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Paola Rosiane Teixeira Hernandes

**ADSORÇÃO DE HERBICIDAS UTILIZANDO BIOCHAR OBTIDO
A PARTIR DE RESÍDUOS DE MADEIRA**

Santa Maria, RS
2022

Paola Rosiane Teixeira Hernandes

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Dissertação apresentada ao Curso de Pós-Graduação em Engenharia Química, da Universidade Federal de Santa Maria (UFSM, RS), como requisito parcial para obtenção do título de **Mestre em Engenharia Química**.

Orientador: Prof. Dr. Guilherme Luiz Dotto

Coorientadora: Prof^a. Dr^a. Nina Paula Gonçalves Salau

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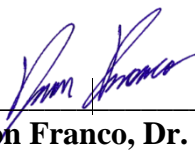
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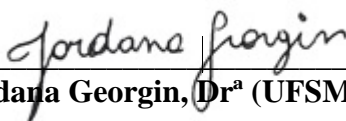
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“Por vezes sentimos que aquilo que fazemos não é senão uma gota de água no mar.

Mas o mar seria menor se lhe faltasse uma gota”.

(MADRE TERESA DE CALCUTÁ)

RESUMO

ADSORÇÃO DE HERBICIDAS UTILIZANDO BIOCHAR OBTIDO A PARTIR DE RESÍDUOS DE MADEIRA

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ORIENTADOR: Prof. Dr. Guilherme Luiz Dotto
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Resíduos de serragem da espécie florestal *Cedrela fissilis* foram modificados, sendo que uma parte da amostra foi modificada apenas fisicamente (BCC), enquanto a outra sofreu também ativação química com cloreto de zinco ($ZnCl_2$) como agente ativador (BACB). O material precursor a serragem de cedro (CBS), assim como BCC e BACB foram caracterizados pelas técnicas de Difração de Raios-X (DRX), Espectroscopia no Infravermelho por Transformada de Fourier (FT-IR), Microscopia Eletrônica de Varredura (MEV), Espectroscopia de Raios-X por Energia Dispersiva (EDS), Ponto de Carga Zero (pH_{pZC}), Isotermas de Adsorção/Dessorção de N_2 (métodos BET e BJH); e tiveram seu potencial avaliado para remoção dos herbicidas atrazina e 2,4-D de efluentes. Testes iniciais indicaram que nenhum dos adsorventes foi eficiente na remoção do 2,4-D, no entanto, demonstraram potencial na remoção da atrazina. Sendo que BCC apresentou desempenho relativamente superior a BACB. Sendo assim, o BCC foi o adsorvente escolhido para dar seguimento nos estudos cinéticos, isotérmicos e termodinâmicos, bem como do efeito do pH, do efluente simulado e de regeneração do material para adsorção do herbicida atrazina. O teste de pH indicou que os melhores resultados de adsorção foram obtidos sob pH 4. Os estudos isotérmicos comprovaram que o processo de adsorção da atrazina foi favorecido em temperaturas mais elevadas. O modelo de Langmuir foi o mais adequado aos dados de equilíbrio experimental, a capacidade máxima de adsorção foi de $7,679 \text{ mg g}^{-1}$ a 328 K. Os parâmetros termodinâmicos confirmaram um processo espontâneo, de natureza endotérmica governado por interações físicas. Estudos cinéticos mostraram que o equilíbrio foi alcançado em 180 min, sendo influenciado pela concentração de atrazina. O modelo de força motriz linear (LDF) apresentou bom ajuste estatístico aos dados experimentais, e o coeficiente de difusão aumentou com a concentração de adsorbato. Quanto à regeneração, o BCC pode ser reutilizado em até três ciclos. Por fim, o adsorvente apresentou boa eficiência de remoção em amostras reais de água de rios contaminados com atrazina, com remoção de 76,58% e 71,29%. Portanto o adsorvente apresenta potencial e pode ser utilizado para remoção de poluentes emergentes de soluções aquosas.

Palavras –chaves: Adsorção, Atrazina, Biocarvão, Regeneração

ABSTRACT

ADSORPTION OF HERBICIDES USING BIOCHAR OBTAINED FROM WOOD WASTE

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ADVISOR: Dr. Guilherme Luiz Dotto
CO-ADVISOR: Dr^a Nina Paula Gonçalves Salau

Residues of sawdust of the forest species *Cedrela fissilis* were modified, with a part of the sample being only physically modified (BCC), while the other was also chemically activated with zinc chloride ($ZnCl_2$) as an activating agent (BACB). The precursor material to cedar sawdust (CBS), as well as BCC and BACB were characterized by the techniques of X-Ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FT-IR), Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Spectroscopy (EDS), Point of Zero Charge (pHPZC), N₂ Adsorption/Desorption Isotherms (BET and BJH methods); and had their potential evaluated for the removal of atrazine and 2,4-D herbicides from effluents. Initial tests indicated that none of the adsorbents were efficient in removing 2,4-D, however, they showed potential in removing atrazine. Since BCC performed relatively better than BACB. Therefore, BCC was the adsorbent chosen to carry out kinetic, isothermal, and thermodynamic studies, as well as the effect of pH, simulated effluent, and material regeneration for atrazine herbicide adsorption. The pH test indicated that the best adsorption results were obtained at pH 4. The isothermal studies proved that the atrazine adsorption process was favored at higher temperatures. The Langmuir model was the most suitable for experimental equilibrium data, the maximum adsorption capacity was 7.679 mg g^{-1} at 328 K. The thermodynamic parameters confirmed a spontaneous process, of an endothermic nature, governed by physical interactions. Kinetic studies showed that equilibrium was reached within 180 min, being influenced by the atrazine concentration. The linear driving force (LDF) model showed a good statistical fit to the experimental data, and the diffusion coefficient increased with the adsorbate concentration. As for regeneration, the BCC can be reused in up to three cycles. Finally, the adsorbent showed good removal efficiency in real samples of water from rivers contaminated with atrazine, with the removal of 76.58% and 71.29%. Therefore, the adsorbent has potential and can be used to remove pollutants emerging from aqueous solutions.

Keywords: Adsorption, Atrazine, Biochar, Regeneration

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LISTA DE ABREVIATURAS E SIGLAS

A_0	Área abaixo da curva antes da adsorção
ARE	Erro Relativo Médio
A_t	Área abaixo da curva depois da adsorção
BACB	Biochar ativado quimicamente da serragem de cedro
BCC	Biochar da serragem de cedro
BET	Método Brunauer-Emmet-Teller
BJH	Método Barret-Joyner-Halenda
C_0	Concentração inicial de adsorbato (mg L^{-1})
CBS	Serragem de cedro
C_e	Concentração de adsorbato no equilíbrio (mg L^{-1})
COOH	Grupo carboxila
C_s	Solubilidade do adsorbato em água (g L^{-1})
C_t	Concentração de adsorbato no tempo t (mg L^{-1})
DRX	Difração de Raios-X
ECs	Contaminantes emergentes
EDC	Desregulador endócrino
EDS	Espectroscopia de Raios-X por Energia Dispersiva
FT-IR	Espectroscopia no Infravermelho por Transformada de Fourier
k_1	Constante cinética de PFO (min^{-1})
k_2	Constante cinética de PSO ($\text{g mg}^{-1} \text{min}^{-1}$)
k_e	Constante de equilíbrio termodinâmico (adimensional)
K_F	Constante de Freundlich ($(\text{mg g}^{-1})(\text{L mg}^{-1})^{1/n}$)
K_L	Constante de Langmuir (L mg^{-1})
k_{LDF}	Coefficiente de transferência de massa LDF (min^{-1}).
LDF	Modelo de força motriz
M	Massa de adsorvente (g),
M_{ADS}	Peso molecular do adsorbato (g mol^{-1})
MEV	Microscopia Eletrônica de Varredura
MOFs	Estruturas metal-orgânicas
$1/n$	Fator de heterogeneidade de Freundlich (adimensional)
OH	Grupo hidroxila

PFO	Pseudo-primeira ordem
$\text{pH}_{(\text{pzc})}$	Ponto de carga zero
PSO	Pseudo-segunda ordem
Q	Capacidade de adsorção (mg g^{-1})
q_1	Capacidade de adsorção obtida por PFO (mg g^{-1})
q_2	Capacidade de adsorção obtida por PSO (mg g^{-1})
q_e	Capacidade de adsorção no equilíbrio (mg g^{-1})
q_L	Máxima capacidade de adsorção de Langmuir (mg g^{-1})
q_t	Capacidade de adsorção no tempo t (mg g^{-1})
q^*	Capacidade de adsorção do adsorbato relacionada à concentração do adsorbato na fase líquida em equilíbrio (mg g^{-1}),
\bar{q}	Capacidade média de adsorção do adsorbato (mg g^{-1})
R	Constante universal dos gases ($8,314 \times 10^{-3} \text{kJ mol}^{-1} \text{K}^{-1}$)
R^2	Coefficiente de Determinação
RMSE	Raiz do erro quadrado médio
SSE	Soma dos Erros Quadrados
T	Temperatura (K)
t	Tempo de contato (min)
UV-Vis	Espectrofotômetro Ultravioleta-Visível
V	Volume de solução (L)
β	Constante de Dubinin-Radushkevich ($\text{mol}^2 \text{kJ}^{-2}$)
γ^{ADS}	Coefficiente de atividade do adsorbato em solução (adimensional, assumindo $\gamma^{ADS} = 1$)
ΔG^0	Varição de energia livre de Gibbs (kJ mol^{-1})
ΔH^0	Varição de entalpia (kJ mol^{-1})
ΔS^0	a variação de entropia ($\text{kJ mol}^{-1} \text{K}^{-1}$)
E	Potencial Polanyi

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1 INTRODUÇÃO

O aumento da população mundial, que no século 20 passou de 1,5 bilhão para 6,9 bilhões (JATOI et al., 2021), levou ao aumento na demanda de alimentos. Neste contexto surgiram os agrotóxicos que se tornaram importantes aliados do setor agrícola para produção em grande escala. No entanto, o seu uso indevido e excessivo afeta todo o ecossistema ao inserir os resíduos na cadeia alimentar e poluir o solo, o ar e as águas superficiais (AHMAD et al., 2010). Muitos estudos mostraram que os herbicidas são tóxicos para os seres humanos e para o ecossistema.

O ácido 2,4-diclorofenoxiacético (2,4-D) é um herbicida comumente aplicado na agricultura para o controle de plantas daninhas de folhas largas e gramíneas, como trigo, milho, aveia, centeio e cana, devido sua ação seletiva e baixo custo (AKSU & KABASAKAL 2005; HAMEED et al. 2009; SALMAN & HAMEED 2010; DEOKAR & MANDAVGANE 2015). A Organização Mundial da Saúde (OMS) determinou que o 2,4-D é moderadamente tóxico para humanos e animais (classe II) (ZHU et al., 2018).

O herbicida atrazina, 2-cloro-4-etilamino-6-isopropilamino-s-triazina, é um dos herbicidas mais aplicados e persistentes no mundo (TAN et al, 2016). Seu uso intensivo e baixa biodegradabilidade tem levado ao acúmulo deste composto no meio ambiente, contaminando as águas superficiais e subterrâneas (SCHLEDER et al , 2017). A atrazina pode atuar como um desregulador endócrino (EDC) que afeta os sistemas nervoso central, endócrino e imunológico (LASSERRE et al., 2009). É uma possível causa para os danos às estruturas reprodutivas em rãs, peixes e outros animais selvagens e apresenta riscos potenciais para a saúde humana (MUIR et al., 2004).

Devido a todas essas características, a remoção de herbicidas de matriz aquosa é uma das maiores preocupações ambientais da atualidade e tem se tornado alvo de várias pesquisas em torno do assunto. Entre os métodos utilizados para a remoção dos herbicidas estão a degradação fotocatalítica, os processos de oxidação avançada, a degradação aeróbia, as membranas de nanofiltração, a ozonização, a coagulação, a extração de fluidos, a extração em fase sólida e a adsorção. A adsorção é um processo de separação de equilíbrio bem conhecido e um método eficaz para aplicação de descontaminação de água. A adsorção mostrou-se

superior a outras técnicas de reutilização de água em termos de custo inicial, flexibilidade e simplicidade de projeto, facilidade de operação e insensibilidade a poluentes tóxicos. A adsorção também não resulta na formação de subprodutos nocivos (AHMAD et al., 2010).

Os materiais residuais e subprodutos da agricultura e outras indústrias são fontes de adsorventes de baixo custo devido à sua abundância na natureza e por possuírem requisitos de processamento. Nos últimos anos, uma nova classe de adsorventes e especificamente materiais lignocelulósicos vem sendo investigada devido sua atratividade decorrente de sua disponibilidade, baixo custo e biodegradabilidade. Alguns estudos anteriores relataram sua capacidade de acumular quantitativamente metais pesados e vários compostos orgânicos, como corantes e pesticidas (AHMAD et al., 2010).

No Brasil, a madeira de cedro tem se destacado devido as suas altas taxas de crescimento e boa adaptabilidade, além de sua durabilidade natural graças a seus extrativos naturais e a qualidade da madeira (GEORGIN et al, 2019). A serragem de cedro é um resíduo abundante do processamento da madeira de cedro, que necessita, portanto de um destino ambientalmente correto como aplicações alternativas. Neste contexto no presente trabalho a serragem de cedro *cedrela fissilis* é utilizada para a produção de biocarvão para remoção de herbicidas. O trabalho está organizado na forma de artigos científicos. Inicialmente, o contexto do trabalho é introduzido, a seguir os objetivos e a revisão bibliográfica. Em sequência, são apresentados artigos científicos na íntegra, contendo os resultados obtidos. Artigo 1 compila as modificações físicas e químicas aplicadas na serragem de cedro, bem como a caracterização do precursor e dos adsorventes gerados. Os adsorventes são utilizados na remoção dos herbicidas 2,4-D e atrazina, avaliando a eficiência de cada um selecionando o material mais eficiente. O Artigo 2 apresenta as caracterizações do material mais eficiente selecionado no Artigo 1 e se aprofunda mais na sua aplicação em estudos cinéticos, de equilíbrio, termodinâmicos, efluente simulado e teste de regeneração.

2 OBJETIVOS

2.1 OBJETIVO GERAL

Sintetizar e caracterizar biochar obtido a partir da serragem de cedro, bem como avaliar seu potencial como adsorvente na remoção de herbicidas em matriz aquosa.

2.2 OBJETIVOS ESPECÍFICOS

- Modificar a serragem de cedro através da pirólise utilizando uma atmosfera inerte de N_2 e temperatura de $800^\circ C$ e, a seguir, ativar quimicamente com $ZnCl_2$;
- Caracterizar a serragem de cedro, e os biochars produzidos utilizando diferentes técnicas: Difração de Raios-X (DRX), Espectroscopia no Infravermelho por Transformada de Fourier (FT-IR), Microscopia Eletrônica de Varredura (MEV), Espectroscopia de Raios-X por Energia Dispersiva (EDS), Ponto de Carga Zero (pH_{PZC}), Isotermas de Adsorção/Dessorção de N_2 (métodos BET e BJH);
- Analisar a serragem de cedro e os adsorventes sintetizados a partir da mesma, na remoção dos herbicidas atrazina e 2,4-D de solução aquosa. Selecionar o material mais eficiente através dos resultados obtidos e aplicá-lo em estudo avançado da adsorção dos herbicidas;
- Determinar as condições ideais de pH e dosagem do adsorvente selecionado na adsorção da atrazina;
- Obter experimentalmente as curvas cinéticas de adsorção do herbicida no adsorvente selecionado e verificar o ajuste de diferentes modelos cinéticos: Pseudo-primeira ordem, Pseudo-segunda ordem, Modelo de força motriz linear (LDF);
- Obter experimentalmente as isotermas de equilíbrio de adsorção da atrazina no adsorvente selecionado e verificar o ajuste de diferentes modelos de isotermas em diferentes temperaturas: Langmuir, Freundlich, Koble-Corrigan, Dubinin-Radushkevich;
- Determinar os parâmetros termodinâmicos de adsorção de atrazina;
- Tratar dois efluentes simulados com água de rio real contendo atrazina empregando o adsorvente selecionado;
- Avaliar a capacidade de regeneração e reutilização do adsorvente selecionado;

- Explicar o mecanismo de adsorção do adsorvente selecionado no herbicida atrazina.

3 REVISÃO BIBLIOGRÁFICA

Nesta seção, apresenta-se os defensivos agrícolas de uma forma geral, seus impactos para o meio-ambiente e a sociedade, bem como a importância de sua remoção. Contém também algumas informações sobre as técnicas de remoção utilizadas com ênfase no processo de adsorção. São apresentados os fundamentos da adsorção, alguns materiais que vem sendo utilizados como adsorventes e alguns materiais já aplicados na adsorção do herbicida atrazina. Sendo que os biochars destacam-se pelas suas características, principalmente os obtidos de resíduos agro-industriais, como é o caso do presente estudo, devido a sua alta disponibilidade e viabilidade ambiental.

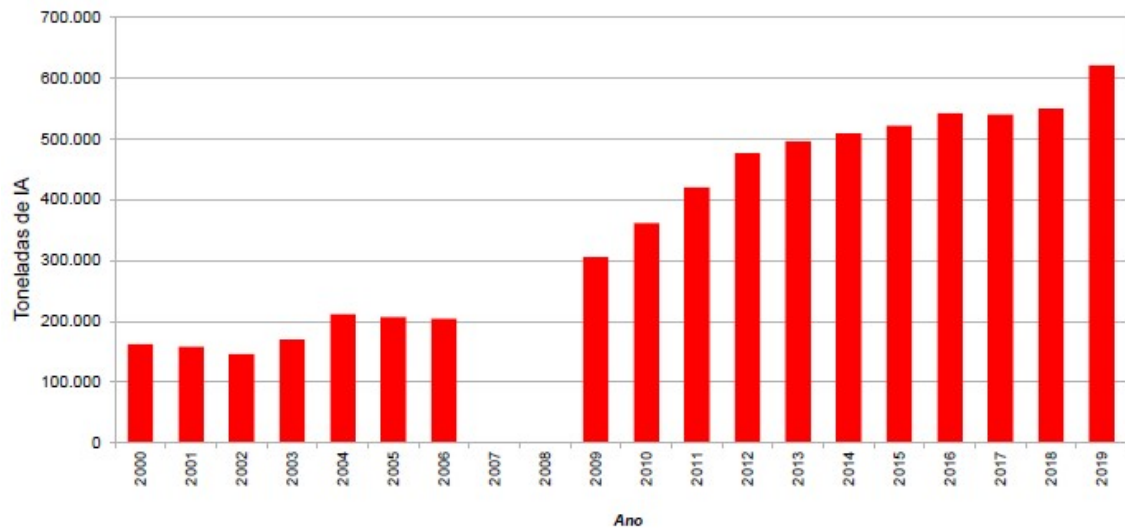
3.1 DEFENSIVOS AGRÍCOLAS

Atualmente, os agrotóxicos são compostos orgânicos amplamente utilizados para melhorar o rendimento agrícola (MACHADO & MARTINS, 2018). Os agrotóxicos também chamados de pesticidas são reconhecidos como poluentes emergentes da água, muitos estudos mostraram que eles são tóxicos para os seres humanos e para o ecossistema.

O termo “pesticida” é uma contração usada para definir uma variedade de agentes que são classificados com base em seu potencial para matar organismos vivos. Eles incluem inseticidas, herbicidas e fungicidas (AHMAD et al.,2010). Quando os pesticidas são aplicados nas plantações, eles podem atingir o solo através da chuva, água de irrigação e vento. Posteriormente, eles entram nos cursos de água superficiais e subterrâneos do solo por meio de processos de escoamento e infiltração, bem como de estações de tratamento de águas residuais (HAMZA et al. 2016).

Segundo os dados registrados pelo IBAMA, expostos na Figura 1, no Brasil em 2000 foram vendidas 160 mil toneladas de agrotóxicos e em 2019 chegou a 620 mil toneladas, aumentando 282% em apenas 19 anos.

Figura 1- Quantitativo das vendas de agrotóxicos e afins por ano



Fonte: Ibama (2020)

Este fato está diretamente ligado a demanda cada vez mais crescente por alimentos, o que consequentemente também se refletiu no aumento de área plantada no Brasil que aumentou de 27 milhões de ha em 2009 para 36 milhões de ha em 2017, aumentando a produção máxima em quase 28% em 8 anos, especialmente no centro-oeste, sul e sudeste (MATIAS et al., 2021). Destacando-se Mato Grosso e Goiás que tiveram um aumento de 255% e 239% de vendas de agrotóxicos, respectivamente, embora sua área plantada não tenha tido aumento significativo em relação ao aumento do uso de agrotóxicos (CAMPOS et al., 2021).

No ano de 2020, foram liberados 493 novos compostos químicos, 19 a mais do que em 2019. Destes produtos, segundo a Agência Nacional de Vigilância Sanitária (ANVISA), 25 foram considerados de moderada a extremamente tóxicos para a saúde humana e 251 como compostos muito ou altamente perigosos ao meio ambiente (MATIAS et al., 2021).

As estruturas dos agrotóxicos são desenvolvidas para imitar e, portanto, substituir moléculas específicas em reações biológicas direcionadas. Os seres humanos são expostos a pesticidas por diferentes vias de exposição, como inalação, ingestão e contato dérmico (AHMAD et al., 2010). O impacto dos agrotóxicos na saúde humana pode ter tanto efeito imediato quanto crônico. Os efeitos imediatos à saúde da exposição a agrotóxicos incluem irritação do nariz, garganta e pele, causando queimação, picadas e coceira, além de erupções cutâneas e bolhas. Náuseas, tonturas e diarreia também são comuns. Os efeitos crônicos à saúde incluem câncer no cérebro e danos no sistema nervoso; defeitos de nascença; infertilidade, danos ao fígado, rins, pulmões e outros órgãos do corpo. Os efeitos

crônicos podem não aparecer por semanas, meses ou mesmo anos após a exposição, dificultando a ligação dos impactos na saúde com o uso de agrotóxicos (JATOI et al, 2021). Portanto, os agrotóxicos são altamente tóxicos e podem causar anormalidades crônicas em humanos, destruindo o meio ambiente e a biodiversidade (JARİYAL et al. 2015). A Tabela 1 apresenta uma lista de ingredientes ativos de grande consumo no Brasil com autorização da Anvisa e sua relação com o câncer.

Tabela 1- Ingredientes ativos e sua relação com o câncer

(Continua)

Nome CAS Nº	Grupo	Classificação Toxicológica (ANVISA)	Classificação Da Carcinogenicidade		Relação Com Câncer
			IARC	USEPA	
2,4-D 94-75-7	Herbicida	Classe I Extremamente tóxico	Grupo 2B: Possivelmente carcinogênico para Humanos	-	Pele, Cavidade nasal, sinonasal, nasofaringe, orofaringe, laringe
Acefato 30560-19-1	Inseticida	Classe III Medianamente Tóxico	ND	Possível carcinogênico para humanos	Leucemias, Linfomas não Hodgkin, pâncreas
Atrazina 1912-24-9	Herbicida	Classe III Medianamente tóxico	Grupo 3: Não é classificável para carcinogenicidad e em humanos	-	Linfomas não Hodgkin
Clorpirifós 2921-88-2	Inseticida	Classe II Altamente Tóxico	ND	Ausência de carcinogenicid ade para seres humanos.	Leucemias, Linfomas não Hodgkin, pâncreas
Diazinona 333-41-5	Inseticida	Classe II Altamente Tóxico	Grupo 2A: Provavelmente carcinogênico para Humanos	-	Leucemias, Linfomas não Hodgkin, câncer de pulmão
Diuron 330-54-1	Herbicida	Classe III Medianamente Tóxico	ND	Provavelment e carcinogênico para humanos	Neoplasia (sem localização definida)
Glifosato 1071-83-6	Herbicida	Classe IV Pouco tóxico	Grupo 2A: Provavelmente carcinogênico para humanos	-	Linfomas não Hodgkin

Tabela 1- Ingredientes ativos e sua relação com o câncer

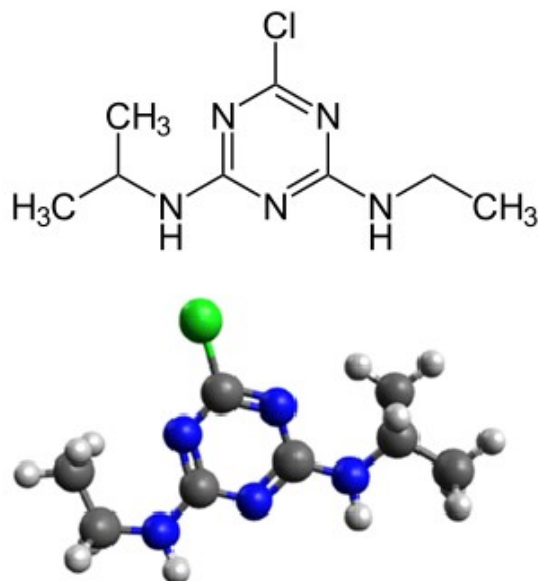
					(Conclusão)
Malationa 121-75-5	Inseticida	Classe III Medianamente Tóxico	Grupo 2A: Provavelmente carcinogênico para humanos	Linfomas não Hodgkin, câncer de próstata.	-
Mancozebe 8018-01-7	Fungicida	Classe III	Grupo 3: Não é classificável para carcinogenicidad e em humanos	-	Linfomas não Hodgkin
Metomil 16752-77-5	Inseticida	Classe I Extremamente Tóxico	ND	Ausência de carcinogenicid ade para seres humanos	-

Fonte: Instituto Nacional do Câncer (INCA).

3.1.1 Atrazina

O herbicida atrazina (2-cloro-4-[etilamino]-6-[isopropilamino]-s- *triazina*) pertence à família das triazinas e tem sido amplamente utilizado no controle de plantas daninhas em lavouras. A atrazina é o quinto agrotóxico mais vendido no Brasil e sexto mais vendido no mundo (AENDA, 2020). É comumente utilizado na produção de milho, e possui autorização para ser aplicado nas plantações de abacaxi, cana-de-açúcar, milho, pinus, seringueira, sisal e sorgo no Brasil. O herbicida também tem registros nos EUA, sendo os principais produtores de milho do mundo. Entretanto, na União Europeia ele foi banido, já que os estudos realizados pelo bloco não comprovaram que o ingrediente ativo não afeta os lençóis freáticos. Outras pesquisas associaram o agrotóxico a impactos no sistema reprodutivo em população de sapos (AENDA, 2020). Sua estrutura está representada na Figura 2.

Figura 2- Estrutura molecular da atrazina



Fonte: Autor.

A atrazina é solúvel em alguns solventes orgânicos, como éter, acetona, benzeno, clorofórmio, etanol e acetato de etila. É um composto fracamente básico, cuja estabilidade se deve a configuração eletrônica do anel heterocíclico. Algumas propriedades físico-químicas da atrazinas estão apresentadas na Tabela 2.

Tabela 2- Propriedades físico-químicas da atrazina

Propriedade	Valores para a atrazina
Solubilidade em água (Sw) a 25 °C	33 mg L ⁻¹
Densidade	1,187 g cm ³
Peso molecular	215 g mol ⁻¹
Pressão de vapor	3.10 ⁷ mmHg
Ponto de fusão	176°C
Log K _{ow} a 25 °C	2,68
pKa a 21 °C	1,7
Constante da Lei de Henry	2,48.10 ⁻⁹ atm m ³ mol ⁻¹

Fonte: Rodrigues & Almeida (1995)

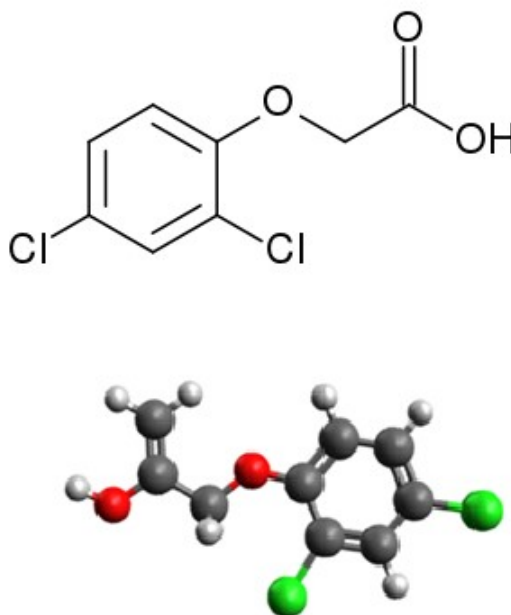
A baixa biodegradabilidade e o uso intensivo da atrazina leva ao acúmulo deste composto no meio ambiente, contaminando as águas superficiais e subterrâneas

(SCHLEDER et al., 2017). A lixiviação da atrazina e seus metabólitos levou a uma séria contaminação das águas superficiais e subterrâneas (SUN et al., 2010). A atrazina também pode atuar como um desregulador endócrino (EDC) que afeta os sistemas nervoso central, endócrino e imunológico (LASSERRE et al., 2009). É uma possível causa para os danos às estruturas reprodutivas em rãs, peixes e outros animais selvagens e apresenta riscos potenciais para a saúde humana (MUIR et al., 2004).

3.1.2 2,4-D

O 2,4-D (ácido 2,4-diclorofenoxiacético) é um ingrediente ativo de pesticida classificado como um herbicida pertencente aos grupos de fenoxi ou ácido fenoxiacético (EPA, 2005). O 2,4-D é uma molécula polar com um pK_a de 2,7 e peso molecular de 221,01; ocorre predominantemente na forma aniônica em valores de pH típicos. Como resultado, a solubilidade em água de 2,4-D é alta cerca de 569 mg L^{-1} (AENDA, 2020). A estrutura molecular do 2,4-D está ilustrada na Figura 3.

Figura 3- Estrutura molecular do 2,4-D



Fonte: Autor.

O 2,4-D é o segundo agrotóxico mais vendido do Brasil com autorização para ser utilizado nas culturas de arroz, aveia, café, cana-de-açúcar, centeio, cevada, eucalipto,

milheto, milho, pastagem, soja, sorgo e trigo (AENDA, 2020). Nos EUA seu uso é liberado, já na União Europeia ele tem autorização restrita apenas para trigo (principal atividade agrícola do bloco), cevada, aveia, centeio e triticale (AENDA, 2020).

O 2,4-D é um herbicida comumente aplicado na agricultura como agente para o controle de plantas daninhas. Tem ação seletiva e de baixo custo (TRIVEDI et al., 2016). Sua estimativa de meia-vida em ambientes aquáticos aeróbicos e anaeróbicos é de 15 dias e 41-333 dias, respectivamente. O limite permitido de 2,4-D na água potável é de 100 ppb (LIANG et al. 2015). O 2,4-D se infiltra em humanos e animais através de vários caminhos, incluindo ar contaminado, água potável, solo e alimentos; e são encontrados em amostras de sêmen e urina humana (QURRATU & REEHAN, 2016). Em relação à saúde humana, o 2,4 D se apresenta como um potencial carcinogênico, suspeito desregulador endócrino e é tóxico para os rins, fígado e sistemas reprodutivos e de desenvolvimento (GILLIOM et al., 2006).

3.2 TÉCNICAS DE REMOÇÃO

Levando-se em conta as legislações vigentes cada vez mais rigorosas e todos os danos que o uso excessivo de agrotóxicos pode causar para a sociedade e o ecossistema, diversas tecnologias têm sido investigadas ao longo dos anos para sua devida remoção dos recursos ambientais. De maneira geral, estes podem ser classificados como métodos físicos, químicos e biológicos, dependendo do mecanismo de descontaminação dos pesticidas (SALEH et al., 2020).

Entre os processos físicos, podem-se citar, como exemplo, as tecnologias de adsorção ou membrana, como nanofiltração e ultrafiltração. Entretanto, estas técnicas apresentam desafios a serem superados, incluindo incrustação que pode alterar as interações entre as membranas e o soluto, prejudicando o desempenho da separação, e também o descarte final das membranas (RODRIGO et al., 2014). Os processos químicos incluem processos de oxidação avançados, incluindo métodos eletroquímicos, sonoquímicos ou fotoquímicos, o ponto fraco desses métodos é a possibilidade de ocorrer reações incompletas, transformação em intermediários e formação de subprodutos perigosos (PONNUCHAMY et al., 2021). Os bioprocessos que incluem biorremediação, bioestimulação e bioaugmentação são conduzidos por micróbios que levam à destruição completa dos pesticidas, porém a desvantagem vem da dificuldade de

realizar o projeto em grande escala, uma vez que manter as condições semelhantes ao laboratório é um desafio para tornar o processo sustentável (PONNUCHAMY et al., 2021).

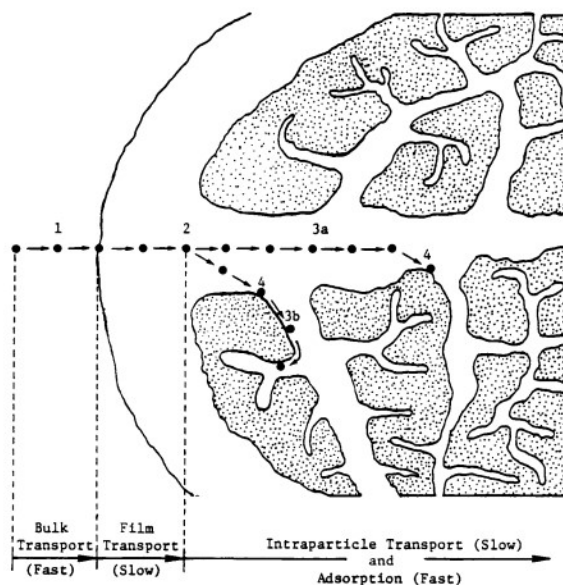
Portanto, dentre as técnicas, a adsorção destaca-se devido a sua simplicidade e conveniência de operação, versatilidade e ausência de formação de subprodutos perigosos. Além disso, a adsorção pode ser facilmente integrada a outros processos para melhorar o desempenho de remediação (PONNUCHAMY et al., 2021).

3.3 ADSORÇÃO

3.3.1 Mecanismos de adsorção

O princípio da adsorção é definido como o fenômeno de transporte de massa que ocorre na interface de duas fases quando elas são colocadas em contato uma com a outra e um determinado componente ou conjunto de componentes se acumula na interface (DEGISI et al., 2016). Adsorvente é o material sólido que fornece a superfície para adsorção e a substância que se acumula na interface é denominada como adsorbato (MATOS, 2015). Segundo Weber e Smith (1986) o fenômeno de adsorção pode ser dividido em quatro etapas básicas, essas etapas estão ilustradas na Figura 4.

Figura 4- Etapas do mecanismo de adsorção



Fonte: Weber e Smith (1986).

As etapas ilustradas na Figura 4 são descritas como: 1) transferência de massa externa: migração do adsorbato do seio da solução até a camada limite hidrodinâmica existente em torno da partícula de adsorvente (*bulk transport*); 2) difusão no filme: transporte difusivo do adsorbato no filme estagnado através da camada limite até a superfície interna do filme (*film transport*); 3) difusão intrapartícula: transporte difusivo do adsorbato a partir da superfície interna do filme estagnado, através do líquido intersticial (a) ou através dos poros internos do adsorvente (b) (*intraparticle transport*); 4) adsorção nos sítios ativos: fixação do adsorbato no sítio receptor disponível do adsorvente (*adsorption*) (WEBER; SMITH, 1986).

Os adsorventes normalmente são caracterizados por possuir estrutura porosa que resulta em um grande número de sítios ativos disponíveis para ligação pelo adsorbato. O tipo de ligação depende da natureza das interações entre a superfície do adsorvente e as espécies moleculares do adsorbato. Quando a natureza da interação é física o fenômeno é denominado como fisissorção, enquanto que quando as ligações químicas predominam nas interações, o fenômeno é denominado quimissorção (PONNUCHAMY et al., 2021).

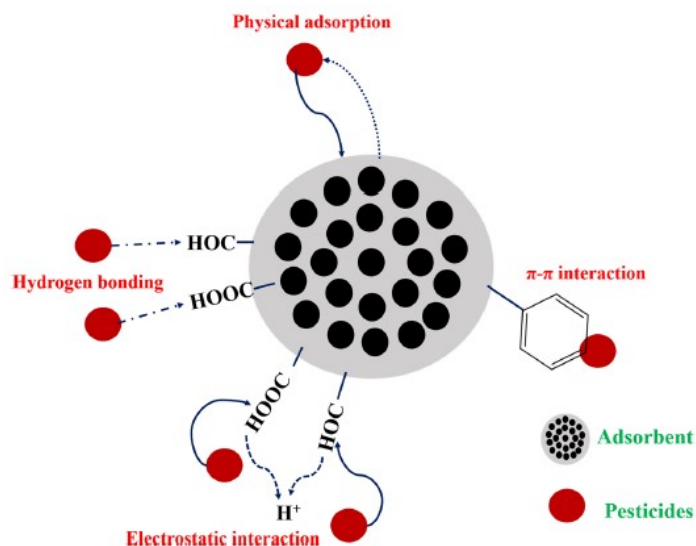
A adsorção por fisissorção envolve forças de Van der Waals fraca ou ligação de hidrogênio, uma camada multimolecular é criada e não necessita de energia de ativação. É um processo reversível, portanto, a regeneração do adsorvente é viável. Geralmente é realizado em baixa temperatura e diminui com o aumento da temperatura. A quimissorção envolve forte ligação eletrostática ou química, como ligação covalente, metálica ou iônica. Portanto, é um processo irreversível e a regeneração do adsorvente não é possível. Ele cria uma camada monomolecular e precisa de energia de ativação (PATEL, 2021).

A dessorção é o processo reverso da adsorção, nela as moléculas de adsorbato são removidas do adsorvente e ela ocorre simultaneamente à adsorção. Quando o adsorvente é mantido em contato com a solução contaminada por um período suficientemente longo, tanto a adsorção quanto a dessorção atingem o estado de equilíbrio dinâmico. Determinando, assim, a máxima adsorção possível do adsorbato pelo adsorvente sob um conjunto específico de condições experimentais. A adsorção máxima é usada como um indicador de desempenho do adsorvente e é denominada como a capacidade de adsorção (PONNUCHAMY et al., 2021).

A adsorção é influenciada por diferentes parâmetros, tais como, dosagem de adsorvente, duração de contato, condições de pH, tamanho de partícula e temperatura (TRIVEDI & MANDAVGANE 2018). Diferentes interações são responsáveis pela remoção

adsortiva, tais como interações hidrofóbicas, forças de Van der Waals, interações eletrostáticas, ligações de hidrogênio e empilhamento π - π entre adsorvente e adsorbato, como mostrado na Figura 5 (PONNUCHAMY et al., 2021).

Figura 5- Interações responsáveis pelo fenômeno de adsorção



Fonte: Ponnuchamy et al. (2021)

Segundo Dotto e McKay (2020) o modo de operação de adsorção é essencial, pois afeta diretamente os custos de tratamento da água, o volume de água tratada, a área física necessária para os equipamentos da estação de tratamento e o tempo necessário para a descontaminação da água. A adsorção pode ser realizada em dois modos convencionais de operação: contínuo (leito fixo) e descontínuo (batelada).

A adsorção em batelada convencional é bastante utilizada em escala laboratorial para fazer o levantamento de parâmetros como a capacidade de adsorção de adsorventes e assim possibilitar o projeto em grande escala através do conhecimento desses dados; no entanto, ele só pode ser usado para tratar pequenos volumes de águas residuais e, como tal, não é popular em aplicações industriais. O sistema de adsorção de leito fixo é comumente usado para controle de poluição de gases e líquidos, seu funcionamento consiste na passagem de um fluido contaminado por uma coluna de forma que ocorra o contato com uma quantidade fixa de adsorvente, criando assim espaço para tratamento de grande volume de fluido efluente com menor necessidade de monitoramento (AUTA & HAMEED, 2014). Neste caso, a operação ocorre até a saturação da coluna, quando as concentrações de contaminantes de entrada e

saída são as mesmas, assim, é possível construir uma curva de ruptura e calcular variáveis como altura do leito e vazão, possibilitando o projeto em grande escala do processo (DOTTO; MCKAY, 2020).

O modo de operação em batelada é realizado em tanques contendo água contaminada, o adsorvente é inserido, e a mistura é então agitada até atingir o equilíbrio. A separação sólido-líquido é realizada por processos como decantação, filtração ou centrifugação (DOTTO; MCKAY, 2020). A quantidade de adsorbato adsorvida no sólido é estimada por meio do balanço de massa dado pela Equação 1.

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

Em que: q (mg g^{-1}) é a capacidade de adsorção, V (L) é o volume da solução, m (g) é a massa de adsorvente, C_0 (mg L^{-1}) é a concentração inicial de adsorbato, e C_t (mg L^{-1}) é a concentração de adsorbato no tempo t .

3.3.2 Fatores que influenciam a adsorção

Como citado anteriormente, diversos fatores podem afetar a adsorção, dentre eles a concentração inicial de adsorbato, a dosagem de adsorvente, o pH, o tempo de contato, a agitação e a temperatura serão discutidos neste item.

A concentração inicial de adsorbato influencia no processo de modo que seu aumento leva a um gradiente maior de concentração entre a solução e a superfície sólida, promovendo o aumento de colisões e conseqüentemente maiores quantidades adsorvidas (BONILLA-PETRICIOLET; MENDOZA-CASTILLO; REYNEL-ÁVILA, 2017a; DOTTO; BURIOL; PINTO, 2014). Porém, ao mesmo tempo, o percentual de remoção tende a diminuir conforme aumenta a concentração inicial, indicando que os sítios ativos foram todos ocupados e encontram-se saturados (HERATH; POH; NG, 2019).

Quanto à dosagem adsorvente, segundo Nascimento et al. (2014) e Worch (2012) o aumento da massa utilizada promove o aumento do número de sítios ativos disponíveis na superfície do material conduzindo ao aumento da remoção. Porém, como o material adsorvente representa um custo ao processo, o objetivo é alcançar bons resultados utilizando a menor quantidade possível de adsorvente.

O pH determina o grau de distribuição das espécies químicas. A intensidade desse efeito pode ser maior ou menor conforme o adsorvente, uma vez que as cargas da superfície do adsorvente dependem da sua composição e das características da superfície. Através do conhecimento do ponto de carga zero (pH_{pzc}), onde a carga do adsorvente é nula, é possível saber a tendência de uma superfície se tornar positiva ou negativamente carregada (NASCIMENTO et al, 2020). Para valores de pH inferiores ao pH_{pzc} , a carga superficial é positiva, e a adsorção de ânions é favorecida; e, para valores de pH superiores ao pH_{pzc} , a carga superficial é negativa, e a adsorção de cátions é favorecida (APEEL; MA; RHUEL, 2003).

O tempo de contato é um fator bastante importante a se avaliar, visto que para a aplicação da operação em escala real, o material deve apresentar alta capacidade adsortiva e atingir o equilíbrio rapidamente para que grandes quantidades de contaminante sejam removidas em curtos períodos de tempo (SEOW; LIM, 2016). Seus efeitos são avaliados por meio da taxa de adsorção.

A agitação do sistema influencia o processo, sendo que seu aumento pode promover a diminuição da resistência à transferência de massa externa, facilitando a migração das moléculas de adsorbato para a superfície do adsorvente (DOTTO; PINTO, 2011; NASCIMENTO et al., 2014).

A temperatura do sistema afeta principalmente a constante de velocidade de adsorção. Um aumento na temperatura pode ocasionar o aumento de energia cinética e na mobilidade das espécies do adsorbato e ainda provocar aumento na taxa de difusão intrapartícula do adsorbato (JIMENEZ; BOSCO; CARVALHO, 2004). Segundo Khattri e Singh (1999), esse fator pode afetar a solubilidade e o potencial químico do adsorbato. Assim, a alteração na temperatura de um processo influencia diretamente na capacidade de adsorção. Além disso, destacam-se dois efeitos importantes da temperatura sobre a adsorção. O primeiro está relacionado com a taxa de difusão das moléculas do adsorbato em toda a camada limite externa e interna nos poros da partícula do adsorvente, já que o aumento da temperatura diminui a viscosidade da solução. O outro efeito está relacionado com o estado de equilíbrio de adsorção para determinado adsorbato. O aumento da temperatura também pode produzir uma desobstrução de poros no interior da estrutura do adsorvente, permitindo a penetração de moléculas maiores do adsorbato (DOGAN; ALKAN; DEMIRBAS, 2006). Assim, a velocidade de vários processos físico-químicos aumenta consideravelmente com o aumento da temperatura (NASCIMENTO et al, 2020).

3.3.3. Cinética de adsorção

O estudo da cinética é muito importante para o processo de adsorção, pois através dele obtêm-se informações sobre a possibilidade de aplicação de determinado adsorvente e as interações que ocorrem na interface adsorbato-adsorvente, também estima-se a taxa de adsorção e o tempo necessário para o processo atingir o equilíbrio, desta forma, pode-se definir os parâmetros de transferência de massa (BONILLA-PETRICIOLET et al., 2019; HO; MCKAY, 1998). A avaliação do perfil cinético é realizada através do ajuste de modelos matemáticos às curvas experimentais de capacidade de adsorção (q_t , mg g^{-1}) em função do tempo de contato (t , min). Entre os modelos cinéticos de adsorção, os modelos de Pseudo-primeira ordem e Pseudo-segunda ordem tem sido os mais utilizados para modelar conjuntos de dados cinéticos dos estudos nas últimas duas décadas. Esses dois modelos têm sido aplicados a uma ampla variedade de sistemas de adsorção, desde biomassa a nanomateriais como adsorventes, e de metais pesados a produtos farmacêuticos como adsorbato ou contaminante (REVELLAME et al, 2020).

O modelo de Pseudo-primeira ordem (Equação 2) assume que a adsorção ocorre como consequência de um gradiente de concentração entre a superfície do adsorvente e a solução (HO; MCKAY, 1998; QIU et al., 2009).

$$q_t = q_1 (1 - \exp(-k_1 t)) \quad (2)$$

Em que: q_1 (mg g^{-1}) é a capacidade de adsorção teórica obtida pelo modelo e k_1 (min^{-1}) é a constante cinética de PPO.

Já o modelo de Pseudo-segunda ordem (Eq 3), reúne os coeficientes interno e externo de transferência de massa na mesma equação, geralmente ele é utilizado para representar processos de quimissorção (HO; MCKAY, 1998; QIU et al., 2009).

$$q_t = \frac{t}{\left(\frac{1}{k_2 q_2^2}\right) + \left(\frac{t}{q_2}\right)} \quad (3)$$

Em que: q_2 (mg g^{-1}) é a capacidade de adsorção teórica obtida pelo modelo e k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) é a constante cinética de PSO.

As características peculiares observadas com relação à partição de compostos orgânicos em partículas suspensas podem ser explicadas satisfatoriamente usando o modelo de força motriz linear (LDF). Em sistemas naturais onde a turbulência perto das partículas é mínima, tanto a difusão intrapartícula dentro dos poros quanto a difusão do filme se tornam importantes. Esses efeitos podem ser incluídos no modelo LDF (VALSARAJ & THIBODEAUX, 1999). O modelo LDF é representado pelas Equações 4 e 5.

$$\frac{d\bar{q}}{dt} = k_{LDF}(q^* - \bar{q}) \quad (4)$$

$$\bar{q}(t=0) = 0 \quad (5)$$

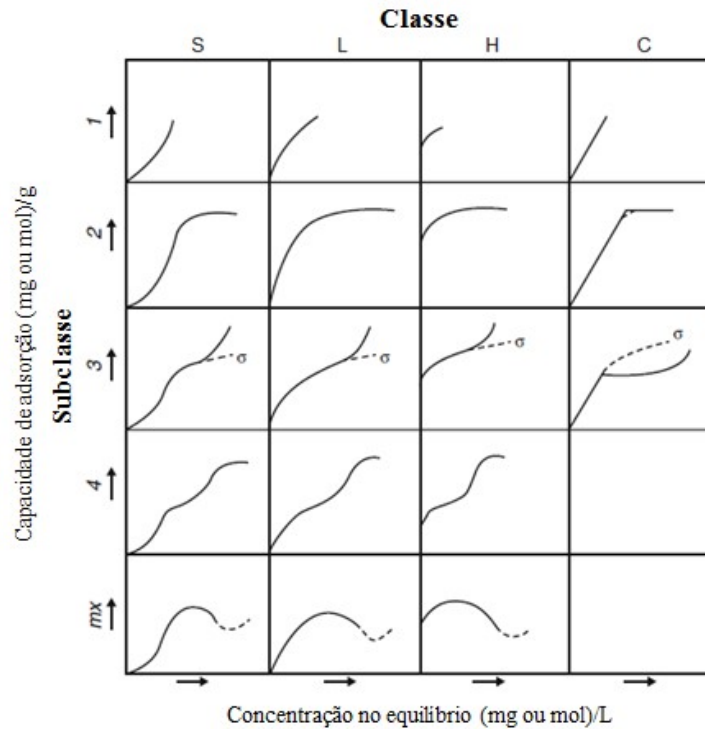
Em que: \bar{q} é a capacidade média de adsorção do adsorbato (mg g^{-1}), q^* a capacidade de adsorção do adsorbato relacionada à concentração do adsorbato na fase líquida em equilíbrio (mg g^{-1}), k_{LDF} é o coeficiente de transferência de massa LDF (min^{-1}).

3.3.4. Equilíbrio de adsorção

O equilíbrio de adsorção é verificado através das curvas de isotermas, as quais correlacionam graficamente a quantidade de adsorbato adsorvida no equilíbrio (q_e , mg g^{-1}) em função da concentração do adsorbato na fase líquida no equilíbrio (C_e , mg L^{-1}), em diferentes temperaturas (GILES et al., 1960). Essas curvas são importantes, pois descrevem a interação do adsorbato com a superfície do adsorvente, estabelecendo a capacidade máxima de adsorção do adsorvente e seus parâmetros termodinâmicos (BONILLA-PETRICIOLET et al., 2019).

A Figura 6 mostra as quatro principais classes em que as isotermas são divididas, Giles et al. (1960) fizeram essa divisão levando em consideração a inclinação inicial das curvas, para representar as variações de cada classe foram estabelecidas subclasses, com base nas formas das partes superiores das curvas e mudanças de inclinação. As classes são nomeadas como S (forma sigmoideal), L (tipo Langmuir), H (alta afinidade) e C (constante de partição), e as subclasses são representadas por números.

Figura 6 – Classificação das isotermas de adsorção



Fonte: Giles et al. (1960).

Existem diversos modelos matemáticos para o ajuste dos dados experimentais das isotermas e, dentre eles, podem-se citar os modelos de Langmuir, Freundlich, Koble-Corrigan e Dubinin-Radushkevich.

A isoterma de Langmuir é válida para a adsorção de monocamada em uma superfície contendo um número finito de sítios idênticos. Ela descreve quantitativamente a formação de um adsorbato de monocamada na superfície externa do adsorvente e, depois disso, não ocorre mais adsorção. O modelo assume energias uniformes de adsorção na superfície e nenhuma passagem do adsorbato no plano da superfície (DADA et al., 2012). A Equação 6 representa o modelo de Langmuir com base nessas suposições.

$$q_e = q_L \frac{K_L C_e}{1 + K_L C_e} \quad (6)$$

Em que: q_e (mg g^{-1}) é a capacidade de adsorção no equilíbrio, C_e (mg L^{-1}) é a concentração de adsorbato no equilíbrio, q_L (mg g^{-1}) é a máxima capacidade de adsorção na monocamada e K_L (L mg^{-1}) é a constante de Langmuir.

O modelo de isoterma de Freundlich é caracterizado por uma equação empírica aplicável em sistemas heterogêneos, não ideais e adsorção em multicamadas (FREUNDLICH, 1906). A isoterma de Freundlich é descrita pela Equação 7.

$$q_e = K_F C_e^{1/n} \quad (7)$$

Em que: $K_F ((\text{mg g}^{-1})(\text{L mg}^{-1})^{1/n})$ é a constante de Freundlich e $1/n$ (adimensional) é o fator de heterogeneidade.

O modelo de Koble-Corrigan combina elementos dos modelos de Freundlich e de Langmuir, sendo normalmente aplicado para a adsorção em superfícies heterogêneas. A Equação 8 representa a isoterma de Koble-Corrigan.

$$q_e = \frac{A c_e^n}{1 + B c_e^n} \quad (8)$$

Em que: A, B e n são os parâmetros Koble-Corrigan, respectivamente.

A isoterma de Dubinin-Radushkevich é geralmente aplicada para expressar o mecanismo de adsorção com uma distribuição de energia gaussiana em uma superfície heterogênea (GÜNAY et al., 2007; DAŹBROWSKI, 2001). A Equação 9 representa o modelo de Dubinin-Radushkevich.

$$q_e = q_{mDR} \exp(-\beta \varepsilon^2) \quad (9a)$$

$$\varepsilon = RT \ln \left(\frac{C_S}{C_e} \right) \quad (9b)$$

Em que: β é a constante de Dubinin-Radushkevich ($\text{mol}^2 \text{kJ}^{-2}$), ε é o Potencial polanyi, R é a constante universal do gás ($8,314 \text{ J mol}^{-1} \text{ K}^{-1}$), C_S é a solubilidade (mg L^{-1})

3.3.5 Termodinâmica

A termodinâmica é avaliada com base nos dados verificados através das isotermas de equilíbrio que são obtidas em diferentes temperaturas e concentrações. Os parâmetros termodinâmicos comumente investigados são a variação de energia livre de Gibbs (ΔG^0 , kJ

mol^{-1}), a variação de entalpia (ΔH^0 , kJ mol^{-1}) e a variação de entropia (ΔS^0 , $\text{kJ mol}^{-1} \text{K}^{-1}$). Estes parâmetros indicam se o processo é espontâneo, exotérmico ou endotérmico, e fornecem informações quanto a heterogeneidade energética da superfície adsorvente (ELWAKEEL, 2009; LIU, 2009).

A entalpia (ΔH) está relacionada ao conteúdo de calor do sistema. Assim, uma entalpia negativa indica que ocorreu liberação de calor e o processo é dito exotérmico, por outro lado, a absorção de calor gera uma entalpia positiva e o processo é endotérmico. A magnitude dos valores de ΔH também é importante, pois indica o tipo de adsorção que ocorre: energias baixas sugerem fisissorção (inferior a 40 kJ mol^{-1}) e altas energias representam quimissorção (40 a 800 kJ mol^{-1}) (BONETTO et al., 2016).

A entropia se refere à desordem do sistema, valores positivos ($\Delta S^0 > 0$) representam um aumento na aleatoriedade do sistema durante a adsorção e valores negativos ($\Delta S^0 < 0$) sugerem a redução da aleatoriedade devido às interações entre o adsorvente e o adsorbato (BONILLA-PETRICIOLET; MENDOZA-CASTILLO; REYNEL-ÁVILA, 2017a; RUTHVEN, 1984).

A energia livre de Gibbs define a espontaneidade do sistema. Ela expressa a quantidade de energia capaz de realizar trabalho durante uma reação a temperatura e pressão constantes. O processo é dito espontâneo quando a energia deixa o sistema ($\Delta G^0 < 0$), e processo é não espontâneo quando energia entra no sistema ($\Delta G^0 > 0$). O ΔG^0 pode ser estimado pela Equação 10.

$$\Delta G^0 = -RT \ln(k_e) \quad (10)$$

Em que: R ($8,314 \times 10^{-3} \text{ kJ mol}^{-1} \text{K}^{-1}$) é a constante universal dos gases, T (K) é a temperatura, e k_e (adimensional) é a constante de equilíbrio termodinâmico, que pode ser obtida pela adimensionalização da Equação 11.

$$k_e = \frac{k M_{\text{ADS}} \gamma^{\text{ADS}}}{\gamma} \quad (11)$$

Onde: k_e é a constante do ajuste de isoterma mais adequado, M_{ADS} (g mol^{-1}) é o peso molecular do adsorbato, γ^{ADS} (adimensional, assumindo $\gamma^{\text{ADS}} = 1$) é o coeficiente de atividade do adsorbato em solução, e γ (1 mol L^{-1}) é o coeficiente de atividade unitário do adsorbato.

A variação da energia livre de Gibbs relaciona-se com a entalpia e a entropia como a diferença entre as duas a uma temperatura constante. Os parâmetros ΔH^0 e ΔS^0 podem ser

determinados ajustando-se os coeficientes angular e linear obtidos pelo gráfico de Van't Hoff ($\ln k_e$ versus $1/T$) na Equação 12 (ELWAKEEL, 2009).

$$\ln(k_e) = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (12)$$

3.3.6 Materiais adsorventes

Segundo Dotto e McKay (2020), a escolha, o desenvolvimento e a caracterização do material adsorvente são essenciais para projetar um processo de adsorção para tratamento de água, sendo que o adsorvente é responsável por 70% dos custos operacionais; desta forma, um adsorvente adequado requer as seguintes características:

- Baixo custo e disponibilidade: grandes quantidades de material adsorvente precisam ser facilmente obtidas (produzidas ou compradas) e transportadas para as estações de tratamento para que seja possível reduzir os custos operacionais com adsorvente;
- Estabilidade química: diferentes matrizes de água possuem diferentes características químicas (pH, força iônica, condutividade, entre outras) que podem afetar o adsorvente, portanto, o material requer estabilidade química;
- Estabilidade mecânica: tendo em vista que o tratamento contínuo da água é realizado em colunas, o adsorvente também requer estabilidade mecânica para evitar quedas de alta pressão e caminhos preferenciais;
- Boas características texturais e físico-químicas: alta área superficial e volume de poros, e grupos funcionais na superfície, que possam interagir com os contaminantes.
- Alta capacidade de adsorção: a quantidade de contaminante adsorvido por grama de adsorvente deve ser elevada, assim a quantidade de adsorvente necessária para o tratamento é reduzida, facilita a separação de fases após a adsorção e diminui a área física necessária para a operação;
- Alta eficiência: alta quantidade de contaminante retirado da água e transferido para o adsorvente garantindo que o padrão de qualidade desejado seja alcançado;
- Cinética rápida: alta capacidade de adsorção e alta eficiência devem ser alcançadas em curtos intervalos de tempo. De modo que o tempo necessário para o tratamento seja curto reduzindo o custo de capital da estação de tratamento;

- Potencial de regeneração e reutilização: O adsorvente deve ser facilmente regenerado e reutilizado por mais de uma vez, reduzindo os custos operacionais.

Desenvolver um material com todas essas características não é fácil, e essas características dependem de uma série de fatores como o tipo de adsorbato e as condições operacionais do processo. Com este intuito, uma série de estudos vêm sendo desenvolvida em busca do adsorvente ideal, dentre os materiais mais comumente utilizados podem-se citar: materiais derivados de carbono como carvões, biochars, carvões ativados, carvões e nanomateriais (DIRAKI et al., 2019; STREIT et al., 2019; ZAZYCKI et al, 2020), quitina e os materiais derivados da quitosana (KWOK et al., 2018; DOTTO, VIEIRA, PINTO, 2012; DOS SANTOS et al., 2019; CRINI & BADOT, 2008), bioissorventes e resíduos agroindustriais (TORRES-PÉREZ et al, 2015; ESCUDERO et al, 2019; MO et al, 2018), materiais de base inorgânica, incluindo zeólitos, hidróxidos duplos em camadas e geopolímeros (BRIÃO et al., 2017), estruturas metal-orgânicas (MOFs) (HALDAR et al., 2020), materiais à base de sílica (FAN et ao, 2012) e nanotubos de carbono (SARKAR et al. 2018). A Tabela 3 reúne alguns adsorventes aplicados na remoção dos herbicidas 2,4-D e atrazina presentes na literatura

Tabela 3- Adsorventes aplicados na remoção de 2,4-D e atrazina

(continua)

Material adsorvente	Adsorbato	Referência
Tecido de carbono de alta área	2,4 - D e atrazina	Ayranci, Erol e Numan Hoda (2004)
Grânulos de borracha de pneu	2,4 - D e atrazina	Alam, JB, AK Dikshit e M. Bandyopadhyay (2005)
Biocarvão de sabugo de milho	2,4-D	Binh, Quach An e Hong-Hai Nguyen (2020)
Argila organofílica comercial	2,4 - D e atrazina	Manzotti, Fernando, Onélia Aparecida André dos Santos (2019)
Casca do amendoim (<i>Arachis hypogaea</i>)	2,4-D	Georgin, J., Franco, DS, Netto, MS, Piccilli, DG, Foletto, EL, & Dotto, GL (2021)

Tabela 3- Adsorventes aplicados na remoção de 2,4-D e atrazina
(conclusão)

Biochar da casca de arroz	2,4 - D e atrazina	Binh, Quach An, et al. (2020)
Organo-beidelitas	Atrazina	Grundgeiger, Emily, et al. (2015)
Cinza de cana de açúcar	Atrazina	Singh, N. (2020)
Carvão ativado de polpa de laranja	2,4-D	Angın, D., & Güneş, S. (2021)
Fibra de carvão ativado	2,4-D	LI, Qun et al (2018)
Bentonita	2,4 - d e atrazina	Pluangklang, C., & Rangriwatananon, K. (2021)
Carvão de forno tradicional	2,4-D	Kearns, JP, Knappe, DR, & Summers, RS (2015)
Cascas de trigo (Fagopyrum esculentum)	2,4-D	Franco, Dison, et al (2021)
Cinza da casca de arroz	Atrazina	N'Diaye, AD, et al (2019)
Castanha carbonizada	2,4-D	Gülen, J.,& Aslan, S. (2020)
Carvão ativado	2,4-D	Kurtoğlu, AE, & Atun, G. (2016)
Óxido de nanofolha de grafeno	Atrazina	de Souza Antônio, Rodrigo, et al.(2021)
Sepiolita modificada com quitosana	Atrazina	Liu, Hc., Chen, W., Cui, B. et al. (2015)
Material grafitico induzido por laser	Atrazina	Bayati, Mohamed, et al. (2020)
Nanopartículas de organossilicato	2,4-D	Bhardwaj, Deepesh, et al. (2015)

Fonte: autor

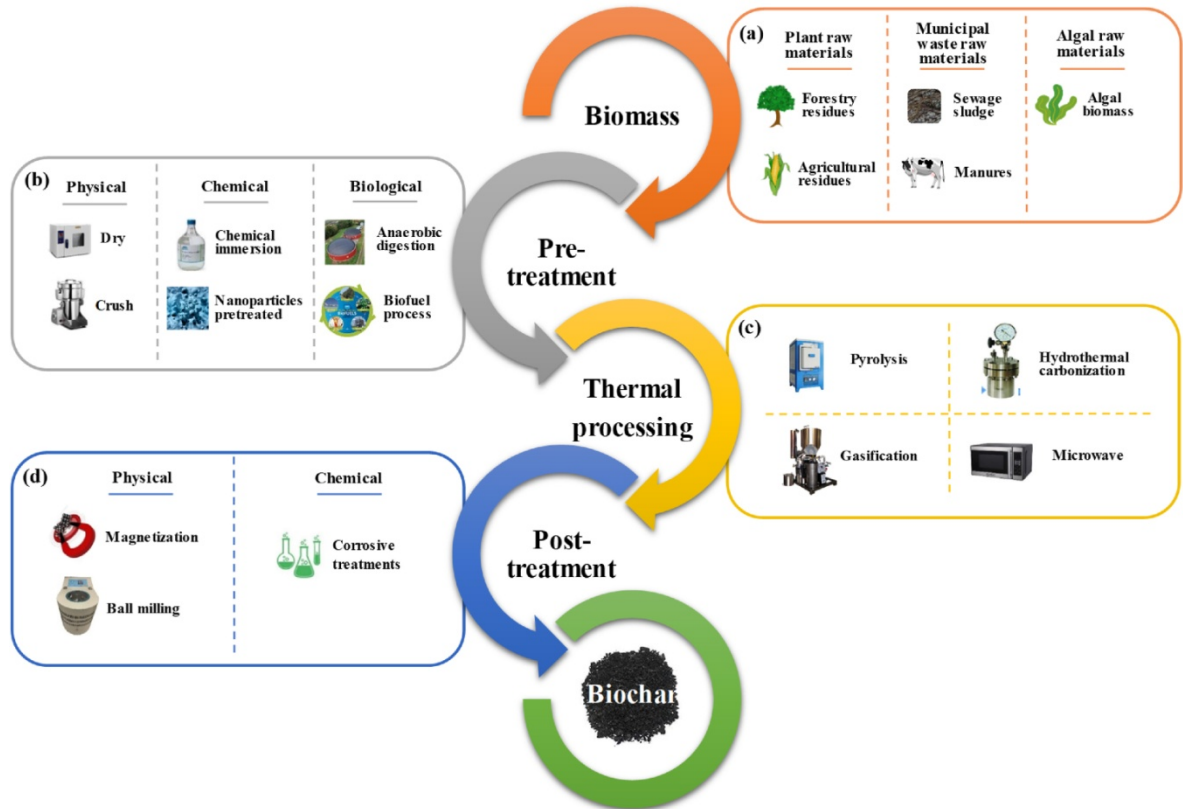
Um dos principais desafios para a produção em escala comercial de carvão ativado é o alto custo (ZHOU et al. 2015), outra questão é a dificuldade de regeneração e sua eliminação em fim de vida. As vantagens apresentadas pela adsorção e as preocupações com os adsorventes existentes levaram os pesquisadores a procurar alternativas ecologicamente corretas (GOPINATH et al., 2021). Os chamados adsorventes sustentáveis são derivados de materiais naturais, apresentando grande disponibilidade na maioria dos casos, eles são econômicos, ecologicamente corretos e biodegradáveis (KYZAS & KOSTOGLU 2014). Vários resíduos agrícolas também têm potencial para serem usados para descontaminação de fluxos de resíduos domésticos e industriais (OMO-OKORO et al., 2018).

3.4 BIOCHAR COMO ADSORVENTE

Biochar (biocarvão) é um produto sólido rico em carbono obtido da conversão térmica de biomassa sob condições com limitação de oxigênio ou anaeróbios (YI et al.2017). Dentre as características presentes no biochar podem-se citar: grande área superficial específica, estrutura porosa, grupos funcionais superficiais abundantes e componentes minerais, o que faz com que ele seja utilizado como adsorvente adequado para remover poluentes de soluções aquosas (ZHANG et al., 2018 ; ZHU et al., 2018).

Como uma espécie de adsorvente, o biochar, com estrutura porosa semelhante ao carvão ativado, é o adsorvente mais utilizado e eficaz no mundo para remover diversos poluentes na água (WU et al., 2018). O biochar é um recurso renovável, sendo ideal para tecnologias ambientais para tratamento de poluentes da água devido aos seus benefícios econômicos e ambientais (DAI et al., 2019). A Figura 7 mostra as etapas comumente utilizadas na produção do biochar.

Figura 7- Etapas para produção de biocarvão.



Fonte: XIANG et al (2020)

Recentemente, o biocarvão tem sido considerado como um substituto potencial para o carvão ativado na remediação ambiental e tratamento de água devido ao seu baixo custo, abundância relativa e capacidade de absorção comparativa (KEARNS et al., 2014).

3.4.1 Precursores

O biochar é feito a partir de resíduos de biomassa. A matéria-prima de biomassa pode ser qualquer resíduo orgânico que inclui resíduos de culturas e florestas, lascas de madeira, algas, lodo de esgoto, esterco e resíduos sólidos urbanos orgânicos (COLANTONI et al., 2016; XIONG et al., 2019).

As matérias-primas do biochar vêm principalmente da biomassa agrícola, sendo um dos mais abundantes recursos renováveis na terra, incluindo principalmente os resíduos de culturas, biomassa de madeira, esterco animal e resíduos sólidos. A composição do biocarvão

(carbono, nitrogênio, potássio, cálcio) depende dos materiais utilizados e da duração e temperatura da pirólise (TAG et al., 2016).

Como exemplo de materiais precursores do biochar tem-se: caroços de frutas (AGGELOPOULOS et al., 2017), bagaço (NIE et al., 2018), esterco animal (AL-WABEL et al., 2017), palha (HUANG et al., 2018), concha (Xu et al., 2018), madeira (CAO et al., 2018), lodo (Vause et al., 2018), bambu (DONG et al., 2018), sabugo de milho (MULLEN et al. 2010), entre outros.

Dentre eles, destacam-se os biocarvões provenientes de biomassa vegetal com lignina e celulose que podem formar estruturas porosas sendo benéficas para a remoção de contaminantes por efeito de preenchimento de poros (KUMAR et al. 2011). Além disso, a biomassa vegetal possui um grande teor de elementos de carbono e oxigênio que podem produzir vários grupos funcionais ($-\text{COOH}$, $-\text{C}-\text{O}-\text{R}$, $-\text{C}-\text{OH}$) na superfície do biochar; esses grupos podem servir como sítios ativos adicionais para melhorar a eficiência de remoção (TAKAYA et al. 2016).

3.4.2. Pirólise

Biochar é definido como o produto da transformação da biomassa através da pirólise. A pirólise da matéria-prima/precursor geralmente ocorre a uma temperatura variando entre 400 e 850 °C na ausência de oxigênio (ABIOYE & ANY, 2015). Durante a carbonização, celulose, hemiceluloses e lignina sofrem reações de decomposição térmica, como despolimerização, reticulação e fragmentação a uma temperatura específica, resultando em produtos finais sólidos, líquidos e gasosos. Os produtos finais sólidos e líquidos são chamados de “biochar” e “bioóleo”, enquanto o produto gasoso é referido como *syngas*, que é uma mistura de monóxido de carbono, dióxido de carbono, hidrogênio e hidrocarbonetos. Na etapa de carbonização, a biomassa depende do fornecimento externo de calor para a combustão do carvão, o que reduz a matéria volátil no carvão e aumenta o teor de carbono (DAI et al., 2019)

O tipo de biochar depende muito do tipo de matéria-prima, da temperatura do craqueamento. Diferentes matérias-primas e diferentes temperaturas de pirólise têm efeitos diferentes no carbono total e no componente cinza do biochar (JINDO et al., 2014).

Devido ao aumento da queima de massa fixa de carbono durante a pirólise, as áreas de superfície e os volumes de poros dos biochars geralmente aumentam com o aumento da temperatura e do tempo de residência (ZABANIOTOU et al., 2008).

3.4.3. Ativação Química

O processo químico é mais comumente usado para ativar o biochar. Essa ativação pode ser realizada tanto tratando o precursor como tratando o carvão obtido após a pirólise. A modificação química pode ser dividida em processos de ativação em uma etapa e em duas etapas. No processo de modificação em uma etapa, a carbonização e a ativação da biomassa são alcançadas simultaneamente usando um agente químico, enquanto no caso do processo de modificação em duas etapas, primeiro é realizada a carbonização da matéria-prima e logo após ativação química do produto final carbonizado resultante na presença de agentes químicos ou, pré-tratamento da biomassa antes do processo de carbonização por meio de mistura com agentes químicos. Porém, é importante ressaltar que, em ambas as abordagens, é necessário lavar o biochar com ácido/base e água deionizada, pois a presença de produtos químicos altera a funcionalidade do biochar (AKHIL et al., 2021).

A modificação química inclui principalmente modificação de ácido, modificação alcalina, modificação de sais metálicos e modificação de agente oxidante, entre outros (PANWAR & PAWAR., 2020).

A área específica e os grupos funcionais presentes na superfície do biochar afetam significativamente a capacidade de adsorção do biochar modificado. A utilização de ácido para a ativação do biochar melhora significativamente as características da superfície. Porém, apresenta a desvantagem das paredes dos microporos serem corroídas devido ao tratamento ácido (SAJJADI et al., 2018). Isto fica evidente, pois de acordo com vários trabalhos encontrados na literatura, o biochar modificado por ácido possui uma área superficial menor em comparação com outros processos de ativação, o que pode ser atribuído à destruição da estrutura dos poros.

O cloreto de zinco ($ZnCl_2$) é um ácido de Lewis que pode ser usado na ativação do biochar. O cloreto de zinco foi utilizado para realizar a ativação do biocarvão de casca de café para aumentar a remoção de corantes. Como resultado foi criado um grande número de poros e a área superficial aumentou de 0,5 para $750 \text{ m}^2/\text{g}$. O tamanho e a área dos poros foram

aumentados devido à remoção de alcatrão, substâncias não voláteis e cinzas pelo ácido de Lewis (KOSAIYAKANON & KUNGSANANT, 2020). Além disso, o cloreto de zinco favorece o desenvolvimento de mesoporos e aglomeração de zinco, melhorando a afinidade de ligação do metal na remoção de contaminantes (GUO et al. 2019).

Levando em consideração todas as informações e dados expostos no item 3, um resíduo da indústria madeireira, a serragem da casca de cedro foi selecionada e utilizada como precursora para a produção de biochars através da ativação física e química. Os adsorventes foram testados na remoção de herbicidas de matriz aquosa. A serragem foi selecionada devido a todas as características que a estrutura da biomassa vegetal possui como possível formação de poros e produção de grupos funcionais, além disso a técnica de remoção utilizada foi a adsorção que destacou-se das demais devido as vantagens como simplicidade de operação, baixo custo e ausência de formação de subprodutos. Os resultados obtidos nos testes estão expostos na forma de artigos que são apresentados a seguir.

4. ARTIGO 1: ADSORÇÃO DOS PESTICIDAS ATRAZINA E 2,4-D EM BIOCHARS ALTERNATIVOS DE SERRAGEM DE CASCA DE CEDRO (*CEDRELLA FÍSSILIS*)

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ADSORPTION OF ATRAZINE AND 2,4-D PESTICIDES ON ALTERNATIVE BIOCHARS FROM CEDAR BARK SAWDUST (*CEDRELLA FISSILIS*)

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Abstract

Bark residues of the forest species *Cedrela fissilis* were physically and chemically modified with zinc chloride ($ZnCl_2$) as an activating agent. The two modified materials were analyzed as adsorbents in removing atrazine and 2,4-D herbicides from effluents. Firstly, the precursor material and the modified ones were characterized by different techniques to identify the structural changes that occurred in the surfaces. Through TGA, it was observed that both modified materials have thermal stability close to each other and are highly superior to the precursor. X-ray diffractions proved that the amorphous structure was not altered, the three materials being highly heterogeneous and irregular. The micrographs showed that the treatments brought new spaces and cavities on the surface, especially for the material carbonized with $ZnCl_2$. The pHPZC of the modified materials was close to 7.5. The physically modified material had a surface area of $47.31 \text{ m}^2 \text{ g}^{-1}$ and pore volume of $0.0095 \text{ cm}^3 \text{ g}^{-1}$, whereas the carbonized material had a surface area of $98.12 \text{ m}^2 \text{ g}^{-1}$ and pore volume of $0.0099 \text{ cm}^3 \text{ g}^{-1}$. Initial tests indicated that none of the adsorbents were efficient in removing 2,4-D. However, they showed good potential for removing atrazine. The Koble-Corrigan

isothermal model best fits the experimental data, with a maximum capacity of 3.44 mg g^{-1} and 2.70 mg g^{-1} for physically modified and with ZnCl_2 , respectively. The kinetic studies showed that the system tends to enter into equilibrium after 120 min, presenting good statistical indicators to the linear driving force model (LDF). The surface diffusion coefficients were 2.18×10^{-9} and $2.37 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ for atrazine adsorption on the physically and chemically modified materials. These results showed that the application of residues from the processing of cedar bark is promising. However, new future studies must be carried out to improve the porous development of the material and obtain greater adsorption capacities.

Keywords: 2,4-D; atrazine; adsorption; biochar; physical activation; chemical activation.

4.1 INTRODUCTION

With the increase in the world population and the growing demand for food and good health, it is necessary to find ways to increase productivity (PIGATTO et al. 2020; STREIT et al. 2021; GEORGIN et al. 2021). However, something that directly interferes with this factor is the various pests that can infest crops, causing damage to food and affecting its marketing. Thus, to eliminate and prevent these pests, they emerged as pesticides, and, currently, their use ends up being essential to ensure high productivity (SALOMÓN et al. 2021; PEREIRA et al. 2021). However, the extensive use of pesticides contaminates soil and water linked to ecosystem functioning and puts human health at risk (GEORGIN et al. 2021; VIEIRA et al. 2021). 2,4-Dichlorophenoxyacetic acid (2,4-D) is one of the oldest and most widely used herbicides to selectively control broadleaf weeds in gardens and agriculture. 2,4-D is generally preferred due to its low cost and good selectivity. However, according to the World Health Organization (WHO), 2,4-D is classified as possibly carcinogenic for humans (LOOMIS et al. 2015). Furthermore, 2,4-D is a poorly biodegradable pollutant; therefore, it has been frequently detected in water bodies in various world regions. (GÜLEN and ASLAN 2020). Atrazine ($\text{C}_8\text{H}_{14}\text{ClN}_5$) has been among the most used pesticides in the world since the 1950s. It is a highly toxic, carcinogenic, and endocrine-disrupting substance. In 2004, it was officially banned in the European Union, but it is still widely used worldwide due to its low cost and high efficiency (AMÉZQUITA-MARROQUÍN et al. 2020). After application, atrazine can pass through different destinations, including runoff or soil leaching, demonstrating that atrazine is persistent in these environments, where it can biodegrade relatively slowly (SHAPIR and MANDELBAUM 1997). Due to the above characteristics of

these compounds, it is necessary to develop an efficient, easily accessible, and inexpensive technology to remove 2,4-D and atrazine from water (DOTTO and MCKAY 2020).

Various chemical and physical treatments, such as adsorption, advanced oxidation process, membrane filtration, and biological treatment, such as phytoremediation, bioremediation, and activated sludge, were used to remove pesticides from aqueous solutions (MOJIRI et al. 2019). However, most remediation technologies have limited flexibility, high cost, low efficiency, and production of secondary contaminants (SHAMSOLLAHI and PARTOVINIA 2019). In this context, adsorption is a promising technique due to its high efficiency, simple operations, low cost, and absence of by-products. Developing a suitable adsorbent in the adsorption field is a key point since it corresponds to 70% of the operational costs (DOTTO and MCKAY 2020).

Biochar has created broad research interest in recent years due to its surface properties, high surface area, pore volume, and pore diameter, making it a strong candidate for removing contaminants from soil and water bodies (MANDAL et al. 2017). In general, biochar production effectively includes two steps: carbonization and activation (SUO et al. 2019). Carbonization is a process of thermal decomposition in an inert atmosphere, with fluxes of nitrogen or helium. Non-carbon species (residues) are eliminated at this stage, and a porous structure is produced. In the activation stage, some treatments are applied to increase the surface area and increase the diameters of the pores formed during the carbonization stage (GÜLEN and ASLAN 2020). Chemical activation is carried out by using a chemical agent such as KOH, HNO₃, and ZnCl₂. The chemical activation method can help synthesize groups to suit and improve the surface area of the biochar (ZHOU et al. 2017, 2019; XIANG et al. 2019). Several studies have been developed in this area, including Alahabadi and Moussavi (2017) using activated biochar prepared from *Calligonum Comosum* biomass activated with K₂CO₃ to adsorb atrazine. Mandal et al. (2017) studied the adsorption mechanisms of 2,4-D on biochar in aqueous solutions. Biochars were prepared from various green residues (tea, cucumber, and hardwood). Kirbiyik et al. (2017) conducted studies on the adsorption of Fe(III) metal ions and 2,4-dichlorophenoxyacetic acid on biomass-based activated carbon (sesame seeds) activated by ZnCl₂.

Based on the abovementioned, the importance of the development of biochars by different routes and based on different precursors and their application for pesticides adsorption can be seen. The present study aims to produce, characterize, and test the efficiency of biochars from

cedar bark sawdust (an available industrial waste) physically and chemically activated with ZnCl_2 to remove 2,4-D pesticides and atrazine from an aqueous solution.

4.2 MATERIAL AND METHODS

4.2.1 Synthesis and characterization of CBS, BCC, and BACB

Cedrella fissilis bark sawdust was obtained directly from a wood processing industry in the Rio Grande do Sul, Brazil. The material was oven-dried at 60 °C for 4 h and sieved. The fraction with particle size lower than 1 mm was named CBS and used for adsorption or as a precursor to producing the biochars. For the physical activation, a part of the CBS material was separated and pyrolyzed at a temperature of 800 °C for 1h with N_2 flow of 25 mL min^{-1} , after which it was dried in an oven at 80 °C for 12 h. This material was named BCC. For the chemical activation, the other part of CBS was placed in contact with water and ZnCl_2 at a ratio of 1:1 under agitation (150 rpm) for 12 h to form a paste. Then the paste was pyrolyzed under the previous conditions; after leaching with 6 mol L^{-1} HCl for 12 h was performed. Finally, the mixture was filtered and washed until pH neutral solution and then dried in an oven at 80 °C for 12 h. The final material was named BACB. The pyrolysis apparatus was according to Zazycki et al. (2017).

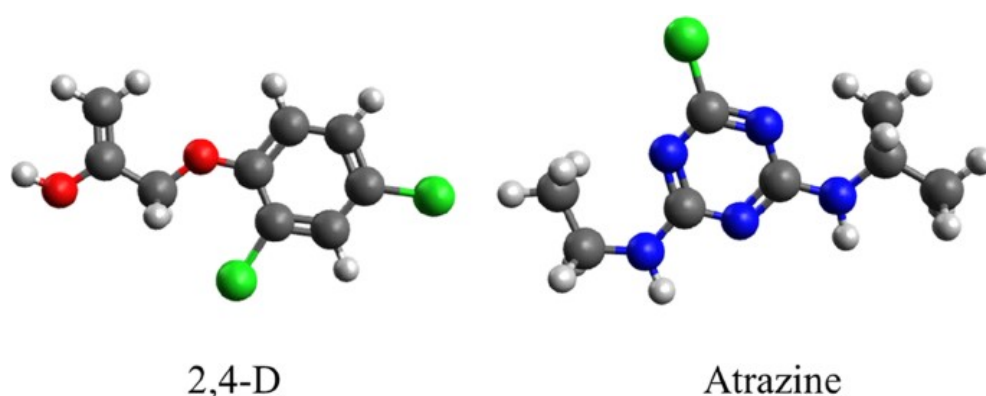
The following techniques characterized CBS, BCC, and BACB: thermogravimetric analysis (TGA), X-ray diffraction (XRD), point of zero charge (pHzpc), scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FT-IR), and BET/BJH methods. Detailed characterization equipment and conditions are reported in previous articles of our group (DOTTO et al. 2012; FRÖHLICH et al. 2019; MEILI et al. 2019a). Some studies previously reported similar analytical procedures (DUARTE et al. 2019; FERRARI et al. 2019; GASPAROTTO et al. 2019; GREDILLA et al. 2019; SAIKIA et al. 2018; OLIVEIRA et al. 2019a, 2019b).

4.2.2 Adsorption tests for atrazine and 2,4-D

The experiments were carried out using previously prepared solutions of the pesticides 2,4-D and atrazine. Figure 8 shows the chemical structure and some relevant chemical data of atrazine and 2,4-D. The pesticide solutions were prepared with distilled water, and analytical grade reagents were used during all experiments. To prepare the stock solution of atrazine,

due to its low solubility in water, it was necessary first to dilute the pesticide in methanol using a 10 mL volumetric flask and then add this solution to a 1000-mL volumetric flask and complete the volume with distilled water, reaching with the concentration of 100 mg L^{-1} . Concerning the 2,4-D, the stock solution was prepared using distilled water without methanol. All the solutions were stored in amber balloons and were further diluted according to the concentration desired. All the batch adsorption experiments were performed using a thermostatic shaker.

Figura 8. Chemical structures of 2,4-D ($221.02 \text{ g mol}^{-1}$) and atrazine ($215.68 \text{ g mol}^{-1}$)



A preliminary test was carried out to compare the adsorption performance of CBS, BCC, and BCAB concerning the pesticides. In this test, the pesticide concentration was 20 mg L^{-1} , the adsorbent dosage was 1.0 g L^{-1} , and the solution volume was 20 mL. The flasks were stirred at 298 K and 200 rpm for 2 h. The adsorbent dosage test was carried out using dosages of 0.5, 1.0, 1.5, 2.0, and 2.5 g L^{-1} of adsorbent. An initial pesticide concentration of 5 mg L^{-1} in 20 mL of solution with the agitation of 150 rpm for 1 h was used.

Kinetic and isothermal experiments were carried out using the best dosage of adsorbent verified in the previous step. For kinetics, a pesticide concentration of 5 mg L^{-1} in 20 mL of solution was used, samples were collected at 0, 5, 10, 20, 30, 40, 50, 60, 120, 180, and 240 min. The isothermal curve was obtained by varying the initial pesticide concentration from 0 to 8 mg L^{-1} in 20 mL of solution, kept under stirring at 150 rpm at 298 K in a thermostatic bath.

Pesticide concentrations were determined by spectrophotometry (Kasuki UV-VIS spectrophotometer, model IL-226-NM). As a result, the percentage of pesticide removal (R , %), adsorption capacity at any time (q_t , mg g^{-1}), and equilibrium adsorption capacity (q_e , mg g^{-1}) were calculated by Eqs. (1)–(3):

$$R = \frac{(C_0 - C_e)}{C_0} \times 100\% \quad (1)$$

$$q_t = \frac{(C_0 - C_t)}{W} \times V \quad (2)$$

$$q_e = \frac{(C_0 - C_e)}{W} \times V \quad (3)$$

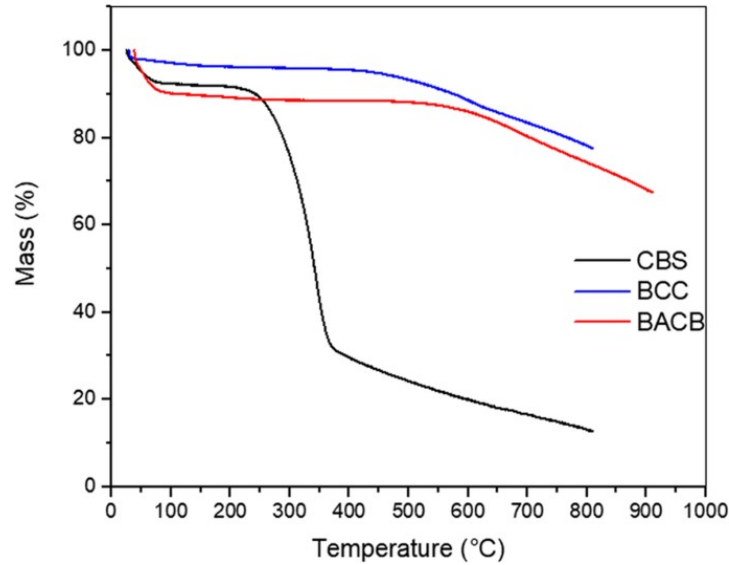
Where: C_0 , C_t , and C_e are the pesticide concentrations at $t=0$, any time and equilibrium, respectively, W is the adsorbent mass (g), and V is the volume of the pesticide solution (L).

4.3. RESULTS AND DISCUSSION

4.3.1. Characteristics of CBS, BCC, and BACB

Observing the TGA profiles of the three adsorbents tested (Fig. 9) makes it possible to verify three phases of mass loss. In the first phase, there is a loss of surface water, in BCC this stage was verified between 29 and 32 °C with mass loss of less than 2%, being the lowest mass loss in this step among the tested adsorbents, as the one with the highest mass loss in this step was BACB about 10% (37.5–100 °C), and CBS had a mass loss of 7.5% (25–85 °C). In the second stage CBS (85–210 °C), BCC (32–420 °C), and BACB (100–550 °C), there is the degradation of the surface functional groups and volatilization of the light compounds. Finally, in the last stage, CBS (>210°C), BCC (>420°C), and BACB (>550°C), the carbon skeletons start to disappear. It is notable that BCC and BACB, due to their physical and chemical activations, respectively, presented a much greater thermal stability than CBS; this can be seen visually in Fig. 9 when comparing the residual mass of the three adsorbents. In the temperature of 800 °C, the residual mass is only 13% for CBS, while for BCC and BACB, respectively, it is 78% and 74%. Therefore, BCC and BACB have thermal stability close to each other and are highly superior to CBS.

Figura 9- TGA curves of CBS, BCC, and BACB



The XRD patterns of CBS, BACB, and BCC are shown in Fig. 10. It is possible to verify the absence of sharp peaks for the three adsorbents, indicating that both do not have a crystalline structure. The tested adsorbents are amorphous due to their lignocellulosic structure confirmed by broad peaks from 10° to 30° for CBS and from 15° to 30° for BCC and BACB, attributed to the lignin content (MEILI et al. 2019a, 2019b). The peaks that appear around 40° to 50° for BCC and BACB correspond to reflections of the disordered micrographic structure, which are characteristic of activated carbon representing the inorganic phase (TOMASSONI et al. 2020).

Figura 10- XRD patterns of CBS, BCC, and BACB

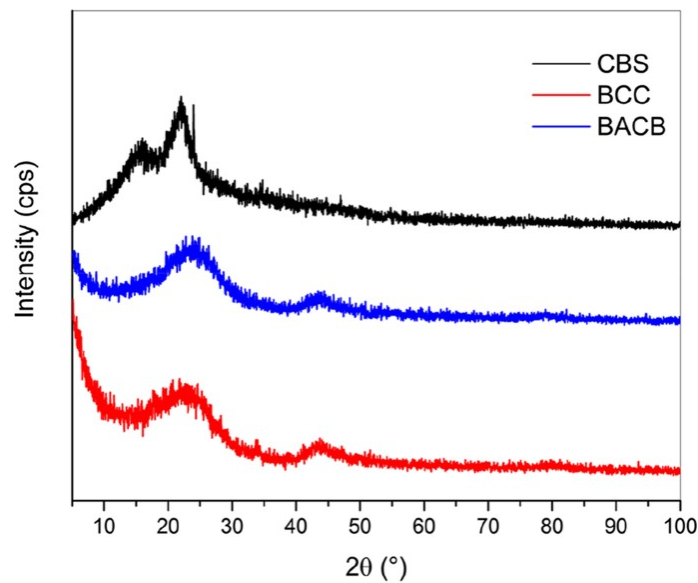


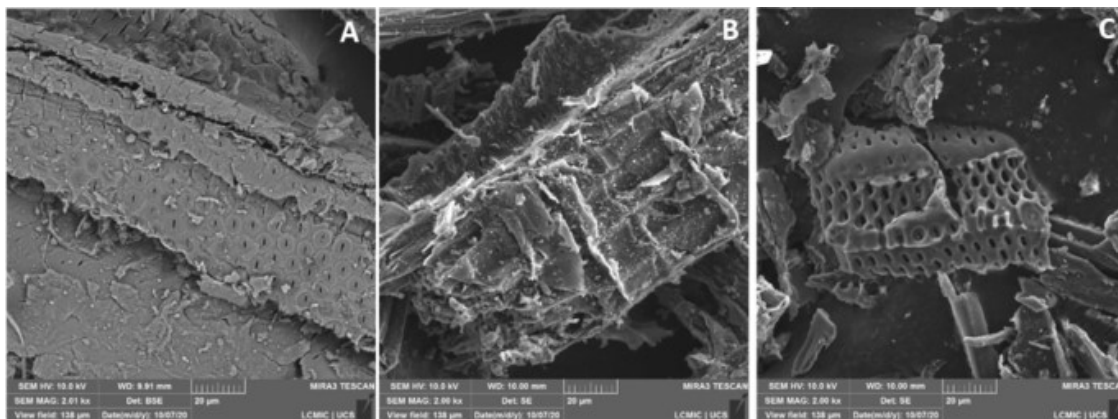
Table 4 shows the values of point of zero charge, surface area, pore volume, and pore diameter for the used adsorbents. The point of zero charge is the pH value at which the charge on the surface of the adsorbent is zero. Thus, in solutions where the pH is lower than pHzpc, the surface of the adsorbent is positively charged. Contrarily, in solutions with a pH greater than pHzpc, the material surface is negative (KHAN et al. 2018). Here, BCC and BCAB presented pHzpc around 7.5, while CBS presented pHzpc of 8.5. This behavior is because the precursor material CBS is composed of lignin, cellulose, hemicellulose, and extractives. These contain N functional groups that are easily protonated, leading to this adsorbent being positive in a wide pH range. However, the chemical and physical activation leads to the volatilization of some of these N groups, making the surface more negative. The volatilization of these light compounds (clear in Fig. 10) also caused an increase in surface area and pore volume values when BCC and BCAB are compared to CBS (Table 4). Thus, it is possible to observe that the pyrolysis with chemical activation causes a higher increase in the specific surface area than the single pyrolysis, where the specific surface area increased from 4.52 to 98.12 m² g⁻¹. Regarding the pore volume and pore diameter, the values were found similar, independent of the method employed, classified as mesoporous materials.

Tabela 4- Textural and physicochemical features of the adsorbents

Adsorbent	pHzpc	Specific surface area (m ² g ⁻¹)	Pore volume (cc g ⁻¹)	Pore diameter (nm)
CBS	8.53	4.52	0.0002	4.12
BCC	7.51	47.31	0.0095	3.66
BCAB	7.47	98.12	0.0099	3.66

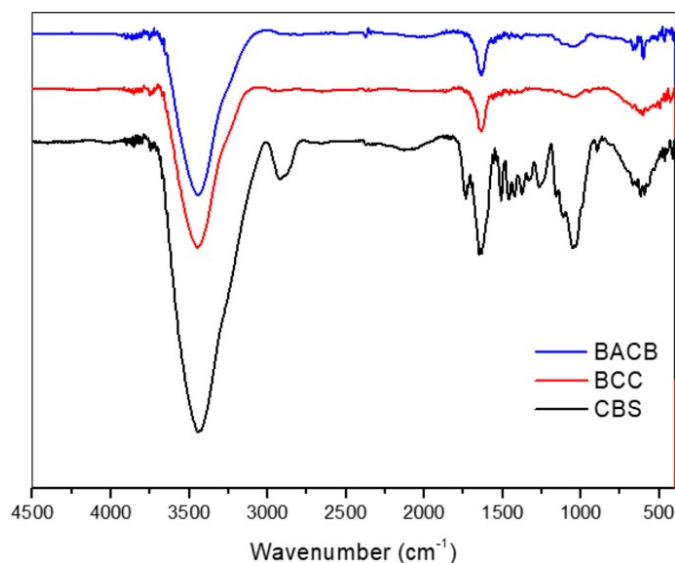
Figure 11 shows the SEM micrograph for the different adsorbents. In Fig. 11a, it is observed that CBS presents a surface with some irregularities and small cavities. This morphology is typical of wood-derived material. After physical activation (BCC) (Fig. 11b), there is a pronounced increase in these irregularities. The pores appear more open; whereas, with chemical activation, there is a visual increase in the area and number of cavities, probably, leading to an increase in porosity (BACB) (Fig. 11c) with the formation of a honeycomb-like structure with regular, well-outlined pores. The increase in surface area and pore volume suggests that the porosity created by ZnCl₂ is due to the spaces left by zinc chloride after washing with acid and water (DEMIRAL et al. 2008).

Figura 11- SEM images of CBS, BCC, and BACB



The FT-IR spectra for each adsorbent are shown in Fig. 12. It is possible to verify several bands showing different functional groups in the structure of cedar bark sawdust (CBS). The main bands observed are those of 3444 cm^{-1} , 2922 cm^{-1} , 1650 cm^{-1} , 1510 cm^{-1} , and 1052 cm^{-1} . At 3444 cm^{-1} , there is a large vibrational elongation typical of the O–H bond in lignin and holocellulose (MEILI et al. 2019b). The signal found at 2922 cm^{-1} is due to the C–H elongation. The 1650 cm^{-1} and 1510 cm^{-1} bands are attributed to the aromatic bond C=C, and the 1052 cm^{-1} band is related to the C–O elongation of the phenolic compounds found in lignin (GEORGIN et al. 2019). After physical and chemical activation (BCC and BACB), the intensity of the bands at 3444 cm^{-1} decreases drastically, indicating that a dehydration reaction occurred in the cellulose after the pyrolysis process (ZHOU et al. 2019). Also, after activations, most organic functional groups are lost (AJMANI et al. 2019).

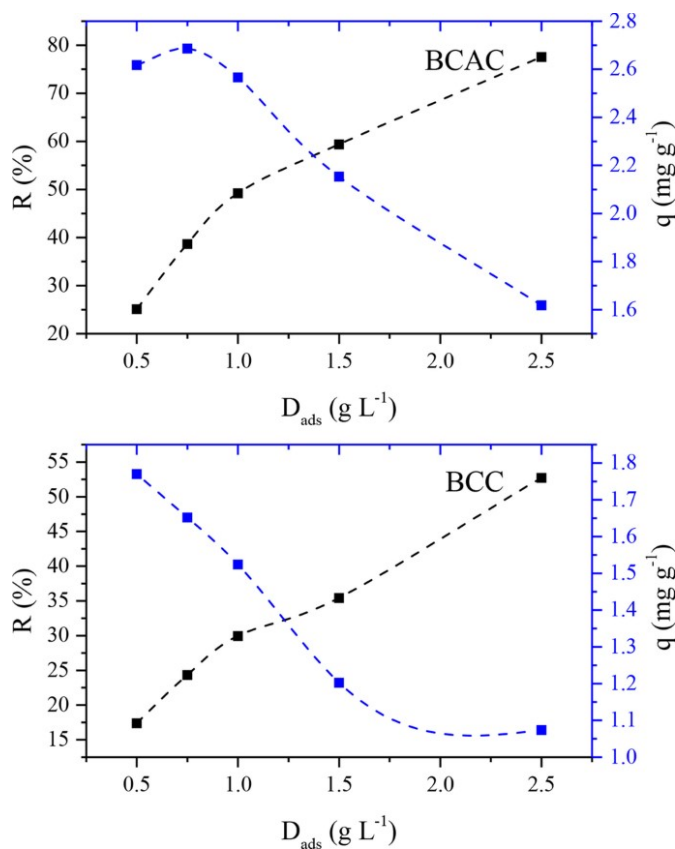
Figura 12- FT-IR vibrational spectra of CBS, BCC, and BACB



4.3.2. Comparison of CBS, BCC, and BCAB as adsorbents and dosage effect

Of the three materials tested, two showed potential to remove the pesticides atrazine and 2,4-D, BCC, and BACB. In contrast, CBS showed zero adsorption capacity, being therefore ineffective in removing these pesticides. This fact justifies the choice to activate CBS for adsorption purposes. Figure 13 shows the effect of BCC and BACB dosages on atrazine adsorption. By varying the dosage of adsorbent from 0.5 to 2.5 g L⁻¹, there was an increase in the percentage of removal from 25 to 77% and from 17 to 52% using BCC and BACB, respectively, which can be explained by the direct relationship between the mass of adsorbent and the number of adsorption sites that interact with the adsorbate. Conversely, the adsorption capacity decreased with the increase of the adsorbent dosage, going from 2.7 to 1.6 mg g⁻¹ and from 1.8 to 1 using BCC and BACB as adsorbents, respectively.

Figura 13. The effect of BCC and BACB dosages on atrazine adsorption



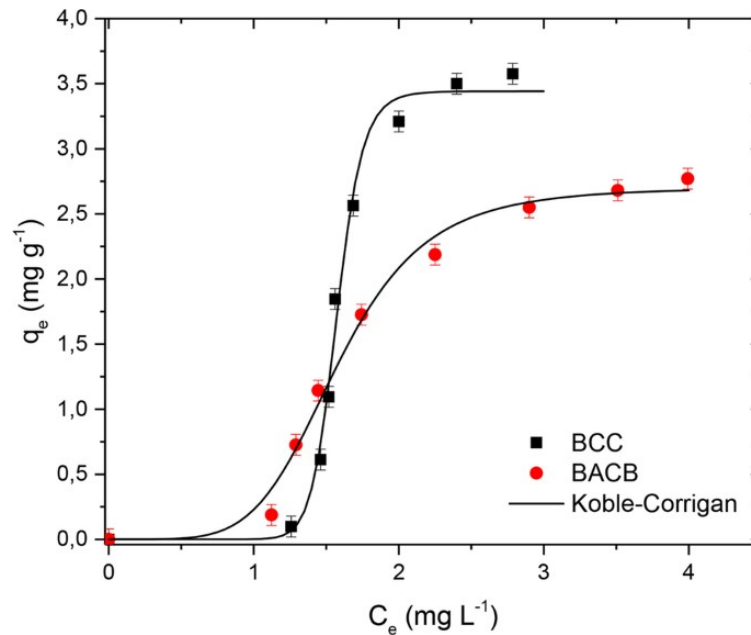
As a good adsorbent must present high adsorption and removal capacity values, the ideal adsorbent dosage was determined by the intersection point of the q and $R\%$ curves, so the dosage of 1.5 g L^{-1} was used for further experiments. In addition, the BCC and the BACB dosage effect were also tested to remove 2,4-D (experimental data is not presented). These tests were conducted using dosages above 2.5 g L^{-1} and concentrations above 20 mg L^{-1} . However, independent of the dosages and the initial 2,4-D concentrations, the adsorption capacities were found below 0.5 mg g^{-1} . Thus, considering this aspect, the adsorbents were considered ineffective for 2,4-D. Therefore, the following experiments were conducted only using atrazine.

4.3.3. Studies of atrazine adsorption isotherms

The isotherm curves for atrazine adsorption by BACB and BCC at 298 K are shown in Fig. 14. Both are favorable, the values of q_e increased with the increase of C_e , and the plateau was reached at the highest values of C_e . However, these isotherms were type S, i.e., at low atrazine concentrations, the adsorption capacity is also low. Subsequently, at certain concentrations, the adsorption capacity suffers a strong increase, tending to a plateau. This

behavior can be explained as follows: when the solution is very diluted (1 mg L^{-1} or less), the atrazine affinity with the adsorbent is low due to the low chemical potential gradient; an increase in concentration make possible a better attraction of the atrazine molecules to the adsorbent surface, increasing the adsorption capacity, and finally, all sites of the BCC and BCAB are occupied.

Figura 14- Atrazine adsorption isotherms on BCC and BACB at 298 K



Again in Fig. 14, it can be seen that the curve of BCC is more inclined and attains a plateau at higher values of adsorption capacity than the curve of BACB. This trend is a clear demonstration that atrazine has a high affinity for BCC. In this sense, we can conclude that, despite the improvements in the textural characteristics caused by the chemical activation, the modifications and rearrangements caused by ZnCl_2 in the surface chemistry of the adsorbent have a negative impact in the case of atrazine adsorption. Finally, it can be stated that for the case of atrazine adsorption, a physical activation (only N_2 pyrolysis) is sufficient.

This work tested three equilibrium models to represent the experimental data: Langmuir, Freundlich (HAMDAOUI and NAFFRECHOUX 2007a), and Koble-Corrigan (HAMDAOUI and NAFFRECHOUX 2007b). The models are presented, respectively, as follows in Eqs. (4)–(6):

$$q_e = \frac{q_m k_L C_e}{1 + k_L C_e} \quad (4)$$

$$q_e = K_F C_e^{1/n_f} \quad (5)$$

$$q_e = \frac{A C_e^{n_{KC}}}{1 + B C_e^{n_{KC}}} \quad (6)$$

Where: q_m is the maximum adsorption capacity for Langmuir (mg g^{-1}), K_L is the Langmuir constant (L mg^{-1}), K_F (mg g^{-1}) $(\text{L mg}^{-1})^{-1/n}$ and $1/n$ are the Freundlich constants; A and B are the Koble-Corrigan constants in $(\text{mg g}^{-1}) (\text{L mg}^{-1})^{n_{KC}}$ and $(\text{L mg}^{-1})^{n_{KC}}$, respectively, and n_{KC} is the exponent constant (dimensionless).

Langmuir and Freundlich's models presented no adequate fitting with the experimental data. For these models, the coefficient of determination (R^2) was lower than 0.80, and the average relative error (ARE) was higher than 30%. Consequently, the parameters were not significant ($p > 0.05$) and consistent in performing any inference. On the contrary, the Koble-Corrigan model represented the experimental data, as presented in Fig. 14 and Table 5. For this model, the values of R^2 were higher than 0.99. Coupled with this, the errors (ARE and MSR) presented little values. In this sense, the atrazine adsorption can be interpreted based on the Koble-Corrigan model and their parameters A , B , and n_{KC} . Koble-Corrigan model combines elements of Freundlich and Langmuir models, being usually applied for adsorption on heterogeneous surfaces. So, it can be stated that BCC and BACB surfaces are heterogeneous with different energy distributions concerning atrazine adsorption. This behavior is corroborated by the different functional groups present on the surface of these materials (Fig. 14). Finally, the n_{KC} value for BCC was three times higher than for BACB (Table 5). This difference is clear in the curve (Fig. 14), where BCC presented a more inclined isotherm. This trend also confirms the high adsorption capacity of BCC.

Tabela 5- Koble-Corrigan parameters for the atrazine adsorption on BCC and BACB

Model	Adsorbent	
	BCC	BACB
	Koble-Corrigan	
A (mg g^{-1}) (L mg^{-1}) ^{nkc}	0.0012	0.2486
B (L mg^{-1}) ^{n_{KC}}	0.0003	0.0920
n _{KC} (dimensionless)	17.59	5.19
R ²	0.9914	0.9910
ARE (%)	11.05	16.77
MSR (mg g^{-1}) ²	0.0238	0.0140

Concerning now the potential of both adsorbents, the maximum value for adsorption capacity found was 3.44 mg g^{-1} for BCC and 2.70 mg g^{-1} for BACB. The comparison of the maximum adsorption capacity results obtained in this study and the conditions for experimenting with other similar works are shown in Table 6. It is noted that comparing the maximum adsorption capacity obtained in this work with studies that used concentrations of atrazine close to that used in the present work, the results obtained in this research were superior and satisfactory. Besides, it can be highlighted that BCC and BACB are adsorbents prepared from eco-friendly and zero-cost wastes.

Tabela 6- Comparison of BCC and BACB with other materials for atrazine adsorption

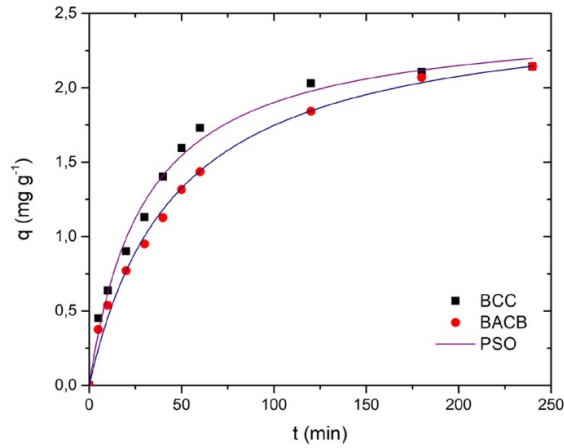
Author	Adsorbent	C ₀ (mg L^{-1})	pH	T (K)	q _{max} (mg g^{-1})
Alahabadi and Moussavi (2017)	Activated biochar from <i>C. Comosum</i>	100	7	338	714.3
Amézquita-Marroquín et al. (2020)	Nanoporous carbons from mangosteen peels	50	7	298	47.7
Chabalala et al. (2021)	PAN nanofibers	10	10	298	0.603
	Modified PAN	10	8	298	0.817

	nanofibers				
Liu et al. (2015)	Chitosan- modified sepiolite	20	6.5	363	17.92
	Activated peanut husk	2.5	6	298	0.42
Grundgeiger et al. (2015)	Organo- beidellites	10	7	298	0.3
This work	BCC	5	7	298	3.44
	BACB	5	7	298	2.70

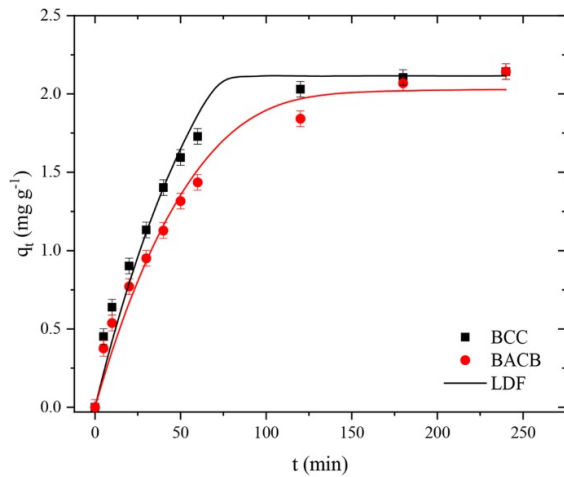
4.3.4. Studies of atrazine adsorption kinetics

Figure 15a shows the atrazine adsorption kinetic profile for BCC and BACB adsorbents. The profiles were typical and similar for both adsorbents. The adsorption capacity was progressively increased until it reached the equilibrium condition at around 240 min. In the first stages, the adsorption rate was fast and then became slow. This behavior occurred because there is a high availability of surface area and adsorption sites for atrazine at the first stages of adsorption. However, along the time, the area and sites are occupied by atrazine.

Figura 15- Atrazine adsorption kinetics on BCC and BCAB at 298 K: a fitted with PSO model and b fitted with the LDF model



(a)



(b)

The pseudo-first-order and pseudo-second-order kinetic models were evaluated in this work. The respective expressions are as follows in Eqs. (7) and (8) (DOTTO et al. 2017):

$$q_t = q_1(1 - \exp(-k_1 t)) \quad (7)$$

$$q_t = \frac{t}{(1/k_2 q_2^2) + (t/q_2)} \quad (8)$$

Where: k_1 (min^{-1}) and k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) are the pseudo-first-order and pseudo-second-order rate constants, respectively; q_1 and q_2 are the theoretical values for the adsorption capacity (mg g^{-1}).

Table 7 shows the kinetic parameters of atrazine adsorption on BCC and BACB. As can be seen in this Table, both models were able to represent the kinetic data. However, the PSO model presented better values for the statistical indicators, and because of this, it was

selected to represent the atrazine adsorption. PFO and PSO are usual reaction models used in many adsorption studies. Still, it is impossible to infer the mass transfer aspects in the adsorption phenomenon from these models. In this sense, for describing the adsorption kinetics, the linear driving force model (LDF) was chosen, where the adsorption rate can be expressed as:

Tabela 7- Kinetic parameters for the atrazine adsorption on BCC and BACB

Adsorbent		
Model	BCC	BACB
Pseudo-first-order		
q_1 (mg g ⁻¹)	2,11	2,09
k_1 (min ⁻¹)	0,0283	0,0205
R^2	0,9900	0,9854
R^2_{adj}	0,9889	0,9838
MSE	0,00577	0,0079
Pseudo-second-order		
q_2 (mg g ⁻¹)	2,47	2,56
k_2 (min ⁻¹)	0,0134	0,0084
R^2	0,9916	0,9938
R^2_{adj}	0,9907	0,9931
MSE	0,0048	0,0034

$$\frac{d\bar{q}}{dt} = k_{LDF}(q^* - \bar{q}) \quad (9)$$

$$\bar{q}(t=0) = 0 \quad (9.a)$$

Where: \bar{q} is the average atrazine adsorption capacity (mg g⁻¹), q^* is the atrazine adsorption capacity related to the atrazine concentration in the liquid phase at equilibrium (mg g⁻¹), and k_{LDF} is the LDF mass transfer coefficient (min⁻¹). The solution of the model starts with the correlation with the best-fitted isotherm model. In this case of this work, the Koble-Corrigan was chosen (Table 5):

$$q^* = \frac{AC_e^{n_{KC}}}{1 + BC_e^{n_{KC}}} \quad (10)$$

The equilibrium concentration can be correlated with the adsorption capacity through the mass balance equation:

$$C_e = C_0 - D_0 \bar{q} \quad (11)$$

C_0 is the initial concentration (mg L^{-1}), and D_0 is the adsorbent dosage (g L^{-1}).

Substituting Eqs. (10) and (1) into (9), we have:

$$\frac{d\bar{q}}{dt} = k_{LDF} \left(\frac{A(C_0 - D_0 \bar{q})^{n_{KC}}}{1 + B(C_0 - D_0 \bar{q})^{n_{KC}}} - \bar{q} \right) \quad (12)$$

Furthermore, the diffusivity for a homogeneous particle can be estimated from the LDF kinetic-lumped parameter:

$$D_S = \frac{R_p^2 k_{LDF}}{15} \quad (13)$$

where R is the adsorbent radius, D_S is the diffusivity ($\text{cm}^2 \text{s}^{-1}$).

The results of LDF implementation are presented in Table 8. The first finding is that the LDF model coupled to the Koble-Corrigan isotherm model could predict the atrazine adsorption kinetics on BCC and BACB (based on the high R^2 and low MSR). This trend implies that, from the mass transport viewpoint, the atrazine adsorption on the adsorbents could be explained based on diffusion in a homogeneous particle. Besides, since the parameters D_S and k_{LDF} were in a near value, it can be seen that, at this initial concentration (5 mg L^{-1}), the BCC and BACB similarly adsorbed atrazine.

Tabela 8- LDF parameters for the atrazine adsorption on BCC and BACB

Model	Adsorbent	
	BCC	BACB
LDF		
$q_{\text{exp}} (\text{mg g}^{-1})$	2.14	2.14
$q_{\text{pred}} (\text{mg g}^{-1})$	2.11	2.03
$k_{LDF} \times 10^4 (\text{s}^{-1})$	2.18	2.37
$D_S \times 10^8 (\text{cm}^2 \text{s}^{-1})$	2.77	2.79
R^2	0.9724	0.9753
MSR ($\text{mg g}^{-1})^2$	0.0144	0.0121

4.4.CONCLUSION

This research has verified the possibility of using cedar bark sawdust (CBS) as a precursor to developing adsorbent materials for atrazine and 2,4-D herbicides. CBS was physically modified by N₂ pyrolysis (BCC) and chemically modified with ZnCl₂+N₂ pyrolysis (BACB). All materials were characterized and applied to remove atrazine and 2,4-D from effluents. The chemical modification has generated material with better textural features, but the surface chemistry depended little on the activation mode. BCC and BACB had the potential to remove atrazine but were not efficient for 2,4-D.

The Koble-Corrigan model was the one that best fit the experimental values, with the maximum value for atrazine adsorption capacity of 3.44 mg g⁻¹ for BCC and 2.70 mg g⁻¹ for BACB. Therefore, it is possible to verify that satisfactory results were obtained, comparing these values with other adsorbents used in similar conditions. Furthermore, the atrazine adsorption on BCC and BACB could be predicted by the LDF model coupled with the Koble-Corrigan isotherm. Finally, it is concluded that BCC and BACB efficiently remove atrazine from water, with BCC having relatively superior performance than BACB. The results demonstrate that it is interesting to conduct new and more detailed experiments to determine the ideal conditions for atrazine adsorption on BCC.

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5. ARTIGO 2: INVESTIGAÇÃO DO BIOCARVÃO DE *CEDRELLA FISSILIS* APLICADO À ADSORÇÃO DO HERBICIDA ATRAZINA DE UM MEIO AQUOSO

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Investigation of biochar from *Cedrella fissilis* applied to the adsorption of atrazine herbicide from an aqueous médium

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Abstract

Biochar was produced from the sawdust of the wood forest species *Cedrella fissilis* and later used as an adsorbent to remove atrazine herbicide from aqueous media. Biochar showed high thermal stability, an amorphous structure, and a highly irregular surface, mainly composed of carbon-containing bonds. The isothermal curves confirmed that the increase in temperature favored the adsorption of the herbicide. The Langmuir model best suited the experimental equilibrium data, with the maximum adsorption capacity of 7.68 mg g⁻¹ at 328 K. The thermodynamic parameters confirmed a spontaneous process of an endothermic nature governed by physical interactions (interactions of van der Waals and hydrogen bonds). Kinetic studies showed that equilibrium was reached within 180 min. The linear driving force model (LDF) showed good statistical adjustment to the experimental data, where it was observed that the diffusion coefficient increased with the concentration of adsorbate. Biochar can be reused in up to three cycles. Finally, the adsorbent showed good efficiency in real water samples from rivers contaminated with atrazine, with 76.58% and 71.29% removal.

Keywords: Adsorption; Atrazine; Biochar; Pesticides; River water.

5.1.INTRODUCTION

Herbicides and pesticides have become increasingly common and necessary in agricultural activities in recent years to control agricultural pests, increase efficiency, and avoid economic damage. Atrazine ($C_8H_{14}ClN_5$) is one of the most widely used chlorine herbicides in agriculture [1,2]. It is a selective herbicide with high efficiency for controlling various broadleaf weeds and grasses, and it is used on a variety of crops, including corn and sugarcane. Because of its harmful effects on health, atrazine has been banned in several European countries since 1991, and the European Union as a whole banned its use in 2004. However, due to the molecule's properties, such as low biodegradability and high persistence, atrazine can still be detected in drinking water samples and even pregnant women's urine [3]. Furthermore, atrazine is still widely used in several developing countries, including China, Brazil, and Iran[4]. Extensive use in agriculture pollutes soil and water, reducing ecosystem function and posing health risks. Serious damage to human organisms includes changes in protein expression, changes at the cellular level, DNA damage, sperm mutagenesis, and disruption of endocrine hormones [2]. In terms of animals, one study found that exposure to certain levels disrupts the sexual evolution of amphibian species in the wild and reduces the overall number of animal species [1]. In addition, the herbicide inhibits photosynthetic activity and, as a result, the development and growth of aquatic plant species in aquatic systems [5,6].

Because of the serious problems caused by atrazine, the scientific community has been working to improve techniques for removing it from the environment in recent years. However, some processes are not flexible, have high costs, are inefficient, and may produce secondary contaminants [7]. Because of its low cost, ease of operation, and high efficiency, adsorption has proven to be a promising alternative [8,9]. The application of transformed biodegradable material onto usable adsorbents such as activated carbon and biochar is a key point in the adsorption process [10]. Biochar can be an effective adsorbent in removing several pollutants due to its highly porous structure, similar to activated carbon [11]. In addition, because activated carbons require reagents in their activation process, whereas biochars do not, the latter have a lower preparation cost and produce fewer effluents[12].

In recent years, several carbonaceous compounds have been successfully used to remove herbicides[13–17,20–24]. The species *Cedrella fissilis* is used in the wood industry. It presents a wood with high resistance, high growth rates, and good adaptability to edaphic

conditions, mainly Minas Gerais and Bahia (Brazil). Due to these factors, commercial plantations have grown, and consequently, the volume of residual biomass in their processing, such as bark and sawdust, has also increased [25]. The bark corresponds to residues generated in the primary splitting of the wood, generally being deposited in the plantation field itself. In contrast, the sawdust corresponds to the waste generated by the secondary splitting and is generated in large volumes in the sawmills. In adsorption studies, the residual bark of the *Cedrella fissilis* was used to remove red 97 from the aqueous solution [25]. However, no reports of the use of *C. fissilis* biochar in the removal of atrazine have been published to date.

In recent years, several carbonaceous compounds have been successfully used to remove herbicides [13–19]. The species *Cedrella fissilis* is used in the wood industry, as it presents a wood with high resistance, in addition to high growth rates and good adaptability to edaphic conditions, mainly in the regions of Minas Gerais and Bahia. Due to these factors, commercial plantations have grown, and consequently, the volume of residual biomass in their processing, such as bark and sawdust, has also increased [20]. The bark corresponds to residues generated in the primary splitting of the wood, generally being deposited in the plantation field itself, whereas the sawdust corresponds to the waste generated by the secondary splitting and is generated in large volumes in the sawmills. In adsorption studies, the residual bark of the *Cedrella fissilis* was used to remove red 97 from the aqueous solution [20]. However, no reports of the use of *C. fissilis* biochar in the removal of atrazine have been published to date.

The current study used sawdust from *Cedrella fissilis* as the raw material for biochar production. Biochar was produced at temperatures of up to 800 °C. Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (DRX), scanning electron microscopy (SEM), thermogravimetric analysis (TGA), and Brunner, Emmet, and Teller (BET) methods were used to examine the properties of the original and carbonized materials. The biochar's ability to absorb atrazine herbicide was then tested. First, dosage and pH analysis were predetermined, followed by isothermal studies and thermodynamic parameter analysis. Next, kinetic studies were investigated and fitted to the linear driving force model (LDF). Following that, studies on adsorbent regeneration were conducted. Finally, the material's performance against a mixture of river water containing atrazine was evaluated.

5.2. MATERIALS AND METHODS

5.2.1. Reactantes employed

For this study, the following compounds were used: hydrochloric acid (HCl), sodium hydroxide (NaOH), and atrazine (chemical formula: $C_8H_{14}ClN_5$, M_w : 215.7 g mol^{-1} , molar volume: $169.8 \text{ cm}^3 \text{ mol}^{-1}$). All chemicals were acquired with an analytical grade from Sigma-Aldrich. Atrazine stock solutions were previously prepared by dissolving 50 mg L^{-1} of atrazine in water. Deionized water was employed in the stock solution preparation and all subsequent dilutions.

5.2.2. Adsorbent synthesis and characterization

Cedrella fissilis sawdust was obtained from a wood industry in the Brazilian state of Rio Grande do Sul. Approximately 600 g of sawdust was oven-dried for 4 h at 333 K. The material was sieved, yielding a fraction with particles smaller than 1 mm in size. The precursor fraction was called CBS, and a portion of it was separated for characterization analysis, while the remainder was used to produce biochar.

Pyrolysis was performed in a quartz tube under an N_2 atmosphere at a flow rate of 0.25 L min^{-1} and a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$ until the temperature reached $800 \text{ }^\circ\text{C}$. When the temperature reached its maximum, the precursor material was kept for 60 min before cooling and maintained for 12 h at 353 K. Finally, the biochar was labeled BBC, with a small portion separated for characterization and the remainder used in atrazine adsorption experiments. The characterization methodology and equipment employed are described in Supplementary Material S1.

5.2.3. BBC and atrazine batch experiments

A thermostatic shaker (MA093, Marconi, Brazil) conducted atrazine adsorption tests on BCC. A spectrophotometer (UV mini 1240, Shimadzu) was used to measure the concentration of atrazine in the liquid phase at a wavelength of 222 nm, corresponding to the herbicide. An initial concentration of 5 mg L^{-1} atrazine in 20 mL was used for the dosage and pH effect studies, with the thermostatic agitator set to 150 rpm and 1 h. The BCC dosages of 0.5, 1.0, 1.5, 2, and 2.5 g L^{-1} were tested. The pH tested ranged from 2 to 10, and the atrazine solutions were adjusted using HCl or NaOH solutions with 0.1 mol L^{-1} concentrations.

The isothermal and kinetic experiments were carried out using the best conditions of pH and dosage of BCC previously verified and a solution volume of 20 mL. Isothermal studies were carried out by varying the temperature in the system at 298, 308, 318, and 328 K for initial concentrations of 0, 5, 8, 10, 15, 18, and 20 mg L⁻¹ of atrazine, kept under stirring at 150 rpm in a thermostatic bath. Kinetic curves were obtained at concentrations of 5, 4, 3, and 2 mg L⁻¹ of atrazine. Samples were collected at 0, 5, 15, 30, 60, 90, 120, 150, 180, 210, and 240 min. Atrazine concentrations were determined by spectrophotometry. The percentage of pesticide removal (R, %), adsorption capacity at any time (qt, mg g⁻¹), and equilibrium adsorption capacity (q_e, mg g⁻¹) were calculated according to the supplementary material S2.

5.2.4. Isotherms and thermodynamic parameters

The Freundlich [26], Dubinin-Radushkevich [27], and Langmuir [28] models were chosen to be fitted to the equilibrium isotherms [29]. Then, according to the methodology proposed elsewhere [30], the thermodynamic parameters were estimated. These equations are listed in Supplementary Material S3 and S4, respectively.

5.2.5. Kinetic modeling

The linear driving force (LDF) model (Equation 1) was chosen to describe the atrazine adsorption onto the BCC. This model considers that the rate of adsorption is dependent on the adsorption gradient between the maximum adsorption capacity and the adsorption capacity at any time [31]. In addition to that, the LDF parameters are related to the diffusion of the atrazine/BCC system. The derivation of the model is shown in Supplementary Material S5.

$$\frac{dq}{dt} = k_{LDF} \left(\frac{q_{mL} K_L (C_0 - D_0 q)}{(1 + K_L (C_0 - D_0 q))} - q \right) \quad (1)$$

$$q(t=0) = 0 \quad (1.1)$$

$$D_S = \frac{R_p^2 k_{LDF}}{15} \quad (2)$$

Where: q is the adsorption capacity (mg g⁻¹), k_{LDF} is the kinetic lumped parameter (min⁻¹), q_L is the Langmuir maximum adsorption capacity (mg g⁻¹), K_L is the Langmuir constant (L mg⁻¹),

C_0 is the initial atrazine concentration (mg L^{-1}), D_0 is the adsorbent dosage (g L^{-1}), R_p is the radius of the adsorbent (cm), and D_s is the diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$).

5.2.6. Parameter estimation and evaluation

The parameter estimations and LDF solutions were done using Matlab. The following built-in functions were chosen for the model parameters: *particleswarm*, *nlinfit*, *lsqnonlin*. Concerning the LDF solution, the *ode15s* was employed for solving the model. In addition, according to the Supplementary material (S5), the best model fit was evaluated.

5.2.7. Thermal regeneration and reuse

The regeneration tests were performed in cycles: first, the adsorbent loaded with atrazine was regenerated through heating. For this, the adsorbent was placed in the oven for 2 h at 300 °C. This process should remove the atrazine from its boiling point (205 °C). Second, 1.5 g L^{-1} of adsorbent was put in contact with atrazine solution (5 mg L^{-1}) and agitated for 4 h at room temperature (298 K) and constant agitation (150 rpm). After that, the atrazine concentration was measured through UV-Vis spectroscopy. This cycle was repeated eight times, always using the previously regenerated adsorbent.

5.2.8. Treatment of river water containing atrazine

As herbicides used in crops are frequently leached by rainwater into water resources, the performance of BCC in real river water samples was analyzed. The Ijuíriver is a watercourse in the state of Rio Grande do Sul, while the Conceição River is a tributary of the Ijuí River. Both are located close to large tracts of crops planted with various crops, mainly corn and soybeans. About 100 mL of sample from each river was contaminated with 5 mg L^{-1} of herbicide. Then, 1.5 g L^{-1} of BCC was added to the solution and stirred at 150 rpm. Samples were collected at 0, 5, 15, 30, 60, 120, and 240 minutes, then centrifuged. The percentage of removal (R, %) was estimated according to Equation 3:

$$R = \left(1 - \frac{A_t}{A_0}\right) 100\% \quad (3)$$

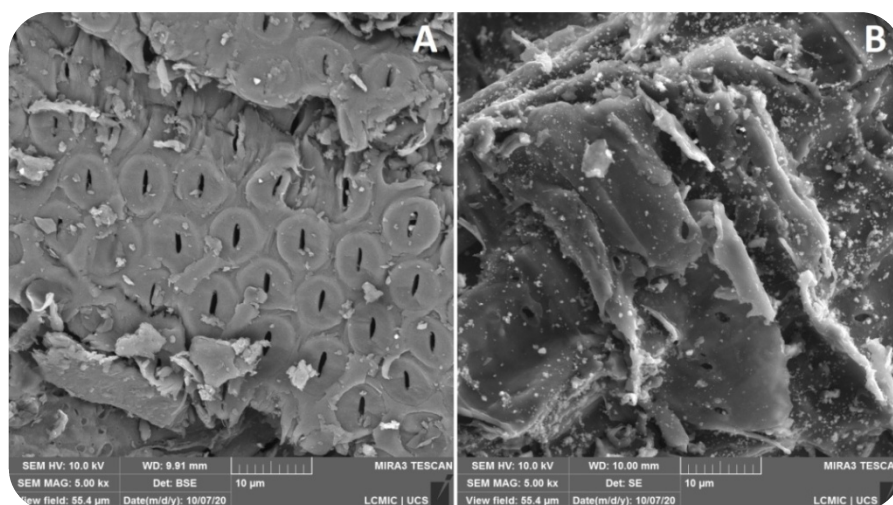
A_0 is the area under the spectrum curve before the adsorption, and A_t is the area under the spectrum curve after the adsorption at different times.

5.3. RESULTS AND DISCUSSION

5.3.1. CBS and CBB characteristics

The scanning electron microscopy images for the CBS (A) and BCC (B) are depicted in Figure 16. The CBS presents a typical morphology of wood-waste-derived biomass, with circular and well-defined structures common for *Cedrella fissilis*. However, after being subjected to pyrolysis up to 800 °C(BCC), the surface presented irregular and uneven shapes, containing new spaces/cavities randomly distributed in the material. Therefore, the structure before and after pyrolysis is defined according to the organic matter present in the biochar [32]. Sbizzaro et al.[33] found a similar behavior when preparing two biochars from bamboo. They observed that the increase in temperature from 350 to 550 °C provided more cavities and irregularities on the material's surface, with greater porosity and, consequently, greater surface area. These new spaces are formed with increased production temperatures due to the release of volatile compounds and a more regular structure[34].

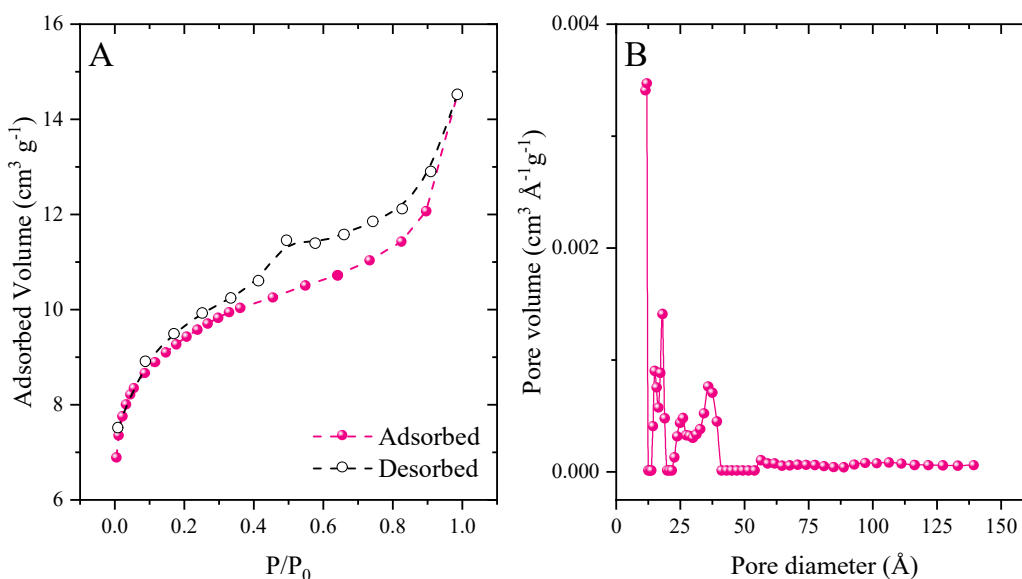
Figura 16- SEM images for CBS (A) and BCC (B) (x5000).



Regarding the textural characteristics, the BCC presented a specific surface area (Figure 17a) of 27.96 m² g⁻¹, which is relatively low when compared to activated carbons [35,36], but high when compared to other existing biochars in the literature[37–39]. Furthermore, the N₂ adsorption isotherms showed a hysteresis loop in the region from 0.4 to 0.9, confirming the presence of mesopores[40]. According to the IUPAC classification, the BCC revealed type IV adsorption-desorption isotherms with a pore volume of 0.018 cm³ g⁻¹ and a pore diameter of 1.13nm (Figure 17b) characteristic of a mesoporous structure [41].

This pore volume value is close to that obtained by Hollister et al.[42], $0.006 \text{ cm}^3 \text{ g}^{-1}$ for corn husk biochar, and by Luo et al. [38], $0.008 \text{ cm}^3 \text{ g}^{-1}$ for corn cob biochar. The modification of the carbon structure of the BCC caused by the increase in temperature in the pyrolysis step results in changes in the textural characteristics, which can favor atrazine adsorption.

Figura 17- N_2 adsorption-desorption isotherms (a) and desorption pore size distribution (b) for the BCC.



The energy-dispersive X-ray spectroscopy (EDS) results are presented in Table 9. It is possible to observe that the carbonization process increases the C % and decreases the O %. This behavior is expected for biochars and activated carbons, where the ratio of oxygen per carbon tends to decrease. Since, during the carbonization process, the hydroxyl groups tend to be broken. Similar results were also reported by Ahmad et al.[43] when studying the pyrolysis of peanut shells and by Peng et al.[44] for the biochar obtained from sugarcane bagasse.

Tabela 9- Amounts of C and O in the biochar.

Element % by weight	CBS	BCC
C (%)	65.65	88.40
O (%)	33.04	10.61
O/C	0.503	0.120

The pH_{pzc} value of the biochar was found 7.51, in this region, the pH presents the smallest variation. In the literature, it is possible to observe that the pH_{pzc} tends to increase as the pyrolysis temperature increases[39]. Therefore, biochars produced at lower temperatures may contain a greater amount of more acidic functional groups, this is due to incomplete degradation [40,41]. Biochars produced at higher temperatures, as is the case in this study, have higher pH_{pzc} values, and a greater amount of basic functional groups[40,41]. This result collaborates with the FT-IR spectra (Table 10), where a reduction of functional groups responsible for decreasing the surface charge was observed.

The main bands observed through the FTIR for CBS and BCC are presented in Table 10. The great vibrational elongation present at 3444 cm^{-1} is typical of the OH bond present in lignin and holocellulose[48]. At 1052 cm^{-1} , there is a CO elongation of the phenolic compounds found in lignin[25]. In BCC, the intensity of the bands at 3444 cm^{-1} decreases drastically, indicating that a dehydration reaction occurred in the cellulose after the pyrolysis process[49].

Tabela 10- Functional groups of CBS and BCC.

Functional Group	Wavenumber (cm^{-1})	
	CBS	BCC
O-H	3444	3444
C-H	2922	-----
C=C	1650	-----
C=C	1510	1510
C-O	1052	-----

The XRD pattern revealed that both adsorbents do not have a crystalline structure due to the absence of sharp peaks. Broad peaks from 10° to 30° for CBS and from 15° to 30° for BCC were verified, confirming its lignocellulosic structure and indicating that the adsorbents are amorphous [48]. For BCC, peaks appearing around 40° to 50° corresponding to reflections of the disordered micrographic structure, which are characteristic of activated carbon, were also verified [44]. The XRD image can be found in Supplementary Material S6.

Figura 18- TGA curves of CBS and BCC.

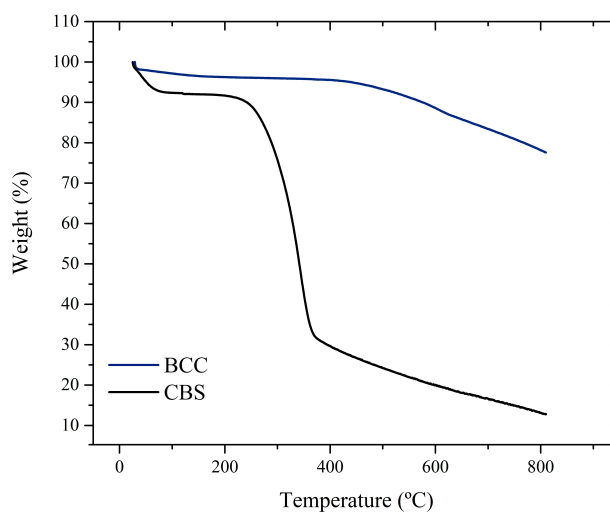
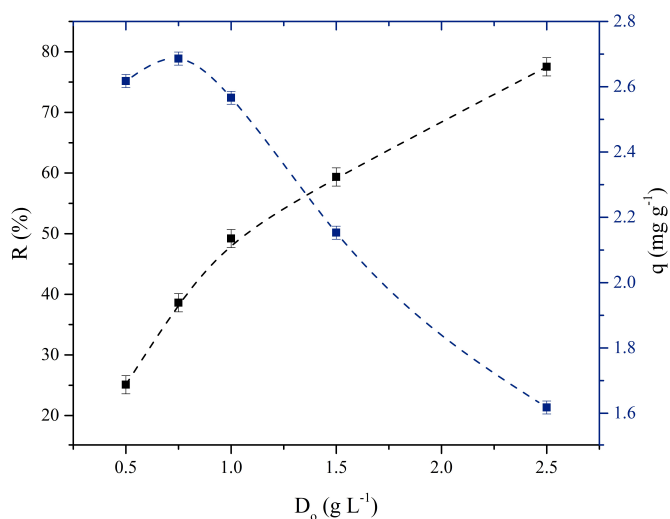


Figure 18 shows the TGA curves for CBS and BCC. For CBS (black line), three well-defined weight loss regions can be visualized. The first stage occurs between 25 to 100 °C and is proportional to the surface water loss [45], corresponding to 7.5% of the total mass. In the second stage, from 290 to 400 °C, around 60% of the total mass was lost. In this stage, the weight loss is relative to the reactions with cellulose and hemicellulose, which release volatile compounds. The final stage was from 400 to 800 °C, and this weight loss could be relative to the lignin degradation or break of the carbonaceous skeleton. The residual weight of CBS was 13%. In parallel, only two weight loss stages were found for BCC (blue line). The first was from 25 to 490 °C, where only 10% was lost. Again, this loss is relative to surface water and the degradation of some remaining functional groups after pyrolysis. The last step was from 490 to 800 °C. This mass loss step is relative to the decomposition of the carbonaceous skeleton but was only 10%. The residual weight of BCC was 78%. These profiles prove that pyrolysis generates biochar with high thermal stability.

5.3.2. Effects of biochar dosage and pH on the atrazine adsorption

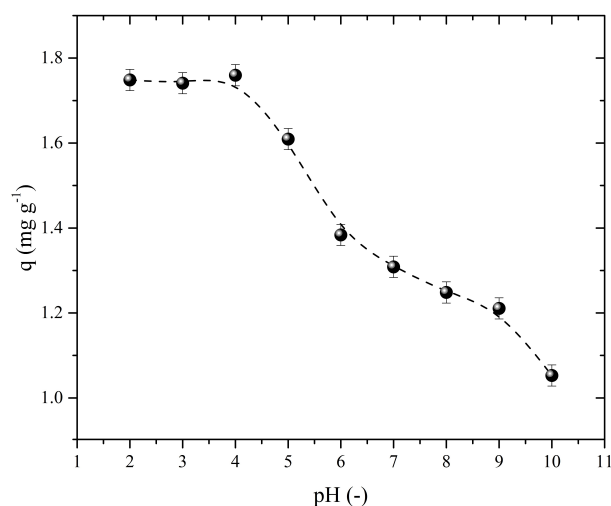
The effect of the BCC dosage on the herbicide adsorption capacity and efficiency is shown in Figure 19.

Figura 19- Effect of BCC dosage on atrazine adsorption.



The increase in removal from 25 to 77% occurred when the dosage was increased from 0.5 to 2.5 g L⁻¹ due to the greater number of adsorption sites. The dosage of 1.5 g L⁻¹ (intersection of the curves) obtained excellent removal values (65%) and capacity (2.3 mg g⁻¹), which were fixed for the following studies. Finally, the adsorption capacity (q) values showed an inverse dependence on removal (R %). Values decreased from 2.6 to 1.6 mg g⁻¹ when the adsorbent dose was increased from 0.5 to 2.5 g L⁻¹ due to the superposition of adsorption sites at higher dosages.

Figura 20- Effect of pH on atrazine adsorption

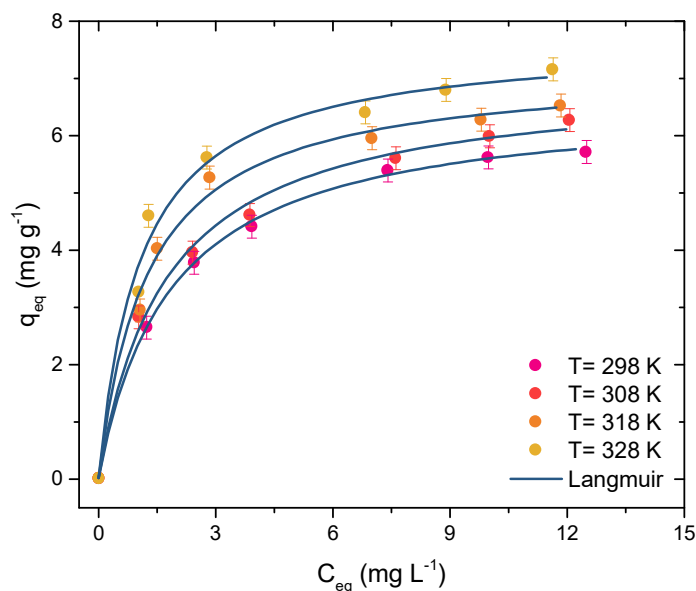


Through Figure 20, it is possible to observe that atrazine adsorption occurs at an acidic pH (between 2 and 4) since as the pH increases from 4 to 10, the capacity decreases drastically. In this pH range (2-4), BCC is protonated since its pH_{pzc} is 7.51. In parallel, atrazine is considered a weak base, with a pK_a at 4.20. At these pH conditions, a fraction of molecules is neutral, and a fraction is in a cationic form of triazine. In this sense, we can point out that the main adsorption interaction type depends less on electrostatic forces. The adsorption interactions are well detailed in the next sections. In the literature, it is possible to find other studies where atrazine adsorption is favored under acidic conditions [23,51,52]. As a result, the pH 4 was set for future experiments.

5.3.3. Adsorption isotherm and thermodynamics

The isothermal curves were determined (Figure 21) to better understand the distribution of adsorbate between liquid and solid phases when equilibrium occurs. The four sequences of experimental data represent the relationship of the herbicide's adsorption capacity (q_{eq}) on the BCC under different concentrations (C_{eq}).

Figura 21- Adsorption isotherms for the atrazine onto the BCC.



First, the shape of the isotherm is analyzed. The curves were convex, with an inclined portion at low C_e values, followed by a plateau. This shape is near to an "L2" type curve. The inclined portion reveals that the proposed adsorbent (BCC) is suitable since higher adsorption capacities coupled with low C_e values could be found. Besides, the plateau shows that the BCC surface was saturated. Concerning now the temperature effect, Figure 21 reveals an endothermic profile. For example, at higher concentrations, the atrazine adsorption capacity on BCC increased from 5.71 to 7.15 mg g⁻¹ with the temperature increase. This behavior may be related to the increase in the energy exchange during the process [53]. Salomon et al.[14] also observed that at the same temperature interval, the atrazine adsorption capacity increased from 194.2 to 211.5 mg g⁻¹, using activated carbon from fruit residues. The same behavior was reported by Alahabadi and Moussavi[54] using activated charcoal prepared from the dry stem of the *Calligonum comosum* plant when the temperature was raised from 283 to 313 K.

The isothermal data fitted the Langmuir, Freundlich, and Dubinin-Radushkevich models (Table 11). The best model was defined through the analysis of statistical coefficients. The Langmuir model provided the best fit, with the highest values of determination coefficient ($R^2 > 0.9870$), adjusted coefficient of determination ($R^2_{adj} > 0.9805$), and lowest

values of ARE (<5.28%) and MSR (<0.099(mg g⁻¹)²). Furthermore, the capacity values of the model are in agreement with the experimental values, increasing with increasing temperature, reaching a maximum capacity of 7.68 mg g⁻¹ at 328 K. It was also observed that the K_L and q_L parameters were directly proportional to temperature, indicating the adsorbate/adsorbent affinity and adsorption capacity were favored at 328 K[25]. In the literature, it is possible to observe several adsorbents that present better adjustment to the Langmuir isotherm in removing atrazine, indicating that herbicide molecules tend to adhere to the surface of the adsorbent through the formation of monolayers, related to homogeneous surfaces[23,33,54–60].

Tabela 11- Isotherm parameters for the atrazine and BCC system.

Model	Temperature (K)			
	298	308	318	328
Langmuir				
q _L (mg g ⁻¹)	6.6403	6.9961	7.1867	7.6791
K _L (L mg ⁻¹)	0.53427	0.57105	0.78507	0.91721
R ²	0.99920	0.99510	0.99281	0.98706
R ² _{adj}	0.99880	0.99265	0.98921	0.98058
ARE (%)	1.0217	3.3252	3.9907	5.2837
MSR (mg g ⁻¹) ²	4.0808×10 ⁻³	2.8646×10 ⁻²	4.7230×10 ⁻²	9.9019×10 ⁻²
Freundlich				
K _F ((mg g ⁻¹)(mg L ⁻¹) ^{-1/n_F})	2.8006	2.9695	3.5193	3.9735
1/n _F (dimensionless)	0.3013	0.3062	0.2608	0.2479
R ²	0.98792	0.99788	0.97333	0.97506
R ² _{adj}	0.98188	0.99682	0.95999	0.96259
ARE (%)	4.9819	2.2524	7.0803	7.0322
MSR (mg g ⁻¹) ²	6.1655×10 ⁻²	1.2406×10 ⁻²	1.7519×10 ⁻¹	1.9076×10 ⁻¹
Dubinin-Radushkevich				
q _{mDR} (mol kg) ⁻¹	0.52530	0.59147	0.40123	0.38685
β (mol J) ²	0.12166	0.11962	0.09867	0.09094
R ²	0.98792	0.99788	0.97333	0.97506
R ² _{adj}	0.98551	0.99745	0.96799	0.97008
ARE (%)	4.2745	1.9304	6.0687	6.0260
MSR (mg g ⁻¹) ²	5.7600×10 ⁻⁴	6.5200×10 ⁻⁴	7.2800×10 ⁻⁴	8.6400×10 ⁻⁴
q _{exp} (mg g ⁻¹)	5.7153	6.2718	6.5275	7.1592
q _{exp} (mol kg) ⁻¹	0.026499	0.029079	0.030265	0.033194

By analyzing the adsorption performance of BCC with other adsorbents present in the literature on atrazine removal, it was possible to observe a good performance of BCC. Salvestrini et al. [51], when using Acid-activated zeolite-rich tufts, they reached a maximum capacity of 1.1 mg g^{-1} , with a concentration varying between 5 and 15 mg L^{-1} . Yue et al.[59] reached a capacity of 5.58 mg g^{-1} for the concentration range of 5 to 20 mg L^{-1} using rice husk as adsorbent. Toledo et al.[61] used bentonite modified with benzyl-chloride-octadecyl-dimethyl-ammonium and reached a capacity of 4.24 mg g^{-1} for a concentration of 10 to 20 mg L^{-1} of atrazine. However, it is also possible to observe adsorbents with higher adsorption capacity values for higher values of concentration ranges. Wei et al.[18,60] reached maximum capacities of 46.3 and 222.22 mg g^{-1} , for minimum and maximum concentrations of 60 to 110 mg L^{-1} , using activated carbon derived from apricot peel and coal-based activated carbon modified with sodium dodecylbenzene sulfonate, respectively.

Table 12 shows the thermodynamic data of atrazine adsorption on BCC. It can be seen that K_e values increased with temperature, and consequently, ΔG^0 values were more negative. This trend indicates that the adsorbate/adsorbent product formation favored 328 K and confirmed the process's spontaneity. Besides, the positive ΔS^0 indicates that some rearrangements occurred on the BCC surface during atrazine adsorption. The positive ΔH^0 sign confirms that atrazine adsorption on BCC was endothermic. The ΔH^0 value of $15.72 \text{ kJ mol}^{-1}$ indicates that physical interactions are involved in atrazine adsorption, specifically Van der Waals interactions or hydrogen bonds, since the value was less than 20 kJ mol^{-1} [62]. This find is consistent with the pH effect, where electrostatic forces were discarded.

Tabela 12- Thermodynamic parameters for the atrazine adsorption onto the BCC.

T(K)	$K_e(-)$	$\Delta G^0 (\text{kJ mol}^{-1})$	$\Delta H^0 (\text{kJ mol}^{-1})$	$\Delta S^0 (\text{kJ mol}^{-1} \text{ K}^{-1})$
298.15	115231.0	-28.899		
308.15	123164.0	-30.029	15.721	0.14920
318.15	169323.0	-31.845		
328.15	197824.0	-33.271		

5.3.4. Kinetics and application of the LDF model

Figure 22 illustrates the kinetic curves of the BCC/atrazine system and represents the time required for the system to reach equilibrium at four concentrations at room temperature (298 K). It was observed that as the concentration was increased, the faster the system came to equilibrium. Thus, the equilibrium was concentration-dependent, being 180, 120, 90, and 60 min for the concentrations of 2, 3, 4, and 5 mg L⁻¹, respectively. As the concentration increased, an increase in the adsorption capacity was also observed, being 0.77, 1.98, 2.09, and 2.3 mg g⁻¹. The behavior was observed mainly for the initial concentrations of 3, 4, and 5 mg L⁻¹, where the capacity increases rapidly in the first minutes, and then the rate decays until reaching equilibrium. A single but suitable explanation for this trend is that the BCC surface is free in the first minutes, causing the molecules to be rapidly adsorbed. Over time, the surface becomes overloaded as where the adsorbate molecules slowly occupy the few available places[63,64].

The linear driving force (LDF) model was applied to the experimental data (Table 13). According to the good values of the statistical parameters ($R^2 \geq 0.9613$; $MSR \leq 0.0379$ (mg g⁻¹)², $ARE \leq 14.86\%$), the LDF force model can be used to represent the BCC/atrazine system. Added to this, the capacity values of the model are in agreement with the values obtained experimentally. Furthermore, the mass transfer coefficient (K_{LDF}) and the diffusion coefficient (D_s) increased with the initial concentration. This behavior confirms that the atrazine adsorption was faster at higher initial concentrations. This effect is related to increasing the atrazine concentration gradient, which leads to higher intraparticle mass transfer and external mass transfer rates [65]. This behavior was also reported by Lazarotto et al.,[13] and Franco et al., [65] when using activated carbons to remove 2,4-dichlorophenoxyacetic and phenol, respectively.

Figura 22- Experimental and predicted data for the adsorption kinetics of atrazine on BCC.

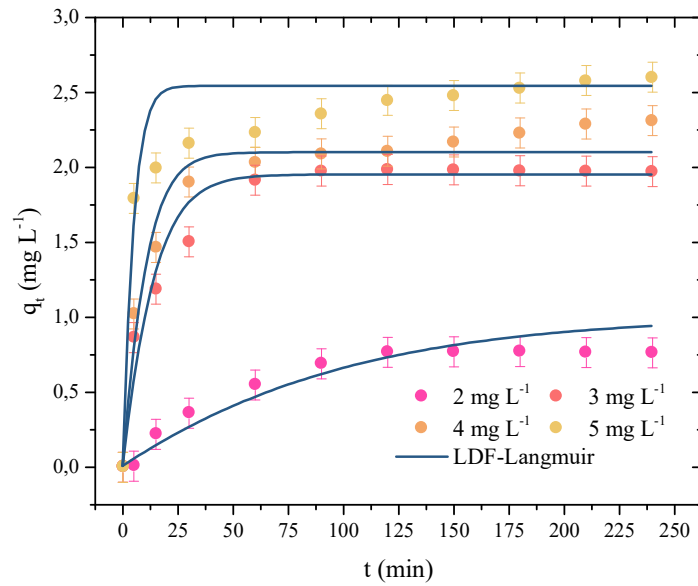


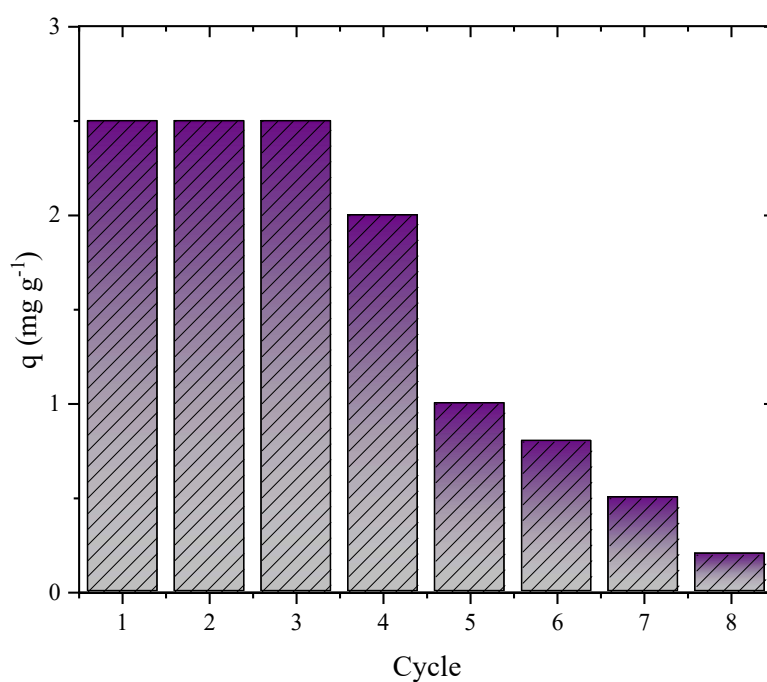
Tabela 13- Estimated parameters for the LDF model.

Model	Atrazine initial concentration (mg L^{-1})			
	2	3	4	5
LDF				
$q_{\text{exp}}(\text{mg g}^{-1})$	0.76330	1.9721	2.3124	2.6019
$q_{\text{pred}}(\text{mg g}^{-1})$	0.83229	2.1213	2.0319	2.4662
$k_{\text{LDF}}(\text{s}^{-1})$	5.9011×10^{-5}	5.4626×10^{-4}	7.5601×10^{-4}	1.7655×10^{-4}
$D_s(\text{cm}^2 \text{s}^{-1})$	1.1866×10^{-8}	5.3105×10^{-8}	1.0393×10^{-7}	2.4898×10^{-5}
R^2	0.98367	0.9182	0.9413	0.9314
ARE (%)	14.030	14.862	9.0507	6.4210
$\text{MSR}(\text{mg g}^{-1})^2$	1.6072×10^{-3}	3.4628×10^{-2}	2.9504×10^{-2}	3.7945×10^{-2}

5.3.5. Regeneration and reuse of BCC

The material's regeneration performance is a major advantage for adsorption technology in terms of economics and sustainability for industrial applications. Therefore, just as the retention of adsorbate is important, its regeneration capacity must also be analyzed. Figure 23 shows the BCC adsorbent regeneration cycles based on the adsorption capacity achieved in each of them. The adsorbent still presents good adsorption in the first three cycles. From the first cycle to the third, the material maintained practically the same efficiency. However, there is a decrease in adsorption capacity from the third cycle. This trend occurred because even though BCC has thermal stability, some adsorption sites on the surface are degraded during consecutive cycles of thermal desorption.

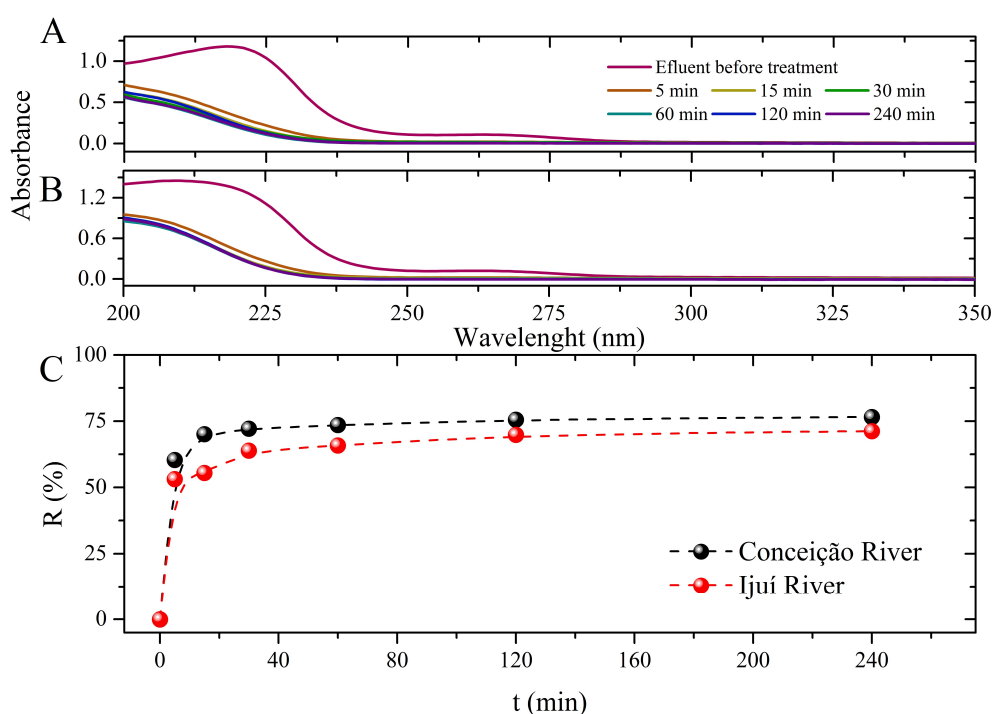
Figura 23- regeneration over eight cycles



5.3.6. River water treatment

The BCC removal efficiency was tested using water from two rivers without any treatment. The two samples containing 5 mg L^{-1} of atrazine were treated with 1.5 g L^{-1} of BCC. The spectrum for the Conceição and Ijuí rivers at different times and the percentage of removal according to time are displayed in Figure 24.

Figura 24- Atrazine spectrum for the (A) Conceição and (B) Ijuí river at different times, percentage of removal according to the river sample, and time (C).

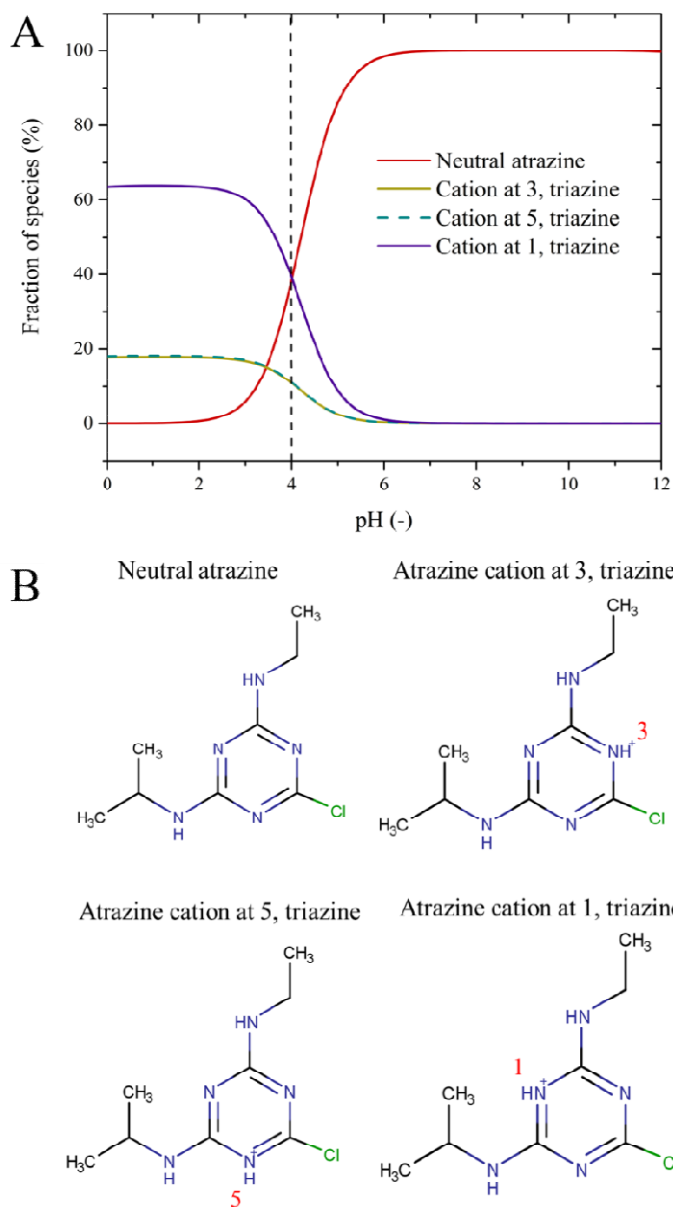


The first aspect to be noticed is that the BCC could adsorb the atrazine from different river samples. Second, equilibrium was achieved in 120 min for both samples, reaching a percentage of removal of 76.58% and 71.29% for the Conceição and Ijuí rivers, respectively. Thus, it is confirmed that BCC has potential atrazine removal in real water samples. In the study by Lazarotto et al. [13], the authors contaminated a water sample from the Jacuí River (Agudo, Rio Grande do Sul, Brazil) with 10 mg L^{-1} of the 2,4-D herbicide. They verified the removal of 70 % using activated charcoal. In the study by Salomon et al.[14], reduced the atrazine concentration from $4.7 \text{ } \mu\text{g L}^{-1}$ to $0.70 \text{ } \mu\text{g L}^{-1}$ in the Jacuí River water, using activated charcoal.

5.3.7. Adsorption mechanism proposal

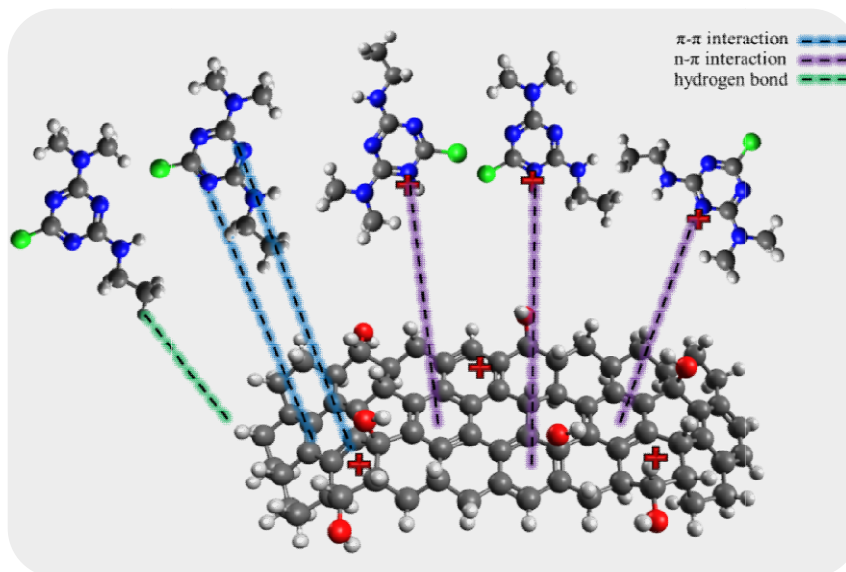
Considering the results from the characterization (FT-IR, EDS, pH_{pzc}), solution pH, pK_a , speciation of the atrazine, and the thermodynamic parameters, it is possible to suggest an adsorption mechanism. The first step is the proposal of the surface of the adsorbent. From the FT-IR before and after the pyrolysis step is expected that the adsorbent surface is mainly constituted of OH and C=C groups, forming aromatic rings and carboxylic groups. In addition to that, for every eight carbons, there is one oxygen. Besides that, the pH_{pzc} was found to be 7.51, meaning that the surface of the BCC will tend to present a positive surface since the optimum pH was found to be 4. Second, the solution pH and pK_a of the atrazine are important to understand how the atrazine is found in the solution. The atrazine is a molecule without oxygen and a triazine (nitrogen/carbon aromatic group), meaning that atrazine has several different ionic states. At pH 4, the atrazine molecules have 4 different states (Figure 25), 38.53% of the atrazine is found in the neutral form; the other percentage is found in the cationic form, divided into three different states: 39.31% of the atrazine is found with nitrogen cation at position 1 of the triazine group; 22% corresponds to the atrazine found with nitrogen cation at positions 3 and 5 of the triazine group (each state is 11%). Last, the enthalpy value indicates that the adsorption has a physical nature. This pattern indicates that the adsorption mainly occurs due to hydrogen bonding, π - π or n - π interactions [66,67].

Figura 25- Atrazine speciation diagram according to MarvinSketch pK_a estimations (A) and different atrazine ionic forms (B).



It should be noted that 61.3% of the atrazine will have a positive charge, and the remaining is found in neutral form. Since at low pH, the surface of the adsorbent may have a positive charge, it is expected that electrostatic force should not occur. However, due to the possibility of the aromatic ring on the surface and the triazine of the atrazine, it is expected that n- π interactions could occur in the form of cation- π interactions. Besides that, traditional hydrogen bonds between the neutral atrazine and adsorbent are also expected. A summary of the possible interactions between the BCC and the atrazine is shown in Figure 26.

Figura 26- Possible interactions in the atrazine adsorption on BCC at pH of 4.



5.4.CONCLUSIONS

The application of residual sawdust from the wood industry chain of the species *Cedrella fissilis* was promising for the production of porous biochar. The developed adsorbent efficiently removed the atrazine herbicide in a synthetic mixture and a contaminated river water sample. Adsorption was favored under acidic conditions for an ideal dosage of 1.5 g L^{-1} of biochar and a temperature of 328 K. The maximum capacity obtained by the Langmuir isotherm was 7.68 mg g^{-1} . Thermodynamic parameters confirmed the endothermic nature. The LDF kinetic model satisfactorily represented the experimental data, obtaining a diffusion coefficient ranging from 5.31×10^{-8} to $2.49 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$. Besides, the biochar can be reused in up to 3 cycles. In water samples from two rivers contaminated with atrazine, biochar obtained maximum removals higher than 70% in a time of 120 min. Finally, it is suggested that n- π , π - π and H-bonds were the main interactions between atrazine-biochar.

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6. DISCUSSÃO GERAL

O primeiro artigo denominado “Adsorção dos pesticidas atrazina e 2,4-D em biochars alternativos de serragem de cedro (*cedrela fissilis*)” teve como objetivo principal averiguar se os materiais adsorventes CBS, BCC e BACB tinham potencial na remoção dos herbicidas 2,4-D e atrazina, bem como determinar suas características e já realizar alguns testes iniciais de determinação de parâmetros. No teste preliminar ficou claro que os adsorventes não foram eficientes na remoção do 2,4-D em baixas concentrações, assim o estudo seguiu apenas com a atrazina como adsorbato, o material precursor CBS também foi descartado do estudo, já que não demonstrou nenhuma eficiência na remoção de ambos os herbicidas. Também foi realizada neste artigo uma série de caracterizações a fim de comparar as características físico-químicas dos adsorventes em estudo. Na maior parte das análises, o BACB e o BCC não apresentaram grandes diferenças entre si, com exceção da micrografia MEV, em que fica evidente que o BACB apresentou um aumento da área e do número de cavidades, com a formação de uma estrutura em forma de favo de mel com contornos regulares e poros bem delineados, devido, provavelmente, aos espaços deixados pelo cloreto de zinco após lavagem com ácido e água, diferentemente do BCC em que essas irregularidades são pouco pronunciadas. Já a diferença entre o BCC e o BACB com relação ao CBS é bem notável, sendo que o BCC e o BACB apresentaram maior estabilidade térmica, diminuição de grupos funcionais e aumento de poros, o que já é esperado resultados das ativações físicas e químicas. Foi determinada a dosagem de adsorvente de $1,5 \text{ g L}^{-1}$ como sendo a ideal para ser utilizada nos próximos estudos.

Considerando o adsorbato e o adsorvente determinados anteriormente, foi produzido o artigo 2 para dar continuidade aos estudos desenvolvidos no primeiro artigo, esse artigo é intitulado “Investigação do biocarvão de *Cedrella fissilis* aplicado à adsorção do herbicida atrazina de um meio aquoso”. Neste artigo os estudos cinéticos, isotérmicos e termodinâmicos são desenvolvidos de uma forma mais ampla, com mais dados. As questões como condição ideal de pH, tratamento de efluente simulado e regeneração também foram abordados. Assim o pH ideal foi verificado como sendo 4, os dados de equilíbrio experimental revelaram uma capacidade máxima de adsorção de $7,679 \text{ mg g}^{-1}$ a 328 K. O processo foi definido como espontâneo, endotérmico e governado por interações físicas. O equilíbrio foi alcançado em 180 min, o que significa um tempo não muito longo para o processo, sendo influenciado pela

concentração de atrazina. O biochar pode ser reutilizado em até três ciclos apresentando baixo custo para regeneração, além disso BCC apresentou boa eficiência de remoção em amostras reais de água de rios contaminados com atrazina, com remoção de 76,58% e 71,29%.

Por fim, os resultados obtidos indicam que o biochar da serragem da casca de cedro (BCC) mostrou-se um adsorvente potencial para ser utilizado na remoção de atrazina da água, sendo um adsorvente ambientalmente correto com bons resultados de adsorção.

7. CONCLUSÃO

Com base nos resultados obtidos foi possível verificar que as modificações aplicadas na serragem da casca de cedro mostraram-se benéficas para o processo de adsorção da atrazina, aumentando a capacidade adsortiva do material precursor.

O adsorvente foi produzido através de uma rota simples derivado de um material natural a serragem de cedro, com alta disponibilidade, sendo um resíduo de baixo custo facilmente encontrado nas indústrias de base florestal. Atingiu a capacidade máxima de adsorção de $7,679 \text{ mg g}^{-1}$ a 328 K. Além disso, o BCC apresentou alta estabilidade térmica, o que permite seu uso em temperaturas mais elevadas, eficiência na remoção do herbicida também em condições próximas às reais, sendo aplicado na água de rio contaminada, obtendo percentual de remoção superior a 70% para as duas amostras testadas. Também verificou-se a possibilidade de regeneração do adsorvente de forma simples e reutilização do mesmo por pelo menos três ciclos. Assim o adsorvente produzido conseguiu aliar economia e alta eficiência de remoção, além de ser ecologicamente correto. Mostrando-se como uma alternativa promissora para o tratamento de águas contaminadas.

Devido a todas essas características e resultados apresentados é interessante dar prosseguimento ao estudo, explorando o potencial do BCC também em outros contaminantes alvos como outros agrotóxicos, fármacos, corantes, entre outros poluentes emergentes de matrizes aquosas.

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APÊNDICE A – MATERIAL SUPLEMENTAR ARTIGO 2

S1. Characterization techniques

The raw material and biochar were characterized according to the following techniques: Fourier transformed infrared spectroscopy (FT-IR; Prestige-21, Shimadzu, Japan). In this step, 50 mg of the adsorbent was pressed with 50 mg dry potassium bromide. The spectra were obtained with a resolution of 4 cm^{-1} with several sequential scans in the range of $4000\text{--}500\text{ cm}^{-1}$. The analyzes were carried out at room temperature (298 K) in a dehumidified room. The analysis regarding particles' surface morphology was performed by scanning electron microscopy (SEM; Vega 3 SB, Tescan, Czech Republic) with a working voltage of 10 kV and magnifications of 500, 1000, and 3000 times. X-ray diffraction (XRD) was used to identify the crystallographic structures with a computer-controlled X-ray diffractometer (Rigaku, Miniflex 300, Japan). A heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ from $25\text{ }^{\circ}\text{C}$ temperature to $800\text{ }^{\circ}\text{C}$ was used. Also, the DSC analysis (DSC, TA instruments) was performed to complement the knowledge about the carbonaceous material's thermal profile

The biochar was characterized as well by the following techniques: The specific surface area (S_{BET}) of the GFRAC sample was estimated based on the Brunauer-Emmett-Teller isotherm (BET), and the total pore volume and average poresize were estimated through the Density functional theory (DFT). The determination of the pH point of zero charge (pH_{pzc}) was performed accordingly: 20 mg of adsorbent was added in 20 mL of 0.1 mol L^{-1} aqueous NaCl solution. The pH was varied from 1 to 12, adjusted with 0.1 mol L^{-1} HCl and NaOH solutions, the experiment was carried out in a thermostatic bath at 298 K and stirring at 150 rpm. Subsequently, the pH was checked with the aid of a pH meter.

S2. Batch adsorption equations

The adsorption capacity at any time (q_t , mg g^{-1}) (Eq. 1), adsorption capacity at the equilibrium (q_e , mg g^{-1}) (Eq. 2), and percentage of removal (R, %) (Eq. 3) are presented as follows:

$$q_t = (C_0 - C_t) \frac{V}{m} \quad (1)$$

$$q_e = (C_0 - C_e) \frac{V}{m} \quad (2)$$

$$R = \frac{(C_0 - C_t)}{C_0} 100\% \quad (3)$$

Where C_0 is the initial concentration of the adsorbate in the liquid phase (mg L^{-1}), C_e is the equilibrium concentration of the adsorbate in the liquid phase (mg L^{-1}), C_t is the concentration of the adsorbate in the liquid phase at any time (mg L^{-1}), m is the mass of adsorbent (g), and V is the volume of solution (L).

S3. Isotherm models

The Langmuir (Eq. 5), Freundlich (Eq.6), Dubinin–Radushkevich (Eq. 7), and Tempkin (Eq. 11) models are represented as follows:

$$q_e = q_L \frac{K_L C_e}{1 + K_L C_e} \quad (5)$$

$$q_e = K_F C_e^{1/n} \quad (6)$$

$$q_e = q_{mDR} \exp(-\beta \varepsilon^2) \quad (7)$$

$$\varepsilon = RT \ln \left(\frac{C_S}{C_e} \right) \quad (7.a)$$

Where q_L is the maximum adsorption capacity of the Langmuir model (mg g^{-1}), K_L is the Langmuir constant (L mg^{-1}), K_F ($(\text{mg g}^{-1}) (\text{mg L}^{-1})^{-1/n}$) is the Freundlich constant, $1/n$ (dimensionless) is the heterogeneity factor, β is the Dubinin–Radushkevich constant ($\text{mol}^2 \text{kJ}^{-2}$), ε Polanyi potential, R is the universal gas constant ($8,314 \text{ J mol}^{-1} \text{ K}^{-1}$), C_S is the solubility (mg L^{-1})

S4. Thermodynamic estimation

The standard Gibbs free energy change (ΔG^0 , kJ mol^{-1}), enthalpy change (ΔH^0 , kJ mol^{-1}), and entropy change (ΔS^0 , $\text{kJ mol}^{-1} \text{ K}^{-1}$) were calculated as the following Equations:

$$K_e = \frac{KM_W \gamma^{ATR}}{\Gamma} \quad (8)$$

$$\Delta G^0 = -RT \ln(K_e) \quad (9)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (10)$$

$$\ln(K_e) = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (11)$$

Where, K_e is the equilibrium constant (dimensionless); K is the constant parameter from the most suitable isotherm fit (L mg^{-1}); M_w is the molecular weight of the atrazine ($215.68 \text{ g mol}^{-1}$), γ^{ATR} is the activity coefficient of atrazine in solution (dimensionless, assuming $\gamma^{\text{ATR}} = 1$), Γ is the unitary activity coefficient of atrazine (1 mol L^{-1}); T is the temperature (K); R is the universal gas constant ($8.31 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1}$).

S5. Adsorption kinetics model

For describing the adsorption kinetics, the linear driving force model (LDFM) was chosen, where the rate of adsorption can be expressed as follows:

$$\frac{dq}{dt} = k_{LDF}(q^* - q) \quad (11)$$

$$q(t=0) = 0 \quad (11.a)$$

Where: q is the adsorption capacity (mg g^{-1}), q^* the ketoprofen adsorption capacity related to the concentration in the liquid phase at equilibrium (mg g^{-1}), k_{LDF} is the LDF mass transfer coefficient (min^{-1}). The solution of the model starts with the correlation with the best-fitted isotherm model. In this case, the Langmuir model was found to be the optimum model for describing the adsorption equilibrium:

$$q^* = q_L \frac{K_L C_e}{1 + K_L C_e} \quad (12)$$

The equilibrium concentration can be correlated with the adsorption capacity through the mass balance equation:

$$C_e = C_0 - D_0 q \quad (13)$$

Where the C_0 is the initial concentration (mg L^{-1}), D_0 is the adsorption dosage (g L^{-1}).

Substituting Equations 5 and 6 into 4:

$$\frac{dq}{dt} = k_{LDF} \left(q_m \frac{K_L(C_0 - D_0 \bar{q})}{1 + K_L(C_0 - D_0 \bar{q})} - q \right) \quad (14)$$

Furthermore, the diffusivity for a homogeneous particle can be estimated from the LDF kinetic lumped parameter:

$$D_S = \frac{R_p^2 k_{LDF}}{15} \quad (15)$$

Where R is the adsorbent radius and D_S is the surface diffusivity ($\text{cm}^2 \text{s}^{-1}$).

S5. Statistical evaluation

The determination coefficient (R^2) (Eq. 12), adjusted determination coefficient (R^2_{adj}) (Eq. 13), average relative error (ARE) (Eq. 14), and mean square error (MSR) (Eq. 15) are represented as follows:

$$R^2 = 1 - \frac{\sum_{i=1}^n (y_{exp} - y_{pred})^2}{\sum_{i=1}^n (y_{exp} - \bar{y}_{exp})^2} \quad (12)$$

$$R^2_{adj} = 1 - (1 - R^2) \frac{(n-1)}{(n-p-1)} \quad (13)$$

$$ARE = \frac{100\%}{n} \sum_{i=1}^n \left| \frac{y_{exp} - y_{pred}}{y_{exp}} \right| \quad (14)$$

$$MSR = \frac{1}{n-p} \sum_{i=1}^n (y_{exp} - y_{pred})^2 \quad (15)$$

Where y_{exp} is the experimental data, y_{pred} is the predicted value, n is the number of experimental values, p is the number of parameters according to the model.

S6. DRX

Figure S27. DRX for CBS and BCC .

