sidak para as interações, Tabela 3.

Tabela 3. Interação entre "Massa de CANaOH" e "Concentração de Fósforo" para a percentagem de remoção de fósforo e a interação entre "Massa de CANaOH" e "concentração de DQO" na percentagem de remoção de matéria orgânica (DQO) em efluente final de fábricas de polpa celulósica.

Carvão Ativado (g)	Remoção (%) a diferentes concentrações de fósforo (mg L^{-1})					Remoção DQO (%)
	0,27	2	4	6	8	
0	0 g	0 g	0 g	0 g	0 g	0 e
0,1	0 g	42,9 f	43,7 f	44,9 f	45,6 f	24,5 d
0,5	53,8 e	71,6 c	70,9 c	78,4 b	71,8 c	44,5 c
1	67,1 d	69,5 cd	65,9 d	87,9 a	81,5 b	49,1 b
1,5	86,3 a	88,6 a	88,1 a	88,1 a	80,1 b	52,8 a

*Letras iguais indicam que não houve diferença estatística significativa na interação entre as médias $P<0,05$, segundo teste Holm-Sidak.

Os resultados mostram que não houve diferença estatística na adsorção de fósforo em concentrações de 0,27, 2, 4 e 6 mg L^{-1} para uma concentração de 15 mg L^{-1} de CANaOH. Entre as diferentes concentrações avaliadas de CANaOH, a maior remoção de fósforo foi encontrada a uma concentração inicial de 2 mg L^{-1} (88,6%) para uma massa de 1,5 g de CA. Os resultados evidenciaram a tendencia de diminuição da eficiência de remoção quando a concentração de fósforo foi aumentada para 8 mg L^{-1}. Esta tendencia em diminuir a remoção de fósforo com o incremento a 8 mg L^{-1} (80,1%), pode ser explicada pelo preenchimento dos locais da superfície do CA com o adsorbato, provocando a saturação do adsorvente (WANG *et al.*, 2016).

O poder de remoção do CANaOH, mesmo com massa de 0,1 g, atingiu valores de remoção de fósforo superior a 40%, para cada uma das concentrações avaliadas, excetuando a concentração inicial de 0,27 mg L^{-1}. Este comportamento pode ser explicado devido à baixa concentração inicial (0,27 mg L^{-1}) de fósforo, a qual não forneceu uma força motriz significativa para superar a resistência à transferência de massa, entre a solução e o adsorvente (ALMASI *et al.*, 2012). A eficiência de remoção de fósforo no estudo de Yin *et al.* (2019) foi influenciada pelo alto teor de compostos metálicos (6,49% Al e 3,32% Fe) que possuía o adsorvente que os autores utilizaram (biocarvão de lodo de esgoto). Isto como consequência da reação entre os metais do adsorvente com o PO_4^{-3} por complexação. Os autores relatam que os elementos metálicos foram parcialmente liberados do adsorvente para a solução reagindo com o PO_4^{-3}; formando posteriormente fosfatos insolúveis como $FePO_4$. Na caracterização do adsorvente (Capitulo 2) foi observado um alto conteúdo de metais, principalmente Fe, 2.6451 mg kg^{-1}, o qual então poderia ter reagido com o PO_4^{-3} e formar $FePO_4$. Assim, o $FePO_4$ (insolúveis) na solução pode estar sendo depositado na superfície do adsorvente, contribuído com a adsorção de fosfatos. Para comprovação desta teoria recomenda-se em trabalhos futuros a realização de espectroscopia de raios X dispersiva (EDS) para examinar a superfície do CA posterior à adsorção de fosfatos e determinar sua composição elementar superficial. Por outro lado, ao ter o CANaOH um ponto de carga zero (pH_{PZC}) de 7 (Capitulo 2), similar ao pH do efluente (pH 7,6), a superfície do adsorvente foi carregada positivamente, enquanto o adsorbato era carregado negativamente (PO_4^{-3}). Então, esta diferença de cargas elétricas entre o adsorvente e o adsorbato poderia também favorecido à adsorção de fosfato (YIN; LIU; REN, 2019). Em relação à remoção de matéria orgânica as moléculas orgânicas são majoritariamente adsorvidas em condições neutras (CECEN; AKTAS, 2011). Este fato pode ter influenciado na adsorção do material orgânico recalcitrante (DQO), já que o efluente e o pH_{PZC} do adsorvente foi entorno de um pH neutro. Cecen e Aktas (2011) atribuem a adsorção de material orgânico à presença de cadeias ramificadas, como o caso dos compostos aromáticos (lignina); os quais são geralmente mais adsorvíveis do que as cadeias retas como compostos alifáticos. Adicionalmente, os autores indicam que os contaminantes orgânicos complexos têm grupos hidrofóbicos e hidrofílicos. Portanto, a parte hidrofóbica da molécula pode ser adsorvida, enquanto a outra parte hidrofílica permanece na solução. Isto pode ter levado a uma eficiência de adsorção de matéria orgânica menor, quando comparada à remoção de fósforo.

3.2. Cinética de adsorção de fósforo e de matéria orgânica (DQO)

Para entender o mecanismo de adsorção do fósforo e de matéria orgânica no carvão ativado foram feitos testes de cinética, avaliando diferentes modelos, cujos resultados são apresentados na Figura 3 e 4 respectivamente. As curvas de cinética são apresentadas no Anexo 2, Figura S1.

Os possíveis mecanismos de adsorção são: i) pela transferência de massa externa no contorno do filme líquido (solução + adsorbato) que envolve o adsorvente; ii) adsorção no sitio na superfície, controlada pela natureza da adsorção (quimissorção ou fisissorção); e iii) pela difusão das moléculas totalmente adsorvidas ao longo da superfície do poro.

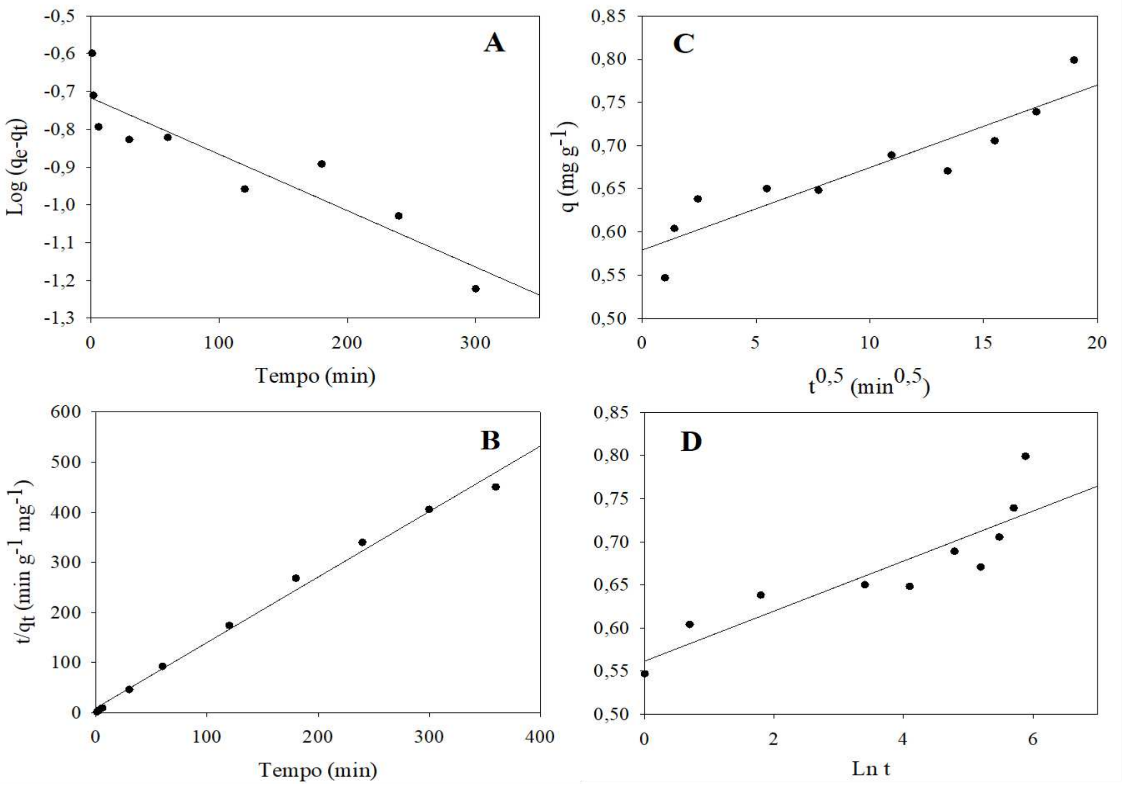

Figura 3. Cinética de adsorção para fósforo total segundo modelo pseudo-primeira ordem (A), pseudo-segunda ordem (B), difusão intrapartícula (C) e Elovich (D).

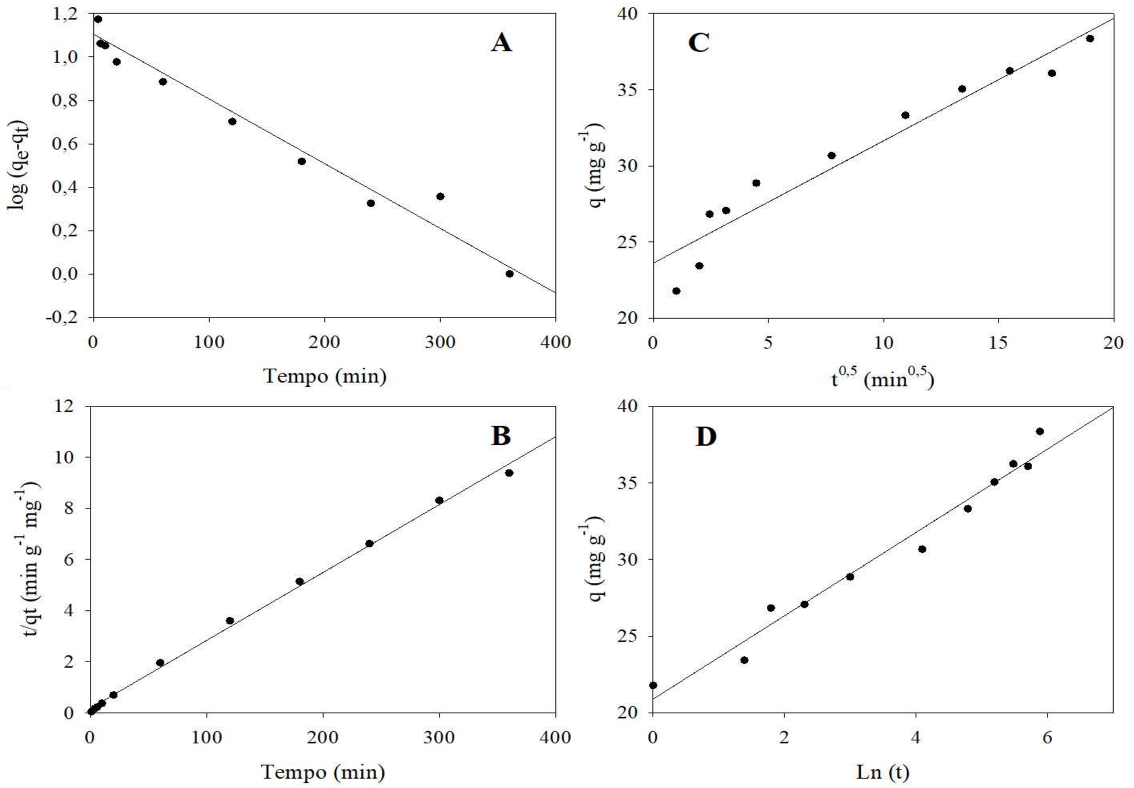

Figura 4. Cinética de adsorção para matéria orgânica (DQO) segundo modelo pseudo-primeira ordem (A), pseudo-segunda ordem (B), difusão intrapartícula (C) e Elovich (D).

A Tabela 4 apresenta os resultados dos parâmetros cinéticos de adsorção, de cada modelo avaliado, para a remoção de fósforo e de matéria orgânica.

Tabela 4. Parâmetros cinéticos de adsorção de fósforo e de matéria orgânica (DQO) referente aos modelos de Pseudo-primeira ordem, Pseudo-segunda ordem, difusão intrapartícula e Elovich.

Adsorbato	Cinética											
	Pseudo-primera ordem			Pseudo-segunda ordem			Difusão Intraparticula			Elovich		
	k_1	q_e	R^2	k_2	q_e	R^2	k_d	C	R^2	A	β	R^2
Fósforo	3,4e^{-3}	0,19	0,84	0,18	0,77	0,99	9,6e^{-3}	0,58	0,85	7,61e^{+6}	34,51	0,79
DQO	6,9e^{-3}	12,74	0,96	4,1e^{-3}	37,59	0,99	0,80	23,61	0,94	5,93e^{+3}	0,37	0,97

O modelo que mais se adequou para a adsorção de fósforo e de matéria orgânica (DQO) pelo CANaOH foi o modelo de pseudo-segunda ordem, verificado pelo valor do coeficiente de determinação (R^2) de 0,99 em ambos casos. O alto coeficiente de determinação sugere então que o mecanismo de adsorção de pseudo-segunda ordem é predominante, e que a taxa geral do processo de adsorção foi principalmente por processos de quimissorção. A constante de velocidade de adsorção K_2 para o fósforo e DQO foram de 0,8 g mg^{-1} min^{-1} e 4,10e^{-3} g mg^{-1} min^{-1}, respectivamente. A constante de velocidade de adsorção no fósforo foi maior ao encontrado na DQO. Isto pode-se explicar, em parte, pela rápida adsorção do fósforo ao possuir um tamanho menor que o material orgânico recalcitrante (DQO). Adicionalmente, a alta eficiência na remoção de fósforo, governada por processos de quimissorção, pode estar atribuída também ao alto teor de compostos metálicos no CANaOH (YIN; LIU; REN, 2019). É importante salientar que a velocidade de adsorção também pode ser influenciada pela temperatura, pH, força iônica, concentração inicial do adsorbato, agitação e distribuição do tamanho dos poros (NASCIMENTO *et al.*, 2014). Valores menores de K_2 (5,3e^{-4} g mg^{-1} min^{-1}) na remoção de fósforo foram encontradas por Yao *et al.* (2013) para uma concentração de fósforo de 30,6 mg L^{-1} usando como adsorvente biochar-Mg. Os autores também sinalaram que o modelo de pseudo-segunda ordem foi o segundo modelo que melhor se ajustou com um R^2 de 0,999.

No caso do modelo de difusão intrapartícula, as retas ajustadas não passaram pela origem (Figura 3C e 4C), tanto na adsorção de fósforo (R^2 0,85) como na matéria orgânica (DQO) (R^2 0,94). Isto indica que o processo de adsorção de fósforo e matéria orgânica pelo CANaOH não foi apenas controlada pela difusão intrapartícula, mas também afetada por outros processo como a transferência de massa externa inicial ou reações químicas (YU *et al.*, 2022). O valor da constante de velocidade de difusão intraparticula (K_d) foi 9,60e^{-3} mg g^{-1} min$^{-0.5}$ e 0,80 mg g^{-1} min$^{-0.5}$ e a constante relacionada com a resistência à difusão (C) de 0,58 mg g^{-1} e 23,61 mg g^{-1} para fósforo e DQO respectivamente. O alto valor de C na DQO no modelo de difusão intrapartícula indica que a adsorção do adsorbato pelo carvão ativado foi feita em parte por processos de difusão externa e/ou interna (JUNG *et al.*, 2015; YIN; LIU; REN, 2019). Entretanto, este modelo não considera parâmetros importantes como a porosidade e o diâmetro da partícula, além de não analisar o comportamento cinético nos tempos iniciais do processo, já que a equação envolve t$^{1/2}$ (NASCIMENTO *et al.*, 2014). Por último, o modelo Elovich apresentou um R^2 de 0,79 e 0,97 na adsorção de fósforo e de matéria orgânica (DQO) respectivamente. O alto coeficiente de determinação no modelo para a adsorção de matéria orgânica, supõe que os sítios ativos do adsorvente podem ser heterogêneos, portanto exibem diferentes energias de ativação (PINZÓN-BEDOYA; VILLAMIZAR, 2009). A heterogeneidade da superfície do carbono surge principalmente aos grupos de oxigênio da superfície, que embora presentes em quantidades relativamente pequenas podem afetar as propriedades da superfície (CECEN; AKTAS, 2011).

O modelo Elovich envolve reações de quimissorção de adsorbato na superfície do adsorvente, como no mecanismo de reação de segunda ordem. O parâmetro α, 5,93e^{+3} g mg^{-1} min^{-1}, teve uma alta taxa inicial da adsorção, relacionado a uma alta energia de quimissorção. O parâmetro β obteve um valor de 0,37 g mg^{-1}, e pode indicar uma possível redução no número de sítios disponíveis da superfície do CA, devido a seu preenchimento com a massa de adsorbato (GÜNAY; ARSLANKAYA; TOSUN, 2007). Mesmo o coeficiente de determinação do fósforo não tenha sido tão alto quanto da DQO, ele apresentou valores superiores de α 7,61e^{+6} g mg^{-1} min^{-1} e β 34,51 g mg^{-1}. Os valores superiores encontrados em α na adsorção de fósforo, em comparação à matéria orgânica, era esperado pela alta taxa de remoção encontrada nos testes de adsorção de fósforo inicial de aproximadamente 88%. Da mesma forma, o valor superior de β na adsorção de fósforo indica que a superfície do adsorvente ainda possui sítios disponíveis para adsorção (PINZÓN-BEDOYA; VILLAMIZAR, 2009). É importante salientar que neste tipo de processo, a velocidade de adsorção depende da quantidade de sítios ativos na superfície do adsorvente. Assim, pode-se dizer que o processo de adsorção de fósforo e de matéria orgânica (DQO) foi governada principalmente por processos de adsorção química, com sítios ativos heterogêneos. No estudo de Yu *et al.* (2022) o processo de adsorção de fosfato também foi dominada por processos de quimissorção, obtendo um R^2 de 0,99 e valores de q_e de 9,39 mg g^{-1} e K_2 de 0,07 g mg^{-1} min^{-1}, menor ao encontrado no presente estudo (0,18 g mg^{-1} min^{-1}). Outros estudos como o de Wu *et al.* (2020) e Yin *et al.* (2019) demostraram que a adsorção de fósforo é melhor ajustado por modelos de pseudo-segunda ordem, o que sugere que a adsorção de fosfato pode envolver uma reação química entre o PO_4^{-3} e grupos funcionais na superfície do adsorvente (YU *et al.*, 2022).

3.3. Equilíbrio de adsorção de fósforo e de matéria orgânica (DQO)

Na remoção de fósforo e de matéria orgânica (DQO) o modelo que melhor se ajustou foi de Freundlich segundo o alto valor do coeficiente de determinação R^2 de 0,99 e 0,95 respectivamente, como apresentados na Tabela 5. Este modelo corresponde a uma correlação logarítmica entre a entalpia de adsorção e a concentração do adsorbato. Isto significa que à medida que a adsorção acorre (preenchimento da superfície do adsorvente pelo adsorbato) a energia de adsorção diminui, devido à heterogeneidade da superfície do CA (NASCIMENTO *et al.*, 2014). Este fato corrobora com o discutido no mecanismo de adsorção do CANaOH, onde após avaliar os diferentes modelos cinéticos se concluiu que a adsorção foi governada principalmente por processos de quimissorção, com sítios ativos heterogêneos.

Tabela 5. Parâmetros dos modelos Langmuir e Freundlich para a adsorção de fósforo e de matéria orgânica (DQO).

Adsorbato	Isotermas						
	Langmuir			Freundlich			
	q_{max}	K_L	R^2	K_F	1/n	n	R^2
Fósforo	1,74	0,51	0,97	0,55	1,65	0,61	0,99
DQO	$1{,}5e^{+9}$	$8{,}9e^{-11}$	0,63	$3{,}34e^{-6}$	0,35	2,90	0,95

Na Figura 5 são apresentadas as curvas dos modelos ajustados de Langmuir e Freundlich para a adsorção de fósforo e matéria orgânica (DQO).

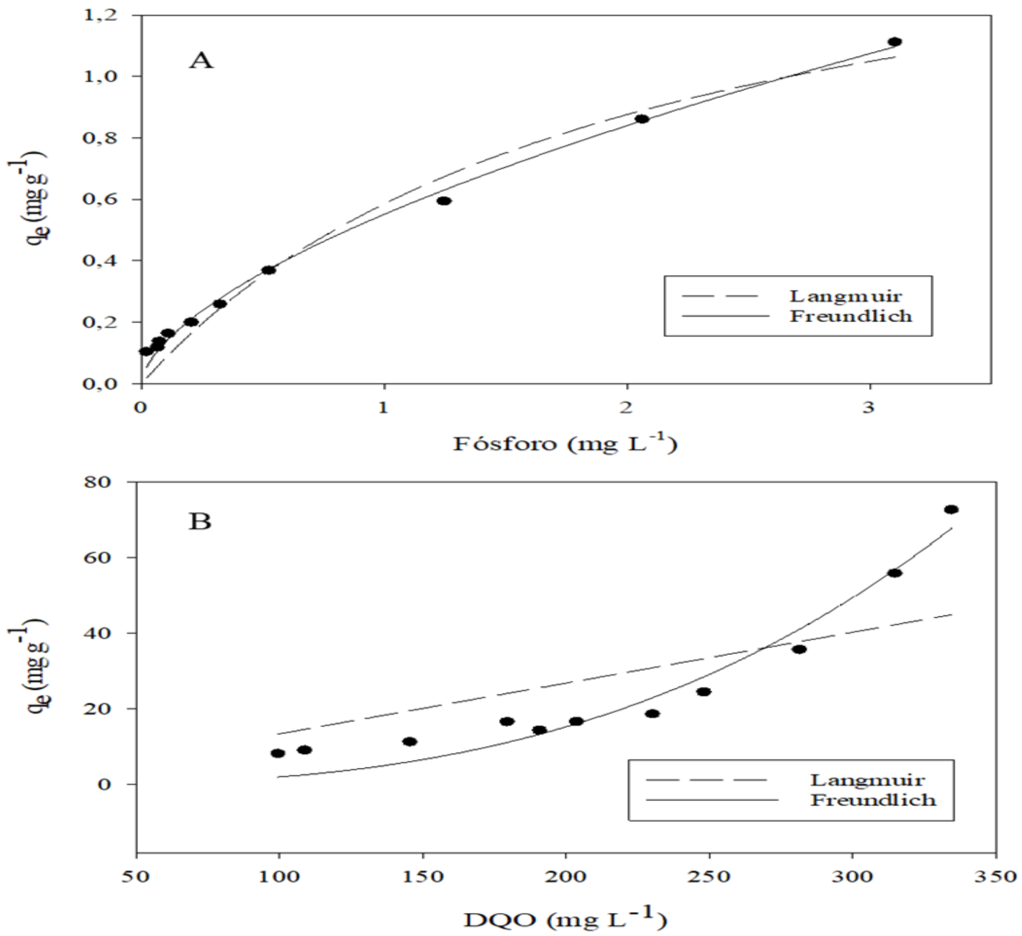

Figura 5. Modelos de isotermas ajustados na adsorção de fósforo (A) e matéria orgânica (DQO) (B) usando carvão ativado com NaOH (CANaOH).

Na Figura 5 A, pode-se observar que a isoterma para a adsorção de fósforo foi favorável. A massa do adsorbato retida por unidade de massa do adsorvente é alta para uma baixa concentração de equilíbrio do adsorbato na fase liquida (NASCIMENTO *et al.*, 2014). O ajuste com o modelo de Freundlich para a adsorção de fósforo também foi encontrado em outros estudos (JACK *et al.*, 2019; YANG *et al.*, 2020), indicando que a adsorção de fosfato pelo adsorvente foi um processo adsortivo heterogêneo (WU *et al.*, 2020). No modelo foi encontrado um valor de 1/n de 1,65. Valores de 1/n > 1 estão relacionados a uma maior afinidade do adsorvente pelo solvente, sugerindo que existe uma forte atração intermolecular entre eles dentro das camadas do adsorvente e, a uma penetração do soluto no adsorvente (DELLE-SITE, 2001). A capacidade máxima de adsorção de fósforo (q_{max}) foi de 1,74 mg g^{-1} para uma concentração inicial de fósforo de 4 mg L^{-1}, o que corresponde um 43,5% de remoção para o modelo de Langmuir. Valores similares de q_{max} (10,43 mg g^{-1}) foram encontradas por Yu *et al.* (2022) para uma concentração inicial de 20 mg L^{-1} (adsorção de um 52,15% de fosfato) usando CA a partir de lodo de fábrica de papel. Jack *et al.* (2019) determinaram uma q_{max} de 2,42 mg g^{-1} para concentrações de 16 mg L^{-1} (adsorção de 15,13% de fosfato) usando como adsorvente um biocarvão magnético (biomassa fúngica derivada de resíduos).

No caso da isoterma de adsorção para a matéria orgânica (DQO) (Figura 5B), a tendencia foi desfavorável. Isto indica que a massa de adsorbato retido por unidade de massa do adsorvente não depende da concentração de equilíbrio do adsorbato na fase liquida, e que a massa de adsorbato retida por unidade de massa do adsorvente é baixa (NASCIMENTO *et al.*, 2014). Uma baixa adsorção de matéria orgânica, pode estar relacionado ao grande tamanho de algumas moléculas orgânicas (maiores à largura dos poros), e/ou à forma dos poros dificultando a entrada das moléculas do adsorbato no interior dos microporos (MENÉNDEZ-DÍAZ; MARTÍN-GULLÓN, 2006b). Adicionalmente as isotermas desfavorável também são características de sistemas onde o adsorbato apresenta maior interação com o solvente do que com o adsorvente (NASCIMENTO *et al.*, 2014). O qual pode ser explicado pela afinidade dos complexos orgânicos hidrofílicos em permanecer na solução, em vez de serem adsorvidos pelo adsorvente (CECEN; AKTAS, 2011). A q_{max} encontrada na adsorção de matéria orgânica (DQO) foi de $1,5e^{+9}$, superior ao relatado por Oda *et al.* (2021) de $1,29e^{+7}$ mg g^{-1} usando como adsorvente lodo biológico ativado com KOH. No modelo Freundlich na adsorção de matéria orgânica (DQO), o valor de 1/n foi menor a 1 (0,35) , o que está relacionado a uma baixa afinidade entre o adsorvente e o solvente (DELLE-SITE, 2001).

4. CONCLUSÕES

Os resultados obtidos no trabalho mostram que o carvão ativado a partir de lignina kraft apresentou-se como um eficiente adsorvente de fósforo e de matéria orgânica (DQO). A eficiência de remoção de fósforo foi superior à remoção de matéria orgânica, no entanto esta última obteve remoções máximas superiores a 50%. Tanto a remoção de fósforo como a de matéria orgânica apresentaram um mecanismo de adsorção de pseudo-segunda ordem predominante, indicando que o mecanismo do processo de adsorção foi por quimissorção. O modelo que melhor se ajustou aos resultados de equilíbrio foi o modelo de Freundlich, correspondente a uma superfície do CANaOH heterogênea. O uso de CANaOH apresenta-se como uma alternativa técnica viável para o tratamento terciário de efluentes de fabricas de polpa celulósica.

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CAPITULO 4

ADSORÇÃO DE MANGANÊS POR CARVÃO ATIVADO PRODUZIDO A PARTIR DE LIGNINA KRAFT

RESUMO

Durante a etapa de branqueamento das fábricas de polpa celulósica kraft, são gerados efluentes ou filtrados ricos em metais, que podem prejudicar a qualidade da polpa além de provocar o consumo de reagentes de branqueio. O Mn contido nos filtrados representa um dos metais mais prejudiciais nesse aspecto. Existem diversos tratamentos para a remoção de Mn, entre ele o uso de carvão ativado (CA). A produção de CA a partir da lignina kraft (LK) mostra-se uma alternativa viável, embora o seu uso para a adsorção de Mn não tenha sido estudado. O objetivo desta pesquisa foi avaliar o comportamento do CA a partir de LK para a adsorção de Mn. Para se conhecer o comportamento do CA na adsorção de Mn, foram feitos testes em batelada em solução sintética, sob delineamento de superfície de resposta Box Behnken (DBB), avaliando-se três fatores, massa de CA (100, 300 e 500 mg), concentração inicial de Mn (0,1, 0,55 e 1 mg L^{-1}) e pH (4, 5 e 6), com um total 16 tratamentos. Como resultado observou-se que nos 16 tratamentos avaliados ocorreu dessorção de Mn, por parte do CA, aumentando a concentração final do elemento na solução. No estudo DBB obteve-se que o CA foi o fator com maior influência na resposta (concentração final de Mn). A liberação de Mn na solução deve-se à alta concentração do elemento tanto na LK como no CA, 65 mg kg^{-1} e 1159 mg kg^{-1} respectivamente. Desta forma, o CA não teve um comportamento adequado como agente adsorvente. Recomenda-se uma purificação da LK ou no CA final para minimizar o conteúdo de Mn no CA.

Palavras-chave: Lignina kraft, Reuso de resíduos, Carvão ativado, Tratamento setorial, Liberação de Mn.

1. INTRODUÇÃO

Na indústria de polpa celulósica kraft são gerados efluentes complexos e que possuem uma alta carga orgânica, que são direcionados à estação de tratamentos de efluentes (ETE). Entre os fluxos líquidos que compõem o efluente bruto final encontram-se aqueles gerados na etapa de branqueamento da polpa. Estes filtrados são responsáveis por mais de 60% do volume dos efluentes, além de possuir a maior carga orgânica (SUHR *et al.*, 2015). Os filtrados do branqueamento são de caráter ácido (estágios ácidos) e alcalino (estágios alcalinos) e são gerados após a lavagem da polpa em cada estágio do branqueamento. Os filtrados são utilizados na lavagem do estágio anterior, em um modo de contra lavagem, obedecendo o pH, buscando a economia de água fresca.

Os filtrados obtido após as lavagens possuem compostos químicos que podem impactar negativamente os processos de deslignificação no branqueamento. Dentre os problemas tem-se o maior consumo de reagentes químicos, as propriedades óticas e físicas da polpa, o aumento da cor e a alta demanda química e bioquímica de oxigênio (DQO e DBO) do efluente bruto final. Os filtrados são constituídos principalmente por material suspenso e dissolvido.

A fração inorgânica está constituída por elementos como cálcio, magnésio, potássio e silício, e em menor concentração manganês, ferro, alumínio, cobre e bário provenientes da matéria prima (FREDDO *et al.*, 1999). Íons metálicos de transição podem ser retidos na polpa devido á complexação com grupos carboxilas, entre eles Fe^{2+}, Fe^{3+}, Cu^{2+} e Mn^{2+}, os quais estão associados a processos de reversão de alvura (COLODETTE; GOMES, 2015). No entanto, uma parte dos metais são removidos durante os estágios ácidos no branqueamento seguem nos filtrados.

Metais de transição como o Mn, Fe e Cu (provenientes maioritariamente da madeira), interferem com a decomposição catalítica dos produtos químicos a base de oxigênio durante os processos de branqueamento da celulose (NORKUS; VAIČIUNIENE; VUORINEN, 2006). O peróxido de hidrogênio é o reagente de branqueamento mais influenciado pela ação destes metais de transição, em especial o manganês. O Mn decompõe de forma rápida o peroxido em condições alcalinas, além de aumentar a degradação das cadeias de carboidratos na polpa. Este fato é explicado uma vez que o Mn catalisa a formação do radical hidroxila (OH^-), que ataca as cadeias de celulose e lignina (COLODETTE; GOMES, 2015; JEMAA *et al.*, 1999). Desta forma a remoção de Mn nos filtrados, beneficia a qualidade do papel, fornece uma maior economia na produção de polpa celulósica, além de diminuir os problemas de corrosão, incrustações e entupimentos nos equipamentos (FREDDO *et al.*, 1999).

O tratamento setorial destes filtrados pode permitir o fechamento de circuitos de água no branqueamento e, consequentemente diminuir a carga orgânica e o volume do efluente bruto final a ser tratado (QUEZADA *et al.*, 2014). Entre os diversos tipos de tratamentos de efluentes para remoção de metais, o tratamento escolhido neste trabalho foi por carvão ativado (CA). O uso de CA vislumbra-se uma alternativa eficiente na remoção de metais e muito avaliada por pesquisadores (GUO; ZHANG; SHAN, 2008; MALDHURE; EKHE, 2011; MOHAN; PITTMAN; STEELE, 2006; ŠĆIBAN; KLAŠNJA; ANTOV, 2011; SCIBAN; KLASNJA, 2004). Na literatura existem inúmeras investigações que estudam a remoção de Mn usando adsorventes, as quais estão resumidas na pesquisa de Patil *et al.* (2016). Não foi encontrado nenhum artigo que avaliasse a remoção de Mn usando CA a partir de LK.

O objetivo do trabalho foi avaliar o uso e comportamento de carvão ativado a partir de lignina kraft para a adsorção de manganês. O estudo foi feito segundo delineamento experimental de superfície de resposta Box Behnken (DBB), usando como fatores independentes o pH, concentração inicial de manganês e massa de carvão ativado, para determinar sua influência na adsorção de Mn.

2. MATERIAIS E MÉTODOS

2.1. Materiais

O carvão ativado utilizado para o estudo foi o mesmo produzido no Capitulo 2 da tese. Os testes de adsorção de Mn foram feitos usando uma solução padrão de 1000 mg L^{-1} de cloreto de magnésio ($MnCl_2$ em H_2O) marca Merck KgaA. A solução estoque de Mn para cada uma das concentrações avaliadas, a solução (água + ácido clorídrico) para cada uns dos pHs avaliados, e as amostras check foram feitas com água ultra pura, para garantir a pureza das soluções.

2.2. Testes de adsorção

Os testes de adsorção foram em batelada usando tubos Falcon de polipropileno de 50 mL (capacidade máxima) e agitados em mesa agitadora a 150 rpm durante 24 h. Os testes foram feitos segundo DBB para determinar a condição ideal onde ocorre a maior adsorção de Mn. Os fatores ou variáveis independentes avaliadas foram o pH, concentração inicial de manganês e massa de carvão ativado e como fator ou variável dependente a concentração final de Mn. A seleção dos fatores para análise foram escolhidos segundo a literatura (FURLAN *et al.*, 2018; MESHRAM; GUNJATE; KHOPE, 2020; OMRI; BENZINA, 2012; SIABI *et al.*, 2021). Os níveis dos fatores analisados foram 4, 5 e 6 para pH; 0,1, 0,55 e 1 mg L^{-1} para concentrações inicias de Mn e 100, 300 e 500 mg para massa de CANaOH. As concentrações iniciais de Mn e pH foram selecionadas sob prévio análise no software MINTEQ2®, para garantir que as concentrações escolhidas não causaram a precipitação de óxidos ou hidróxidos. Análise de capacidade de troca catiônica (CTC) foi realizada para conhecer a concentração dos elementos químicos na superfície do CANaOH disponíveis para intercambio catiônico, em especial o Mn.

Segundo a concentração de Mn para intercambio catiônico (mg kg^{-1}) foi determinado as massas de CANaOH utilizadas nos testes de adsorção.

Em cada tubo Falcon era adicionado uma quantidade de massa de CANaOH, a solução base a determinado pH e a solução de Mn segundo a combinação dos fatores apresentados na Tabela 1.

Tabela 1. Combinação dos fatores e os níveis avaliados do delineamento Box Behnken.

Tratamento	pH	Massa CANaOH (mg)	Concentração inicial Mn (mg L^{-1})
1	4	100	0,55
2	6	100	0,55
3	4	500	0,55
4	6	500	0,55
5	4	300	0,1
6	6	300	0,1
7	4	300	1
8	6	300	1
9	5	100	0,1
10	5	500	0,1
11	5	100	1
12	5	500	1
13	5	300	0,55
14	5	300	0,55
15	5	300	0,55
16	5	300	0,55

Cada uma das alíquotas das soluções de Mn colocadas no tubo Falcon para os 16 tratamentos foram calculadas baseadas no volume final de 40 mL e na concentração inicial de Mn a avaliar. Para chegar à faixa de concentração avaliadas, foi feita uma solução estoque intermediaria de Mn (mg L^{-1}), diluindo-se 100 vezes o padrão original. No caso da solução estoque com pH desejado foi feita diluindo HCl em água ultrapura, e mensurado por medidor de pH da Marconi, com precisão de 0,01.

Após transcorrido o tempo de 24 h cada tratamento foi filtrado com membranas Whatman 40 e uma alíquota de cada tratamento foi armazenado para posterior leitura.

2.3. Análise de espectrofotometria

A determinação da concentração final de Mn para cada uns dos tratamentos avaliados foi feita por espectrometria de emissão ótica com plasma indutivamente acoplado (ICP-OES), usando um espectrômetro da marca Perkin Elmer, modelo Optima DV 7300. Adicionalmente foram analisadas amostras check e brancos para conferir as concentrações iniciais e a pureza das soluções do ajuste de pH.

2.4. Delineamento de superfície de resposta Box Behnken

O delineamento de superfície de resposta Box Behnken foi escolhido por demandar um menor número de experimentos resultando em um menor gasto de reagentes e um menor tempo de trabalho. Este tipo de método permite o desenvolvimento de modelos matemáticos de superfície de resposta de primeira ou segunda ordem com os melhores ajustes. Também proporciona o conjunto ótimo dos parâmetros experimentais que produzem o valor máximo ou mínimo de resposta; representando os efeitos dos parâmetros ou fatores do processo por meio de gráficos bidimensionais e tridimensionais. O número de experimentos necessários para o desenvolvimento do DBB foi definido de acordo com a Equação 1 (FERREIRA *et al.*, 2007).

$$N = 2k\ (k - 1) + C_o \qquad (1)$$

Onde N é o número de experimentos necessários para o desenvolvimento do DBB; k é o número de fatores e C_o é o número de pontos centrais.

Ao ser três os fatores selecionados e realizadas quatro repetições no ponto central no DBB o número total de tratamentos foram 16. A resposta ou variável dependente foi expressa como a concentração final de Mn. Os resultados foram analisados considerando a análise de variância (ANOVA) e gráficos de superfície de resposta através do software Minitab® 18.

3. RESULTADOS E DISCUSSÕES

Para praticidade e entendimento da dessorção do Mn que ocorreu nos testes de adsorção os resultados da concentração de metais e capacidade de troca catiônica (CTC) da LK e do CANaOH são apresentados na Tabela 2.

Tabela 2. Concentração de metais e capacidade de troca catiônica (CTC) da lignina kraft (LK) e carvão ativado com NaOH (CANaOH).

Amostra	Concentração (mg kg^{-1})							
	S	Na	Zn	Ni	Cu	Fe	Mn	Cr
LK	13948	2054	4,0	nd	0,7	144	65	5.9
CANaOH	2488	5760	84	5587	101	26451	1159	9688

Amostra	CTC, T (cmol$_c$kg^{-1})	Cátions para intercambio (mg kg^{-1})						
		Na	K	P	Zn	Cu	Fe	Mn
LK	-	-	-	-	-	-	-	-
CANaOH	52,4	3320	200	2	57	8,6	18700	327

O poder de adsorção de metais depende principalmente da capacidade de troca catiônica e da química superficial favorável do adsorvente (SMITH *et al.*, 2009). Segundo Tag *et al.* (2016) a CTC pode ser altamente variável dependendo da matéria prima e de suas condições de pirolise. Os autores relataram que obtiveram uma CTC de 81,23 cmol$_c$kg^{-1}, quando a temperatura de pirolise na produção do bioadsorvente foi de 250 ºC, e uma diminuição para 49,80 cmol$_c$kg^{-1} quando a temperatura aumento a 600 ºC. O valor obtido na CTC do CANaOH foi de 52,4 cmol$_c$kg^{-1}, superior ao encontrado pelos autores a uma temperatura de 700 ºC (temperatura de ativação). Tag *et al.* (2016) relatam que a diminuição da CTC ocorreu pela remoção de grupos funcionais da superfície do CA e à formação de carbono aromático. Outros estudos também concordam com as variações da CTC pelo incremento da temperatura (CELY *et al.*, 2015; SONG; GUO, 2012). O valor da CTC encontrada no CANaOH vislumbra que o adsorvente pode ter certa capacidade de intercambio de cátions. Adicionalmente pode-se observar na Tabela 2 que o Mn possui uma fração importante (327 mg kg^{-1}) que está disponível para intercambio na superfície do adsorvente.

Em relação à concentração de metais no CANaOH foi notavelmente alta para Fe (26.451 mg kg^{-1}), Cr (9.688 mg kg^{-1}), Ni (5.587 mg kg^{-1}) e Mn (1.159 mg kg^{-1}). O incremento na concentração destes metais da LK para o CANaOH pode ser atribuído à reação entre os metais e o oxigênio contido no CANaOH. Estas reações podem ter formado óxidos como oxido ferroso, oxido de cromo, oxido de níquel e oxido de manganês, com ponto de fusão >1000ºC e insolubilidade em água; portanto não foi possível sua remoção durante a etapa de lavagem do carvão ativado. Adicionalmente, o incremento de metais também pode estar associado a uma possível corrosão do reator durante a ativação do CA com o NaOH, e às sais residuais deste reagente após ativação.

3.1. Teste de adsorção de Mn

O resultado dos testes de adsorção segundo a combinação das variáveis pH, massa de CANaOH e concentração inicial de Mn gerado pelo DBB são apresentados na Tabela 3.

Tabela 3. Concentração final de Mn e recuperação para cada um dos tratamentos avaliados.

Número	pH	Massa CANaOH (mg)	Concentração inicial Mn (mg L^{-1})	Concentração final Mn (mg L^{-1})	Recuperação (%)
1	4	100	0,55	1,02	186
2	6	100	0,55	1,02	185
3	4	500	0,55	3,43	623
4	6	500	0,55	2,78	505
5	4	300	0,1	1,34	1343
6	6	300	0,1	1,58	1575
7	4	300	1	2,21	221
8	6	300	1	2,27	227
9	5	100	0,1	0,52	520
10	5	500	0,1	3,19	3188
11	5	100	1	1,29	129
12	5	500	1	3,07	307
13	5	300	0,55	1,66	302
14	5	300	0,55	1,94	353
15	5	300	0,55	1,78	324
16	5	300	0,55	1,81	329

Segundo Tabela 3 torna-se evidente que existe uma maior concentração final de Mn na solução do que a concentração inicial avaliada. O excedente de Mn na solução foi quantificado como recuperação (%), termo relacionado com a quantidade de determinado analito recuperado no processo, em relação à quantidade real presente na amostra. Possíveis interferências nos resultados foram descartadas após análise dos brancos e das amostras referências. Os resultados mostraram que em concentrações iniciais de Mn de 0,1 mg L^{-1} e massas de CANaOH de 300 e 500 mg, ocorreram os maiores percentuais de recuperação de Mn (entre 1343% até 3188% respectivamente). Em concentrações iniciais de Mn maiores (1 mg L^{-1}) e nas mesmas massas de 300 mg e 500 mg, ocorreram uma recuperação entre 221% e 307% respectivamente, as duas situações em valores de pH distintos. Para uma massa de CANaOH de 100 mg e concentrações inicias de Mn de 0,55 mg L^{-1} obteve uma recuperação de 186% e 185% para um pH de 4 e 6 respectivamente. A menor recuperação obtida foi de 129%, para uma massa de CANaOH de 100 mg, concentração inicial de Mn de 1 mg L^{-1} e pH de 5.

Em geral, pode-se dizer que quanto menores massas de CANaOH foram avaliadas, menor foi a taxa de recuperação de Mn, é dizer uma menor dessorção de Mn ocorreu. A liberação de Mn pode ser influenciada pelo alto conteúdo do elemento no CANaOH 1159 mg kg^{-1}, dos quais 327 mg kg^{-1} se encontram na superfície do adsorvente para intercambio de cátions. O Mn no CANaOH pode estar na forma de óxidos, de sulfetos e de sulfatos. A formação de sulfetos é possível pela reação entre o enxofre remanescente e o Mn contido na LK e/ou no CANaOH (SHELTON; LONG, 2003). A presença de enxofre na LK é devido ao uso de Na_2S como agente deslignificante da madeira. Segundo Rose *et al.* (2003) o Mn é relativamente solúvel na forma de sulfatos ($MnSO_4$), pelo menos até um pH de 8. Os autores também indicam que a maior parte das formas solúveis de Mn encontra-se no estado de oxidação 2+. Caso contrário do Mn com estado de oxidação 3+ e 4+ que são praticamente insolúveis na forma de MnO_2, Mn_2O_3, Mn_3O_4 e $MnCO_3$. Assim a possível presencia de Mn^{2+} e de $MnSO_4$ no CANaOH podem ter ocasionado a solubilidade do elemento em meio ácido (pH 4-5-6).

3.2. Delineamento de superfície de resposta Box Behnken

No resultado do DBB a massa do CANaOH foi o fator mais significativo no processo de adsorção, verificado no gráfico de Pareto (Figura 1), com um valor de 15,52 dos efeitos padronizados, enquanto o pH foi o único termo linear não significativo.

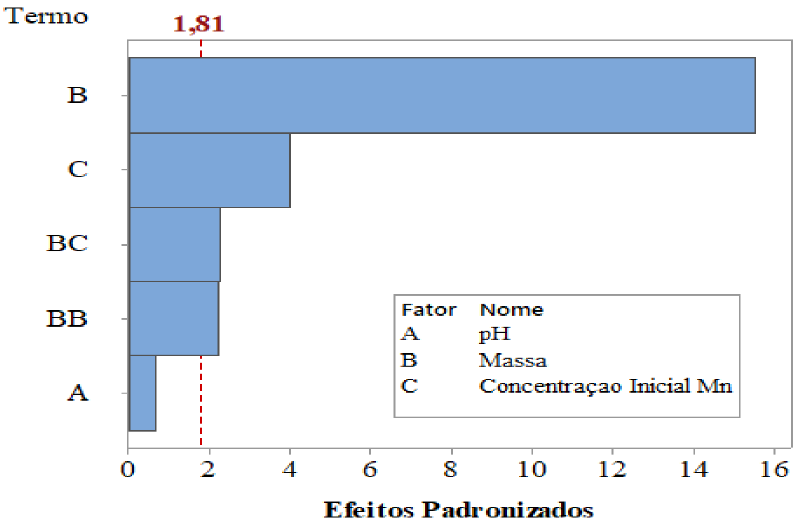

Figura 1. Análise de Pareto dos efeitos padronizados, tendo como resposta concentração final de Mn; $P < 0,1$.

Na Tabela 4 apresenta-se os coeficientes do modelo matemático estimado pelo software, o erro padrão dos coeficientes, o Valor F e as significâncias de cada coeficiente da regressão através do Valor-P. O valor de significância adotado no estudo foi de 10%. Só os coeficientes estatisticamente significativos ($P<0,1$) foram considerados para o modelo matemático; com a exceção do coeficiente do pH por ser um termo linear. Os termos quadráticos e suas interações não significativos (da ANOVA gerada pelo software) foram descartados. Assim verificou-se que as variáveis independentes massa CANaOH (X_2), concentração inicial de Mn (X_3), a variável quadrática de X_2^2 e a interação X_2*X_3 foram estatisticamente significativas. Material suplementar do modelo apresenta-se no Anexo 3.

Tabela 4. ANOVA dos fatores "massa de CANaOH", "concentração inicial de Mn", "pH" e suas interações para a resposta "concentração final de Mn".

Resposta	Fatores	Coeficiente	Erro Padrão Coeficiente	Valor F	Valor-P
Concentração final Mn	Intercepto	1,823	0,069	53,44	0,000
	X_1	-0,047	0,069	0,45	0,516
	X_2	1,076	0,069	240,84	0,000
	X_3	0,276	0,069	15,88	0,003
	X_2^2	0,216	0,098	4,87	0,052
	X_2*X_3	-0,223	0,098	5,15	0,047

X_1 = pH; X_2 = Massa CANaOH; X_3 = Concentração inicial Mn

O grande predomínio da massa do CANaOH influencia diretamente (valor positivo do coeficiente) na concentração final de Mn, quanto maiores os seus níveis, maior será a concentração final de Mn na solução. Por outro lado, a grande ação exercida pela massa do CANaOH pode ter encoberto a influência do pH, fazendo dele um fator não significativo com um Valor-P de 0,516. O modelo matemático que descreve a resposta apresentou um R^2 de 96,4%, enquanto o Valor-P para o mesmo foi de $1,0e^{-6}$, confirmando sua significância estadística ($P<0,10$).

As condições ótimas do processo, foram determinados pelo software obtendo como os níveis ótimos, o valor de 6 para pH, 100 mg para a massa de CANaOH e 0,1 mg L^{-1} para a concentração inicial de Mn. Cabe destacar que mesmo com condições ótimas a concentração final (teórica) foi de 0,4179 mg L^{-1}, ainda superior à concentração inicial de Mn adotada.

No gráfico de contorno e superfície de resposta, Figura 2A e 2B respectivamente, é possível visualizar rapidamente as condições ótimas, fixando-se o pH em 6. Em este cenário observa-se que nas menores massas de CANaOH (100 mg), e nas menores concentrações inicias (0,1 mg L^{-1}) se obtém as concentrações finais de Mn mais baixas (concentração Mn<0,5).

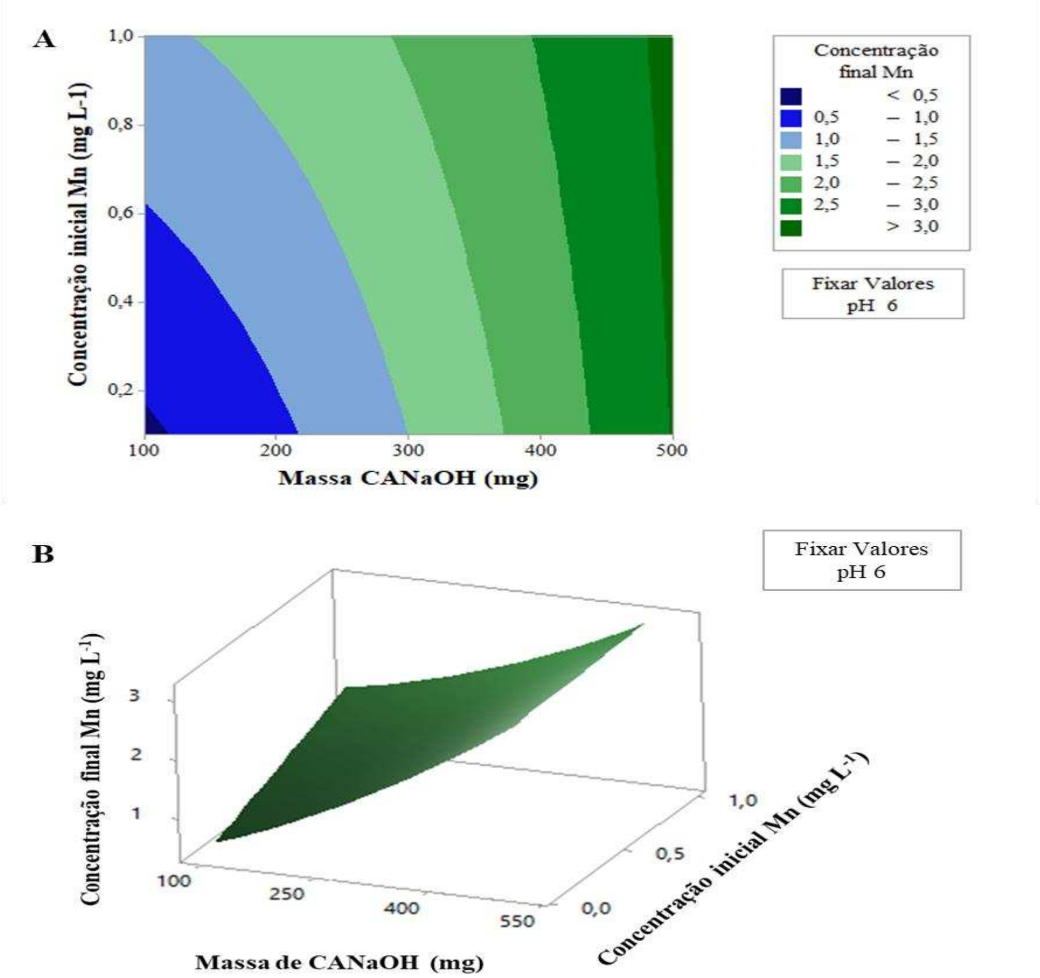

Figura 2. Analise de contorno (A) e de superfície de resposta (B) avaliando massa de CANaOH versus concentração inicial de Mn a um pH fixo de 6.

Na Figura 3 avaliou-se a massa de CANaOH versus pH a uma concentração fixa de 1 mg L^{-1}. Aqui pode-se visualizar facilmente que a massa do CANaOH pode estar camuflando o verdadeiro efeito do pH. Neste caso, foi possível observar que para uma massa de 100 mg de CANaOH, quanto mais perto de 6 está o pH menor será a concentração final de Mn. Este fato tem relação ao relatado por Rose *et al.* (2003), ao indicar que em pHs mais ácidos maior é a solubilidade do Mn, é dizer uma maior fração de Mn contido no CANaOH poderia ser dessorvido na solução.

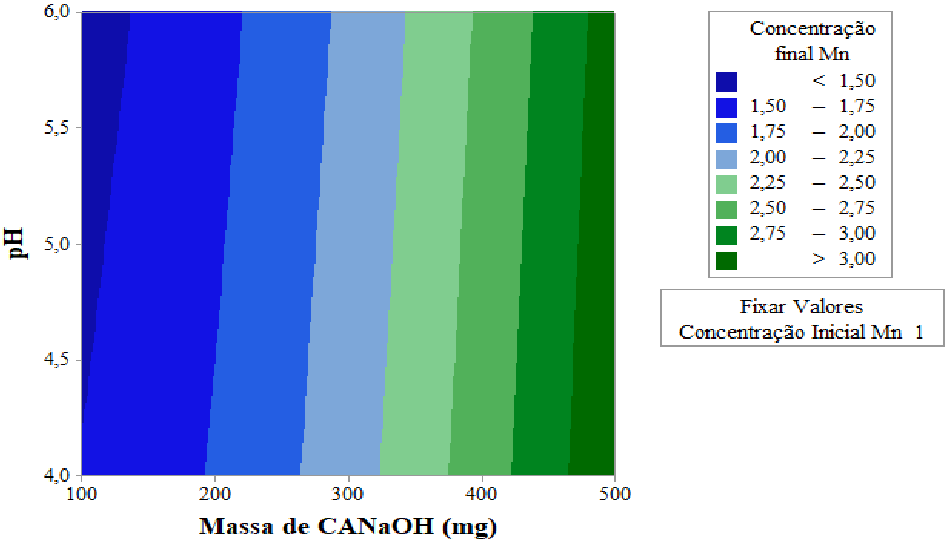

Figura 3. Gráfico de contorno avaliando massa de CANaOH versus pH, a uma concentração inicial de Mn de 1 mg L^{-1}.

A inexistente capacidade de adsorção de Mn por parte do carvão ativado produzido, e a alta influência da massa do CANaOH durante o processo de adsorção, determinado pela análise do DBB, indica que o alto conteúdo de metais no carvão ativado afetou diretamente a adsorção do elemento. Recomenda-se estudar a viabilidade, econômica e ambiental, da aplicação de pré-tratamentos à lignina kraft ou no CA final (antes de seu uso) para a diminuição do material inorgânico (metais). Pré-tratamentos como a desmineralização da lignina com H_2SO_4, permite a redução de compostos inorgânicos (CASTRO-DÍAZ *et al.*, 2019). No entanto, a desmineralização da lignina pode ser prejudicial para a obtenção de adsorventes eficientes (FIERRO *et al.*, 2007). Sharma *et al.* (2004) indicaram que a remoção parcial de sódio e potássio da lignina, catalisou sua pirolise prejudicando o rendimento do carvão. Fierro *et al.* (2007) também relataram que a desmineralização da lignina pode ser prejudicial (para a adsorção de corantes como azul de metileno), portanto sugerem que a desmineralização seja no CA e não no precursor. Karaca, Gurses e Bayrak (2004) observaram que a diminuição na eficiência de remoção de azul de metileno (em amostras desmineralizadas), está relacionada à remoção de minerais silicatados os quais permitem interações eletrostáticas entre íons silicato e íons adsorvato. Outro tipo de tratamento utilizado para a remoção de cátions é a lavagem acida do CA. Esta alternativa pode remover os cátions solúveis, através do intercambio de H$^+$ pelos cátions trocáveis, embora isto pode levar à acidificação das soluções finais (MÉNDEZ; GASCÓ, 2005).

4. CONCLUSÕES

O uso de carvão ativado a partir de lignina kraft para a adsorção de Mn não apresentou qualquer capacidade de adsorção do elemento. O alto conteúdo de Mn presente no carvão ativado afetou negativamente o processo de adsorção desse elemento, e ao contrário provocou a sua dessorção na solução. Uma prévia purificação da lignina kraft ou no carvão ativado final, para remoção de Mn se torna necessária para tornar o CANaOH adequado para a adsorção de metais.

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CONCLUSÕES E RECOMENDAÇÕES FINAIS

A precipitação da lignina kraft contida no licor preto para a produção de carvão ativado representou uma alternativa atrativa, ao obter um produto de alto valor agregado dentro do conceito de biorrefinaria. Ao mesmo tempo, a produção e utilização do carvão ativado dentro de uma fábrica de polpa celulósica, oferece vantagens econômicas, operacionais e ambientais.

O carvão ativado produzido a partir de lignina kraft obteve boas características físico-químicas que estão dentro dos padrões atribuídos aos adsorventes, embora tenha apresentado um alto teor de material inorgânico (cinzas), constituído principalmente por metais pesados. A presença destes metais provem da lignina, que após produção do carvão ativado foi incrementada consideravelmente. De esta forma, no intento de minimizar a concentração dos metais no carvão ativado, uma desmineralização da lignina como pré-tratamento pode ser adotada em estudos futuros.

O emprego do carvão ativado como tratamento terciário apresentou resultados satisfatórios, com eficiências de remoção de até 88% para fósforo e eficiências superiores a 50% para matéria orgânica (DQO). O adsorvente produzido mostrou a grande capacidade de remover concentrações de fósforo superiores às encontradas normalmente nos efluentes finais da indústria de polpa celulósica. Recomenda-se que sejam desenvolvidos estudos onde se avalie o uso de carvão ativado dentro do tratamento biológico sem necessidade de construção de novas unidades de tratamento.

O uso do carvão ativado na adsorção de Mn não apresentou bons resultados nos 16 tratamentos avaliados, por ter ocorrido dessorção de Mn no meio. Segundo a análise do delineamento de superfície de resposta Box Behnken, o fator mais influente, avaliado no processo, foi a massa de carvão ativado. Na otimização do modelo observa-se que enquanto menor for a massa de carvão ativado, menor concentração inicial de Mn e em pH de 6, menor será a concentração final de Mn na solução, ou seja, maior será a remoção do elemento.

ANEXOS

Anexo 1. Material suplementar do artigo 2.

Tabela S1. Análise de Variância no analise MEV-EDS para lignina kraft.

Fonte	GL	SQ (Aj.)	QM (Aj.)	Valor F	Valor-P
Elemento químico	11	42151,8	3831,98	61838,18	0,000
Erro	89	5,5	0,06		
Total	100	42157,3			

Tabela S2. Análise de Variância no analise MEV-EDS para carvão da lignina kraft.

Fonte	GL	SQ (Aj.)	QM (Aj.)	Valor F	Valor-P
Elemento químico	11	34100,3	3100,03	1376,15	0,000
Erro	82	184,7	2,25		
Total	93	34285,1			

Tabela S3. Análise de Variância no analise MEV-EDS para carvão ativado com NaOH.

Fonte	GL	SQ (Aj.)	QM (Aj.)	Valor F	Valor-P
Elemento químico	11	14710,0	1337,27	812,36	0,000
Erro	85	139,9	1,65		
Total	96	14849,9			

Anexo 2. Material suplementar do artigo 3.

Tabela S1. Delineamento experimental para os testes de adsorção de fósforo total.

Tratamentos	Fatores	
	Massa CANaOH (g)	Concentração Fósforo (mg L^{-1})
1	0	0,27
2		2
3		4
4		6
5		8
6	0,1	0,27
7		2
8		4
9		6
10		8
11	0,5	0,27
12		2
13		4
14		6
15		8
16	1	0,27
17		2
18		4
19		6
20		8
21	1,5	0,27
22		2
23		4
24		6
25		8

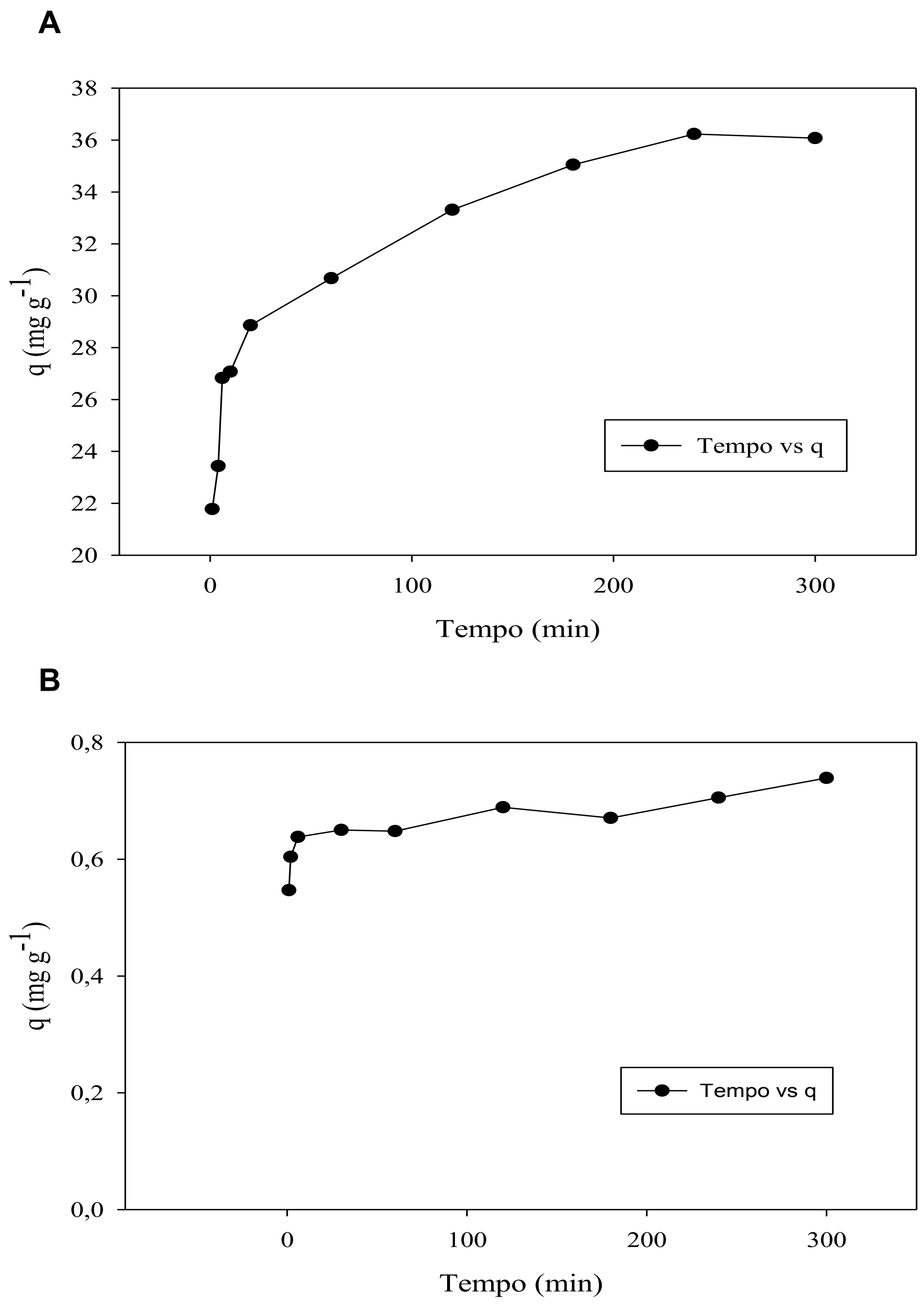

Figura S1. Curvas de cinética de adsorção de fósforo (A) e matéria orgânica (DQO) (B).

Anexo 3. Material suplementar do artigo 4.

Tabela S1. ANOVA do delineamento Box Behnken (DBB).

Fonte	GL	SQ (Aj)	QM (Aj)	Valor F	Valor-P
Modelo	5	10.27	2.05	53.44	0.000
Linear	3	9.89	3.30	85.72	0.000
pH	1	0.02	0.02	0.45	0.516
Massa CANaOH	1	9.26	9.26	240.84	0.000
Concentração inicial Mn	1	0.61	0.61	15.88	0.003
Quadrado	1	0.19	0.19	4.87	0.052
Massa*Massa	1	0.19	0.19	4.87	0.052
Interações com 2 fatores	1	0.20	0.20	5.15	0.047
Massa*Concentração inicial Mn	1	0.20	0.20	5.15	0.047
Erro	10	0.38	0.04		
Falta de ajuste	7	0.34	0.05	3.65	0.157
Erro puro	3	0.04	0.01		
Total	15	10.66			

Tabela S2. Sumário do Modelo.

S	R2	R2(aj)	R2(pred)
0,196085	96,39%	94,59%	88,81%

Tabela S3. Coeficientes codificados do modelo DBB.

Termo	Coef	EP de Coef	Valor-T	Valor-P	VIF
Constante	1,8228	0,0693	26,29	0,000	
pH	-0,0466	0,0693	-0,67	0,516	1,00
Massa CANaOH	1,0759	0,0693	15,52	0,000	1,00
Concentração Inicial Mn	0,2762	0,0693	3,98	0,003	1,00
Massa*Massa	0,2163	0,0980	2,21	0,052	1,00
Massa*Concentração Inicial Mn	-0,2225	0,0980	-2,27	0,047	1,00

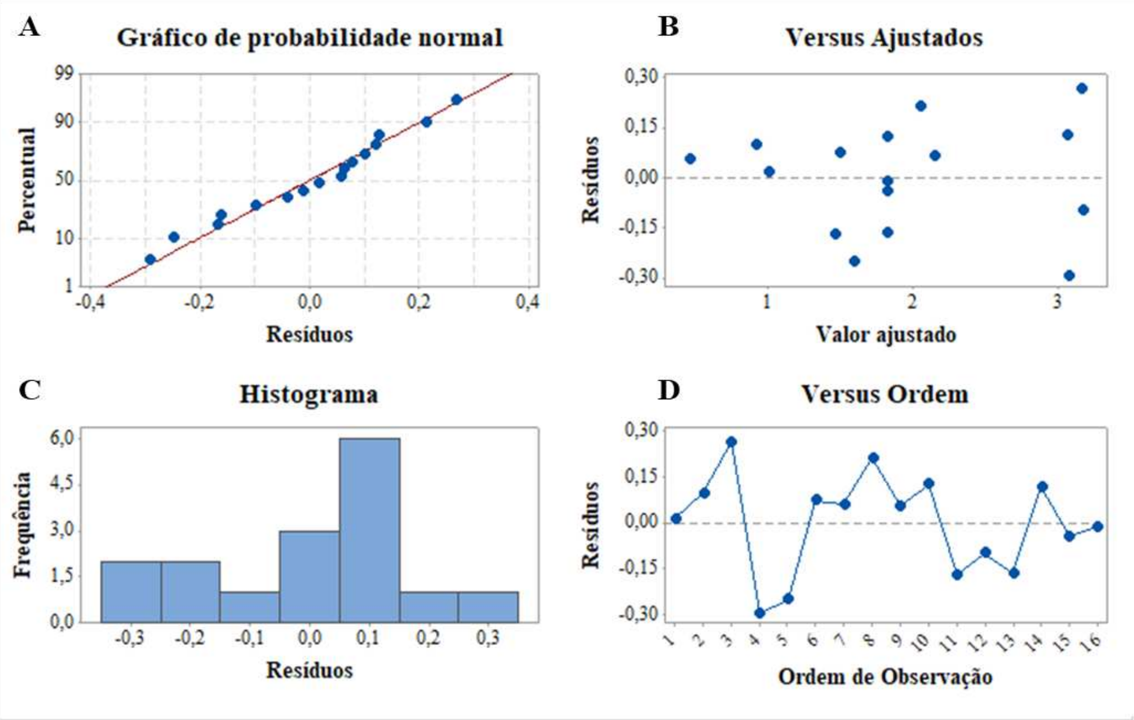

Figura S1. Gráficos de resíduos: gráfico de probabilidade normal (A), resíduos versus valores ajustados (B), histograma (C), resíduos versus ordem (D).

Equação S1. Equação de Regressão do modelo, em Unidades Não codificadas gerado pelo software.

Concentração final Mn = 0,183 - 0,0466 pH + 0,00349 Massa + 1,356 Concentração Inicial Mn + 0,000005 Massa*Massa - 0,00247 Massa*Concentração Inicial Mn

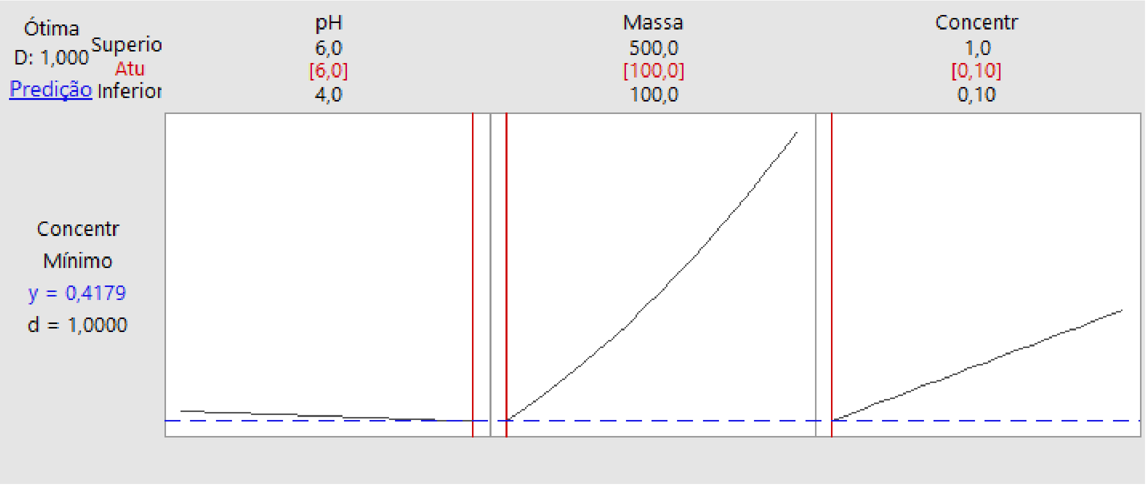

Figura S2. Gráfico de otimização do DBB.