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**Estudo da adsorção de íons metálicos Cu (II) e Pb (II) a
partir das cascas de *Caryocar Coriaceum* Wittm (Pequi)**

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Tese apresentada ao Programa de Pós-Graduação em Química Biológica, da Universidade Regional do Cariri, como requisito para obtenção do Título de Doutor em Química Biológica.

Orientador: Prof. Dr. Raimundo Nonato Pereira Teixeira

Coorientador: Prof. Dr. Francisco José de Paula Filho

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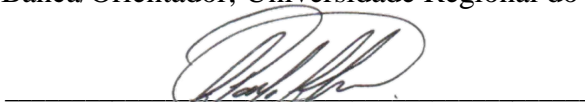
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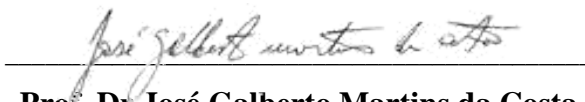
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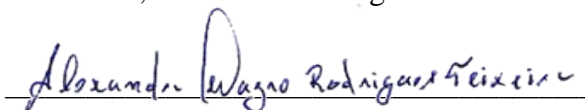
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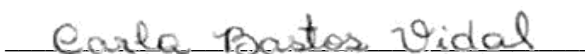
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SÍMBOLOS, SIGLAS E ABREVIATURAS

ΔG° - Variação da energia livre de Gibbs

ΔH - Variação da entalpia

ΔS - Variação da entropia

As - Arsênio

B - Boro

Bd - Constante de Boyd

Bi - Bismuto

b_T - Constante de Temkin

C - Espessura do filme

CCB - Casca do *Caryocar coriaceum* Wittm

Cd - Cádmiio

Ce - Concentração de soluto em equilíbrio na solução

Co - Cobalto

CONAMA - Conselho Nacional do Meio Ambiente

Cr - Cromo

Cu - Cobre

D - Coeficiente de Difusão

D - R - Dubinin-Radushkevich

E - Energia livre

FAAS - Espectrofotometria de Absorção Atômica por Chama

FRX - Fluorescência de Raio X

Hg - Mercúrio

IBGE - Instituto Brasileiro de Geografia e Estatística

K_0 - Constante de adsorção

K_d - Coeficiente de Difusão Intrapartícula

K_F - Constante de capacidade de adsorção de Freundlich

K_L - Constante de Langmuir

K_T - Constante Isotérmica de Temkin

MEV - Microscopia Eletrônica de Varredura

Mn - Manganês

Mo - Molibdênio

Ni - Níquel

Pb - Chumbo

pH_{pzc} - pH de potencial de carga zero

q_D - Constante de D – R

q_e - Capacidade adsorptiva em equilíbrio

q_{máx} - Capacidade máxima de adsorção do adsorvente

R - Constante universal dos gases

Sb - Antimônio

Se - Selênio

SEBRAE - Serviço Brasileiro de Apoio às Micro e Pequenas Empresas

SEMACE - Superintendência Estadual do Meio Ambiente

T - Temperatura

T_{ex} - Tempo de exaustão

TGA - Análise Termogravimétrica

Zn – Zinco

ZTM – Zona de transferência de massa

β - Constante relacionada à energia livre

ε - Potencial de Polanyi

Estudo da adsorção de íons metálicos Cu (II) e Pb (II) a partir das cascas de *Caryocar Coriaceum* Wittm (Pequi)

RESUMO

Introdução: O descarte inadequado de resíduos contendo metais tóxicos resulta em grandes problemas ambientais. A adsorção destaca-se, dentre outras técnicas, como poderosa alternativa tecnológica na remoção de contaminantes tóxicos presentes em soluções aquosas, caracterizando-se por ser técnica eficiente, de fácil operação e de baixo custo, pois faz uso de materiais abundantes e de origem natural. **Objetivo:** Este estudo objetivou avaliar o uso das cascas do *Caryocar Coriaceum* Wittm, resíduo da fruta conhecida como Pequi, como possível bioadsorvente para a remoção de íons Cu^{+2} e Pb^{+2} de soluções aquosas sintéticas. **Metodologia:** Para isso, resíduos deste material foram coletados em um mercado público municipal, onde foram lavados, secos à temperatura ambiente, triturados, peneirados em malha de 32 mesh, lavados e então secos em estufa. Após preparado o material, este foi submetido às técnicas de caracterização e utilizado nos ensaios de cinética, isoterma e termodinâmica de bioadsorção dos íons Cu^{+2} e Pb^{+2} . **Resultados e discussões:** Após os experimentos, foi observado que a capacidade de adsorção foi favorecida com o aumento da temperatura para a adsorção dos íons Cu^{+2} , aumentando de 16,8 (5 °C) para 20,4 mg. L⁻¹ (35 °C), caracterizando processo endotérmico, enquanto para os íons Pb^{+2} , reduziu de 15,6 (5 °C) para 13,5 mg. L⁻¹ (35 °C), caracterizado por ser processo exotérmico. O modelo cinético que melhor se enquadrou ao processo adsorptivo dos íons metálicos estudados foi o de pseudo segunda ordem. A adsorção em ambos os casos ocorreu por quimissorção. O modelo isotérmico de Langmuir foi o que apresentou melhores enquadramentos dos dados experimentais, indicando capacidade máxima de adsorção de 26,9 mg g⁻¹ para os íons Cu^{+2} e 106,38 mg g⁻¹ para os íons Pb^{+2} . **Conclusões:** Portanto, pode-se concluir que a casca do *Caryocar Coriaceum* Wittm, apresentou-se como boa alternativa para ser usada como bioadsorvente para processos adsorptivos de íons Cu^{+2} e Pb^{+2} presentes em soluções aquosas sintéticas.

Palavras-Chave: Adsorção, Metais Tóxicos, Casca do Pequi, *Caryocar Coriaceum* Wittm, Pequi.

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Study of the adsorption of Cu (II) and Pb (II) metal ions from the barks of *Caryocar Coriaceum* Wittm (Pequi)

Introduction: The improper disposal of waste containing toxic metals results in major environmental problems. Bioadsorption stands out, among other techniques, as a powerful technological alternative in the removal of toxic contaminants present in aqueous solutions, characterized as an efficient, easy-to-operate and low-cost technique, as it uses materials of natural origin and plentiful. **Objective:** This study aimed to evaluate the use of the bark of *Caryocar Coriaceum* Wittm, a residue from the fruit known as Pequi, as a possible bioadsorbent for the removal of Cu⁺² and Pb⁺² ions from synthetic aqueous solutions. **Methodology:** For this purpose, residues of this material were collected in a municipal public market, where they were washed, dried naturally, crushed, sieved in a 32 mesh sieve, washed and then dried in an oven. After preparing the material, it was submitted to characterization techniques and used in the kinetic, isotherm and thermodynamic tests of the bioadsorption of Cu⁺² and Pb⁺² ions. **Results and discussion:** After the experiments, it was observed that the adsorption capacity was favored with the increase of the temperature for the adsorption of the Cu⁺² ions, increasing from 16.8 (5 °C) to 20.4 mg. L⁻¹ (35 °C), featuring an endothermic process, while for Pb⁺² ions, it decreased from 15.6 (5 °C) to 13.5 mg. L⁻¹ (35 °C), characterized by being an exothermic process. The kinetic model that best fit the adsorptive process of the studied metal ions was the pseudo second order. Adsorption in both cases occurred by chemisorption. The Langmuir isothermal model fitted better to the experimental data, indicating a maximum adsorption capacity of 26.9 mg g⁻¹ for Cu⁺² ions and 106.38 mg g⁻¹ for Pb⁺² ions. **Conclusions:** Therefore, it can be concluded that the bark of *Caryocar Coriaceum* Wittm, is a good alternative to be used as a bio-adsorbent for adsorptive processes of Cu⁺² and Pb⁺² ions present in synthetic aqueous solutions.

Keywords: Adsorption, Toxic Metals, Pequi's Bark, *Caryocar Coriaceum* Wittm, Pequi.

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IMPORTÂNCIA/RELEVÂNCIA PARA A SOCIEDADE

O descarte inapropriado de resíduos contendo metais tóxicos ocasiona sérios problemas ambientais e de saúde humana, causando dores gástricas, náuseas, vômitos, diarreia severa, câncer nos pulmões e trato digestivo, como também outras doenças como Alzheimer, Parkinson e Menkes. Para tanto devem ser aplicados tratamentos nestes resíduos, de modo a evitar tais problemas. Um dos tratamentos de resíduos contendo metais tóxicos em destaque é a bioadsorção, por se tratar de técnica barata e de fácil operação. Neste estudo objetivou-se preparar um adsorvente a partir do rejeito descartado das cascas do pequi, resíduo facilmente encontrado no meio ambiente, em feiras ou mercados, durante sua safra, e verificar se este seria capaz de remover metais tóxicos de ambientes aquáticos, por meio da técnica da adsorção, buscando assim solucionar tanto o problema ambiental de seu descarte no meio ambiente, como o tratamento econômico de águas contendo metais tóxicos.

1 INTRODUÇÃO GERAL

O crescimento industrial das civilizações trouxe consigo grandes benefícios para o desenvolvimento humano, melhorando sua qualidade de vida por meio da criação de novos produtos, bem como tornando estes mais resistentes, elevando assim sua vida útil.

Dentre os diversos setores industriais, o setor galvanoplástico, apresenta relativa importância, visto o crescente número de produtos que se encontram disponíveis no mercado com tratamento de cobertura metálica em sua superfície para promover sua funcionalidade.

Segundo Barros (2016), diversas indústrias apresentam processos galvanoplásticos como etapa produtiva, como indústrias metal mecânicas, microeletrônicas, eletroeletrônicas, automobilísticas, mobiliárias e de semi joias, todas visando adquirir vantagens, como proteção contra corrosão, maior resistência mecânica, maior condutibilidade elétrica e efeitos estéticos desejados, fazendo assim com que seja etapa importante durante o processo industrial.

Porém, apesar de contribuir com melhoria de vida humana, esse crescimento industrial também promoveu aumento de impactos ambientais negativos, onde muitas vezes são gerados rejeitos líquidos, sólidos ou gasosos que ao serem descartados de forma inadequada, acabam por comprometer a qualidade do meio ambiente (HUSSAIN et al., 2021).

Do ponto de vista do setor galvanoplástico, efluentes contendo concentrações elevadas de metais tóxicos são gerados e por constituir-se de contaminante altamente tóxico para o ambiente, estes devem ser tratados de maneira a gerar efluente compatível com as normas preconizadas pela legislação ambiental vigente (MORENO-BENAVIDES; PEÑA-SALAMANCA; BENÍTEZ-CAMPO, 2019).

Atualmente, os efluentes produzidos pelo setor supracitado, sofrem apenas alteração do seu pH como forma de tratamento, gerando precipitado com elevada concentração de metais tóxicos, fazendo com que empresas tenham gastos, quanto ao seu descarte, uma vez que deverá ser destinada à aterros sanitários de classe I.

De acordo com Rengel (2004) e Tavana, Pahlavanzadeh e Zarei (2020) em pequenas quantidades, alguns metais desempenham papel essencial para plantas e alguns animais, participando de processos de biossíntese e de outros processos essenciais envolvendo ácidos nucleicos e carboidratos, melhoria de ossos e tecido no corpo humano, bem como na manutenção da integridade das membranas biológicas. Porém, quando disposto em concentrações excessivas, estudos como os de Acharya, kumar e rafi (2018); Costa, Mendonça e Wysard junior (2017), Kovács et al.(2009), Maaloul et al. (2020) e Rodrigues et al. (2007),

apontam que tais metais configuram-se como grandes impactantes ao meio ambiente, podendo provocar danos aos seres vivos e efeitos como dores gástricas, náuseas, diarreia, sangramentos, câncer dentre outras.

Com isso a busca por alternativas tecnológicas viáveis para o tratamento deste tipo de efluente torna-se importante, uma vez que devem ser minimizados os impactos ambientais, porém sem gerar gastos elevados para o seu tratamento.

Diante disto, destaca-se a técnica de biossorção, onde são utilizados materiais lignocelulósicos como base adsorvente de substâncias dissolvidas em soluções líquidas, pois os mesmos se enquadram no grupo de materiais porosos e do ponto de vista financeiro, apresentam baixo custo, uma vez que são encontrados facilmente na natureza e muitas vezes tratados como resíduos.

O *Caryocar Coriaceum* Wittm, conhecido popularmente por pequi, trata-se de um fruto encontrado no bioma do cerrado Brasileiro, apresentando grande produção na região da Chapada do Araripe, entre os estados do Ceará, Pernambuco e Piauí, e exerce importante papel socioeconômico para esta região, sendo facilmente encontrado à venda em mercados e em pequenas barracas em rodovias. De acordo Morais et al.(2016), do fruto, muitas vezes apenas o caroço é utilizado, para a preparação de pratos típicos e obtenção da amêndoa, sendo que esta fração corresponde a aproximadamente 6% de seu peso, enquanto que a casca corresponde à 84%.

Alguns estudos como os de Maciel et al. (2017) e Ramos e Souza (2011), indicam algumas aplicações para a casca do pequi, que variam desde a preparação de farelos para a alimentação de bovinos e caprinos até a preparação de adubos orgânicos (compostagem) para a produção de hortaliças, porém como as cascas não apresentam mais valor comercial, facilmente encontram – se descartadas nos mercados públicos e feiras livres, gerando grandes volumes de resíduos a serem dispostos em lixões ou aterros.

Com isso, este estudo almejou avaliar a aplicabilidade de tecnologia alternativa para o tratamento de efluentes contendo metais tóxicos, fazendo-se uso da técnica de adsorção utilizando-se como adsorvente, as cascas do *Caryocar Coriaceum* Wittm.

1.1 ESTRATÉGIAS DE PESQUISA

Para ser possível obter análise crítica a respeito da real capacidade de aplicação do material em estudo como bioadsorvente de metais tóxicos em soluções aquosas, torna-se necessário o uso de técnicas analíticas com o intuito de se obter informações acerca das características físicas e químicas deste material, para com estas, determinar se tais condições

são favoráveis ao processo de adsorção, bem como possibilitar a previsão de determinados parâmetros operacionais do processo adsorptivo.

Com isso, algumas técnicas de caracterização de materiais foram utilizadas tanto antes, como após a aplicação do adsorvente ao processo de adsorção de metais tóxicos, objetivando-se avaliar o efeito da adsorção sobre os resultados obtidos por tais técnicas.

Assim, a espectroscopia na região do infravermelho por transformada de Fourier (FTIR), foi aplicada com o intuito de se determinar os possíveis grupos funcionais presentes no material adsorvente e com isso, verificar se houve alguma alteração no espectro apresentado antes e após o processo adsorptivo, possibilitando assim, inferir o provável mecanismo adsorptivo envolvido no sistema (LOULIDI et al., 2020; RAY; MISHRA; KALAMDHAD, 2021; TAVANA; PAHLAVANZADEH; ZAREI, 2020).

Outra técnica utilizada, que foi aplicada com o intuito de reforçar os dados apresentados pela técnica de FTIR, bem como verificar um possível favorecimento de determinados grupos funcionais em adsorver os metais tóxicos, foi a titulação de Boehm, em que determina a presença de grupos funcionais oxigenados (Carboxílico, Fenólicos e Lactônicos) presentes na superfície do adsorvente (ARSLANOĞLU et al., 2021; CUI et al., 2021; SALAME; BANDOSZ, 2001).

Através da análise termogravimétrica (TGA) verifica-se as perdas de massas do adsorvente através do aumento da temperatura e possibilita o estudo da estabilidade térmica do material, bem como indica possíveis temperaturas para gerar modificações químicas que podem, ou não, favorecer o processo adsorptivo (BREDA et al., 2017).

A morfologia do adsorvente foi estudada através das técnicas de Microscopia Eletrônica de Varredura (MEV) e Difração de Raios-X (DRX), onde foram verificadas características da superfície do material, tais como porosidade e se a mesma apresenta tendências de ser amorfa ou não, bem como se houve alguma modificação em sua estrutura após a realização ensaios adsorptivos. Estas informações que podem justificar o favorecimento de processos adsorptivos (BANERJEE et al., 2018; DENG et al., 2017).

Com a Fluorescência de Raios X (FRX) e a Microscopia Eletrônica de Varredura acoplada de detector por Espectroscopia por Energia Dispersiva (MEV-EDS), permitiu-se inferir a respeito da composição química do adsorvente antes e após o processo de adsorção de metais tóxicos, indicando se houve ou não alteração na concentração de tal metal após realizada a adsorção (LIU; LIAN, 2019).

Os materiais apresentam diferentes comportamentos adsorptivos quando submetidos em condições de pH diferentes, podendo serem favorecidos a atrair determinadas espécies com a variação deste parâmetro. A determinação do pH_{pzc} , possibilita conhecer o valor de pH da

solução em que o adsorvente apresentará características neutras, assim, para valores abaixo ou acima deste, a carga líquida no adsorvente torna-se positiva ou negativa, respectivamente (AL-QODAH; YAHYA; AL-SHANNAG, 2017; LOULIDI et al., 2020).

Por fim, todos os ensaios adsortivos (cinética, isoterma e termodinâmica) foram avaliados mediante a determinação da concentração do metal em estudo presente na solução, antes e após o processo de adsorção, e foram determinados através da técnica de espectrofotometria de absorção atômica por chama (FAAS), técnica esta fortemente aplicada para realização de tal estudo (COSTA et al., 2020; ŠABANOVI et al., 2020; ŠABANOVIĆ et al., 2015; SANTANA et al., 2020; TARLEY; ARRUDA, 2004).

Este estudo está estruturado em formas de capítulos, tendo em vista favorecer o repasse das informações relacionadas à pesquisa. No capítulo I é apresentada toda a revisão teórica embasadora do trabalho, onde contemplam-se informações a respeito de setor galvanoplástico no Brasil e na região do Cariri Cearense, os efeitos negativos causados pelos metais tóxicos aos seres vivos, a legislação vigente para lançamento de metais tóxicos em corpos aquáticos no Brasil e no estado do Ceará, uma breve indicação dos métodos de remoção de metais tóxicos em meios líquidos, destacando-se o processo adsortivo e a biossorção, comentando a respeito dos fatores que influenciam esta técnica e os tipos de adsorventes, contextualizando o pequi. Também é apresentada toda a fundamentação teórica por trás dos estudos de cinética, isoterma e termodinâmica utilizados.

No capítulo II, III e IV são apresentados os manuscritos dos artigos técnicos aceitos e submetidos, com os resultados deste estudo, em periódicos científicos. Sendo no capítulo II, o artigo intitulado de **“Equilibrium, kinetics and thermodynamics of lead (II) adsorption in bioadsorbent composed by *Caryocar coriaceum* Wittm barks”**, publicado no periódico científico **“Chemosphere”**, Fator de impacto **“IF: 7.086 (2022)”**, **“Qualis A1”** na área CBII, no capítulo III o artigo técnico publicado no periódico científico **“Sustainable Chemistry and Pharmacy”**, Fator de impacto **“IF: 4.508 (2022)”**, **“Qualis A1”** na área CBII, intitulado de **“Kinetic and thermodynamic study of copper (II) IONS biosorption by *Caryocar Coriaceum* Wittm bark”** e, por fim, no capítulo IV o artigo técnico submetido no periódico científico **“Process Safety and Environmental Protection”**, Fator de impacto **“IF: 6.158 (2022)”**, **“Qualis A1”** na área CBII, intitulado de **“Competitive Bioadsorption of Pb⁺² and Cu⁺² Ions by *Caryocar Coriaceum* Wittm Barks”**. As primeiras páginas das versões publicadas dos artigos, são apresentadas nos anexos A e B.

Por fim, no capítulo V apontam-se as considerações finais, bem como as perspectivas para investigações futuras obtidas no estudo.

2.1. OBJETIVO GERAL

Estudar a aplicação como adsorvente das cascas do *Caryocar coriaceum* WITTM, popularmente conhecido como Pequi, na remoção de íons metálicos Cu^{+2} e Pb^{+2} , em sistemas de batelada mono e multielementares, presentes em soluções aquosas sintéticas.

2.2. OBJETIVOS ESPECÍFICOS

- Caracterizar o bioadsorvente desenvolvido antes e após os ensaios de bioadsorção, utilizando-se as técnicas analíticas instrumentais MEV-EDS, FTIR, FRX, DRX e TGA.
- Estudar a Cinética de adsorção dos íons metálicos Cu^{+2} e Pb^{+2} , pelo bioadsorvente, investigando os mecanismos envolvidos neste processo.
- Realizar estudo termodinâmico para determinação de espontaneidade da adsorção.
- Determinar o grau de eficiência de adsorção dos íons metálicos Cu^{+2} e Pb^{+2} pelo bioadsorvente em estudo.

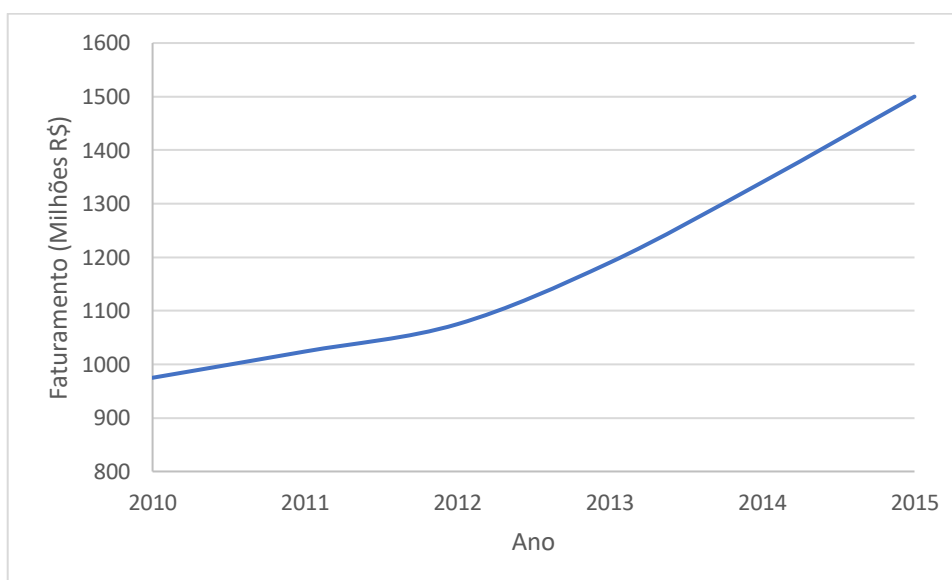
2.3. OBJETIVOS E QUESTIONAMENTOS

O principal motivo da realização deste estudo científico foi estudar um material adsorvente, capaz de remover íons metálicos Cu (II) e Pb (II), presentes em soluções aquosas, possibilitando o tratamento dessas águas e, com isso, ocasionando a remediação de ambientes contaminados com metais tóxicos. Um requisito essencial atribuído para a iniciação da pesquisa foi que o material fosse facilmente encontrado no ambiente e que apresentasse baixo custo, com isso pensou-se na utilização dos resíduos das cascas do pequi, pois durante sua safra, facilmente encontram-se descartados nos mercados e como normalmente é consumido apenas o seu caroço, muitos volumes de resíduos são gerados. Com isso, pensou-se em resolver tanto a problemática da redução/reutilização dos resíduos de casca de pequi, quanto a remoção de contaminantes de íons metálicos presentes em ambientes aquáticos utilizando a técnica de bioadsorção.

3.1. GALVANOPLASTIA NO BRASIL E NA REGIÃO DO CARIRI – CE

Segundo Perez; Corrêa; Pires, (2014), a galvanoplastia pode ser descrita como o processo de depositar camadas metálicas sobre um objeto através da aplicação dos princípios fundamentais do fenômeno da eletrólise, como reações de oxidação e redução, geralmente com o objetivo de proteger contra a corrosão ou para fins estético-decorativos.

O setor galvanoplástico envolve vários tipos de indústrias, com as mais diversas aplicações, como por exemplo, a indústria automobilística, da construção civil, de utensílios domésticos, informática, telefonia, joias e bijuterias, dentre outros. Levando-se em consideração o setor de Bijuterias e Folheados, tal setor apresenta grande crescimento no Brasil, onde conforme dados apresentados na Figura 1, obtidos do estudo de mercado realizado pelo Serviço Brasileiro de Apoio às Micro e Pequenas Empresas (SEBRAE), em 2017, é possível observar que o segmento apresenta, desde 2010, crescimento no faturamento obtido, atingindo aproximadamente R\$ 1500 milhões em 2015.



Fonte: adaptado de SEBRAE (2017)

Figura 1:Faturamento do setor de Bijuterias e Folheados no Brasil.

Para a região Metropolitana do Cariri, localizada ao extremo Sul do estado do Ceará, no Nordeste brasileiro, e constituída pelos municípios de Barbalha, Caririagu, Crato, Farias Brito, Jardim, Juazeiro do Norte, Missão Velha, Nova Olinda e Santana do Cariri (Figura 2), o setor de joias e folheados apresenta-se como de grande importância econômica. De acordo com Cordeiro (2015), este setor conta com 40 empresas formais e cerca de 250 informais, sendo responsável por gerar um faturamento anual de aproximadamente R\$ 60 milhões, na venda de cerca de 30 toneladas de produtos por mês.

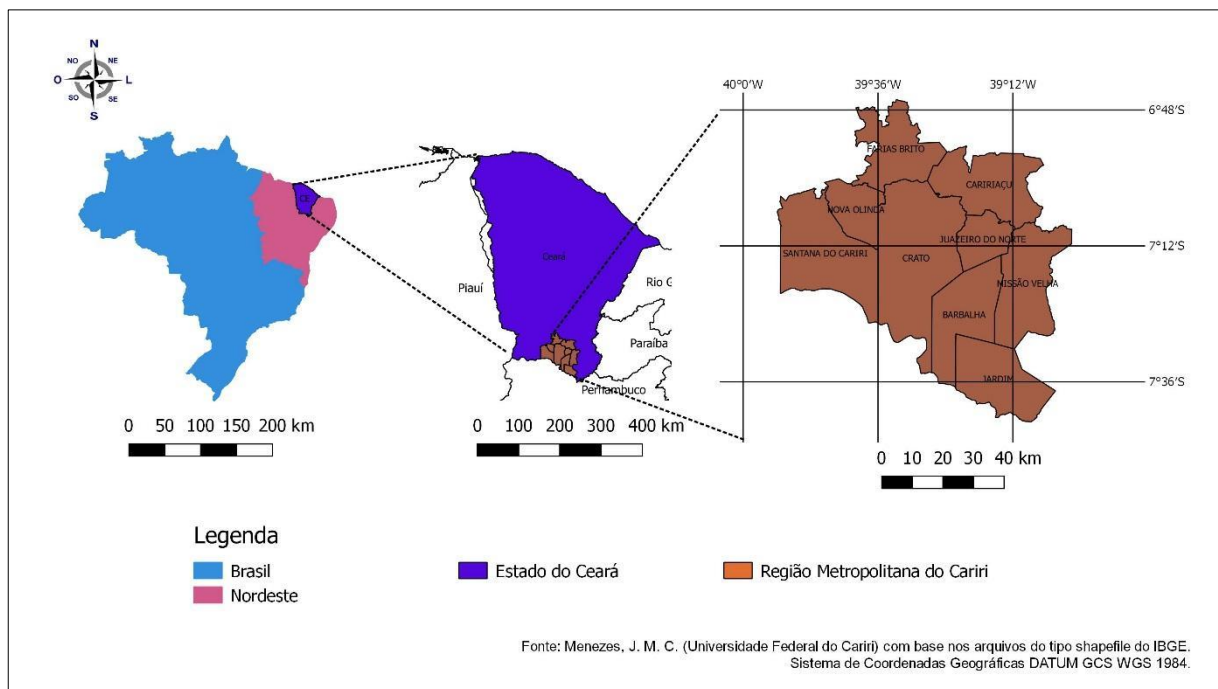


Figura 2: Localização da Região Metropolitana do Cariri.

Conforme a notícia divulgada pelo SEBRAE (2007), a cidade de Juazeiro do Norte situa-se em terceiro lugar como centro produtor de folheados no Brasil, ficando atrás de Limeira, no estado de São Paulo (aproximadamente 450 empresas), e Guaporé, no Rio Grande do Sul (com cerca de 160 empresas).

Delbianco (2008), ressalta que o setor galvanoplástico gera resíduos contendo diversas substâncias químicas que oferecem sérios riscos à saúde da população, tais como ácidos, peróxidos, sais de cianeto, álcalis fortes e metais tóxicos, destacando este último por seu potencial de toxicidade e por apresentar característica bioacumuladora nos seres vivos.

3.2. METAIS TÓXICOS

Lima e Merçon (2011); Pereira (2017) e Pino (2005), destacam que o grupo dos metais tóxicos abrange um total de 40 elementos químicos, com densidade superior a 5 g/cm³ ou número atômico superior a 20. Geralmente esta designação é atribuída aos elementos Cádmio (Cd), Cobre (Cu), Chumbo (Pb), Cromo (Cr), Mercúrio (Hg), Níquel (Ni) e Zinco (Zn), ou mesmo a uma substância tóxica oriunda de um descarte inadequado de um rejeito no meio ambiente.

De acordo com Acharya; Kumar e Rafi (2018), os metais tóxicos podem entrar no suprimento de água através de resíduos industriais e domésticos, ou até mesmo pela chuva ácida que pode solubilizar metais tóxicos nos solos e arrastá-los para córregos, lagos, rios e lençóis freáticos.

Para Shamim (2018), os metais tóxicos apresentam orbitais 'd' incompletos eletronicamente, permitindo a formação de compostos complexos, podendo ou não serem redox ativos, e com isso apresentam importante papel como "oligoelementos" em reações bioquímicas sofisticadas e são cofatores importantes para metaloproteínas e enzimas.

Para Costa, Mendonça e Wysard Junior (2017), do ponto de vista biológico, os metais tóxicos são divididos em 2 grupos, sendo eles os micronutrientes, que são aqueles essenciais para o crescimento de todos os tipos de organismos, porém em pequenas concentrações (elementos Arsênio (As), Boro (B), Cobalto (Co), Cobre (Cu), Molibdênio (Mo), Manganês (Mn), Níquel (Ni), Selênio (Se) e Zinco (Zn), e o grupo sem função biológica determinada, onde são tóxicos, promovem a ocorrência de doenças e bioacumulação, quando encontrados em elevadas concentrações (elementos Cd, Hg, Pb, Antimônio (Sb) e Bismuto (Bi)).

Segundo Santana (2018), em ambientes aquáticos, aéreos e no solo, sejam por origens naturais ou antrópicas, os metais tóxicos podem ser adsorvidos pelos vegetais e animais, causando graves intoxicações ao longo da cadeia alimentar, devido às suas elevadas reatividades.

Acharya; Kumar; Rafi, (2018), Barros et al. (2006); Costa; Mendonça; Wysard Junior (2017) e Rodrigues et al. (2007), ressaltam que os metais tóxicos, têm recebido atenção especial, pois estes apresentam-se como extremamente tóxicos, não são degradados quimicamente e nem biologicamente, são bioacumulados na cadeia produtiva, afetando uma grande variedade de organismos e causando sérias doenças, tais como dor gástrica, náuseas,

vômitos, diarreia grave, hemorragia e até câncer no trato digestivo e nos pulmões, mesmo em concentrações em torno de mili ou microgramas.

3.3. EFLUENTES E LEGISLAÇÕES

Tendo em vista minimizar os impactos ambientais, algumas legislações são estabelecidas quanto às condições e padrões de lançamento de efluentes, como é o caso da resolução nº 430, de 13 de maio de 2011, do Conselho Nacional do Meio Ambiente (CONAMA, 2011). Nela são encontrados alguns padrões nacionais para lançamentos de metais tóxicos em corpo receptor. Os parâmetros estão representados na Tabela 1.

No estado do Ceará, a responsável pela legislação ambiental é a Superintendência Estadual do Meio Ambiente (SEMACE), onde disponibiliza na resolução do Conselho estadual de meio ambiente COEMA nº02, de 02 de fevereiro de 2017, com padrões para lançamentos de efluentes com metais tóxicos, sendo este construído baseado na legislação federal do CONAMA.

Oliveira (2011), destaca que 96% de toda a água doce disponível para consumo é proveniente de água subterrânea e, de acordo com do o Instituto Brasileiro de Geografia e Estatística (IBGE), em 2017, cerca de 68,5 % dos municípios eram abastecidos por água subterrânea. Para a região do Cariri cearense, Veríssimo e Cavalcante (2000) ressaltam que o abastecimento público de água nas cidades de Juazeiro do Norte e Barbalha, é feito através de água subterrânea, complementado por fontes no município do Crato.

Tendo em vista isso, além de padrões de lançamento de efluentes para água de corpos aquáticos superficiais, também devem ser observados os padrões para qualidade de águas subterrâneas, uma vez que este apresenta relativa importância regional, bem como nacional.

Tabela 1: Padrões de lançamento de metais tóxicos em corpo receptor, segundo CONAMA 430/2011.

PARÂMETROS	CONCENTRAÇÃO MÁXIMA*
ALUMÍNIO	10
ARSÊNIO TOTAL	0,5
BÁRIO TOTAL	5,0
BORO TOTAL	5,0
CÁDMIO TOTAL	0,2
CHUMBO TOTAL	0,5
COBRE DISSOLVIDO	1,0
CROMO HEXAVALENTE	0,1
CROMO TRIVALENTE	1,0
ESTANHO TOTAL	4,0
FERRO DISSOLVIDO	15,0
MANGANÊS DISSOLVIDO	1,0
MERCÚRIO TOTAL	0,01
NÍQUEL TOTAL	2,0
PRATA TOTAL	0,1
SELÊNIO TOTAL	0,30
ZINCO TOTAL	5,0

*dados indicados em mg/L.

Fonte: Adaptação CONAMA (2011).

Diante disso, o Ministério da Saúde (2011) apresentou , os padrões de potabilidade de água, relacionados às substâncias químicas que representam riscos à saúde, onde são destacados dados mais rigorosos para nos valores máximos permitidos, como exemplo: As (0,01 mg.L⁻¹), Cd (0,005 mg.L⁻¹), Pb (0,01 mg.L⁻¹), Cu (2,0 mg.L⁻¹), Cr (0,05 mg.L⁻¹), Hg (0,001 mg.L⁻¹), Ni (0,07 mg.L⁻¹) e Se (0,01 mg.L⁻¹).

3.4. MÉTODOS DE REMOÇÃO DE METAIS TÓXICOS

Muitos processos podem ser utilizados para a remoção de metais tóxicos em águas, podendo serem divididos em três grupos, segundo a natureza de seu método, são eles Métodos químicos, físicos e biológicos. Alguns desses processos são apresentados na Tabela 2.

Como pode-se observar na Tabela 2, a maioria dos processos necessitam de condições especiais para atendê-las, onerando-o e conseqüentemente inviabilizando sua aplicação.

Diante disto, surge-se a necessidade de serem desenvolvidas novas alternativas tecnológicas para remoção de metais tóxicos em águas e águas residuárias. De acordo com Maaloul et al. (2020), várias investigações sustentam a visão de que a adsorção continua sendo uma das técnicas preferidas para a remoção de poluentes de meios aquosos, uma vez que é segura, barata e fácil de usar, porém, a busca por adsorvente de fácil obtenção, destacou-se atualmente, por gerar maior oferta de material e com custo ainda mais reduzido, passando a chamar a técnica de bioadsorção.

Tabela 2: Processos para remoção de metais tóxicos.

Natureza	Processo	Descrição	Vantagem	Desvantagem
Método Físico	Osiose Reversa	Separação por membrana semipermeável a uma pressão superior à pressão osmótica.	Elevada eficiência	Custo elevado
	Ultrafiltração	Separação por membranas porosas e pressão	Elevada eficiência	Custo elevado
	Troca iônica	Separação por forças eletrostáticas usando resinas de troca	Seletividade de Metais	Disponível para poucos números de metais
Método Químico	Eletrodiálise	Separação por membrana íon – seletiva semipermeável	Elevada seletividade	Custo elevado
	Precipitação química	Adição de coagulantes	Barato Fácil operação	Lodo Tóxico
	Adsorção (carvão ativado)	Adsorção de metais em uma matriz	Elevada eficiência	Redução da eficiência adsortiva após sua regeneração.
Método Biológico	Fitoremetiação	Bioacumulação dos metais em plantas	Barato Fácil operação	Longo tempo para remoção e regeneração da planta

Fonte: Adaptado de Ahayla e Ramachandra (1995), Al-Qodah, Yahya e Al-Shannag (2017), Shamim (2018) e Tarley e Arruda (2004)

3.4.1 Adsorção e o Processo Adsorptivo

De acordo com Ruthven (1984), A adsorção é uma operação de transferência de massa, na qual se estuda a capacidade de substâncias presentes em fluidos líquidos ou gasosos (adsorvatos) de serem concentrados na superfície de um determinado sólido (adsorvente) aplicado a este meio, com isso possibilitando a separação dos componentes desses fluidos.

Quando utilizado materiais de origem biológicas como adsorventes, a adsorção passa a ser chamada de bioadsorção. Os bioadsorventes podem ser compostos por microrganismos, vegetais macroscópicos ou mesmo por biomassa morta como partes de tecidos específicos de vegetais, fibras naturais, plantas, algodão, dentre outras (WANG; GUO, 2020; BARROS, 2006; MORIN-CRINI et al., 2018; PINO; TOREM, 2011).

Trabalhos na literatura como os de Acharya, Kumar e Rafi (2018) e Morin-Crini et al. (2018), ressaltam que o fato desses biomateriais serem abundantes na natureza, disponíveis em grandes quantidades, apresentar baixo custo, e poderem ter potencial como materiais bioadsorventes devido às suas características físico-químicas e estrutura particular, podendo ou não apresentar modificações químicas, os tornam grandes alternativas para a sua aplicação em processos de adsorção.

Crini et al. (2018) apontam que a separação é baseada na adsorção seletiva, ou seja, seletividade termodinâmica e/ou cinética dos contaminantes por um adsorvente devido a interações específicas entre a superfície do material adsorvente e os contaminantes adsorvidos (transferência de massa simples da fase líquida para a fase sólida).

Ruthven (1984), ressalta que o processo adsorptivo pode ocorrer por dois caminhos, sendo eles a adsorção física e a química, diferenciados pela força de atração existente entre o adsorvente e o adsorbato, conforme é apresentado na Tabela 3.

Tabela 3: Tipos de Adsorção.

TIPO DE ADSORÇÃO	CARACTERÍSTICAS
FÍSICA	<ul style="list-style-type: none"> ● Baixo calor de adsorção; ● Interações adsorbato-adsorvente regidas por forças de Van der Waals; ● Processo reversível (Moléculas adsorvidas podem ser desprendidas sem nenhuma alteração em suas estruturas quando desorvidas). ● $\Delta H^\circ < 25 \text{ KJ/mol}$
QUÍMICA	<ul style="list-style-type: none"> ● Sítios adsorptivos carregados positivamente, negativamente; ● Quimissorção (ligações químicas entre as valências livres do adsorvente e do adsorbato); ● Adsorção específica (Depende da natureza das espécies envolvidas). ● $\Delta H^\circ > 25 \text{ KJ/mol}$

Fonte: Adaptado de Teixeira (2015) e (ATKINS; JONES; LAVERMAN, 2018).

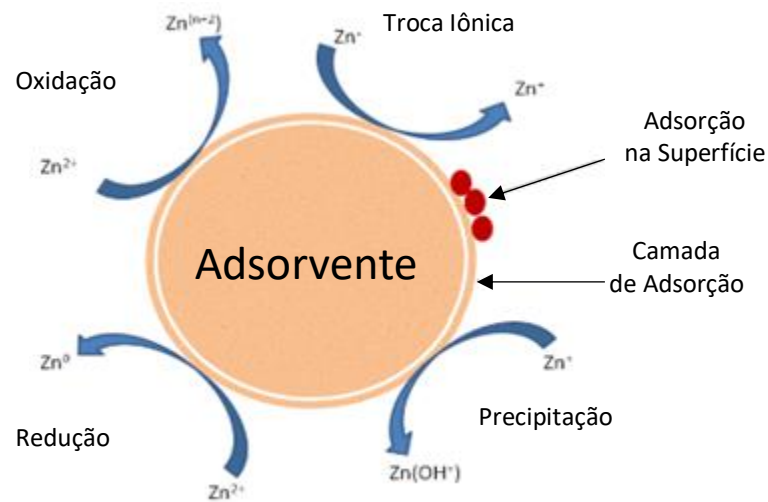
No que diz respeito aos mecanismos envolvidos no processo de adsorção, Malik, Jain e Yadav (2018) destacam que estes podem se configurar como adsorção superficial, troca iônica, oxidação, redução e precipitação (Figura 3).

As principais características dos mecanismos de adsorção de íons de metais são apresentadas na Tabela 4.

Tabela 4: Mecanismos envolvidos no processo de adsorção e sua descrição.

MECANISMO	DESCRIÇÃO
ADSORÇÃO SUPERFICIAL	<ul style="list-style-type: none"> ● Ocorre por forças van-der-Waals e eletrostáticas fracas. ● As ligações contendo oxigênio também são responsáveis pela adsorção de cátions e ânions. ● Os outros mecanismos possíveis são a energia de adesão na superfície do adsorvente. ● Governadas por fatores como ligações covalentes entre íons metálicos e a estrutura superficial do adsorvente.
TROCA IÔNICA	<ul style="list-style-type: none"> ● Troca de íons catiônicos e aniônicos entre o metal e a superfície do adsorvente. ● Íons trocados devido a fenômenos eletrostáticos.
OXIDAÇÃO	<ul style="list-style-type: none"> ● Em alta temperatura e baixa pressão, ocorre formação de óxidos ou ilhas de óxidos metálicos. ● A difusão de íons metálicos e a interação electrónica criam filmes de óxido na superfície de íons metálicos do adsorvente
REDUÇÃO	<ul style="list-style-type: none"> ● Redução dos estados de oxidação dos metais convertendo-os em espécies menos tóxicas.
PRECIPITAÇÃO	<ul style="list-style-type: none"> ● Envolve reação química seguida de precipitação como hidróxido de metal e formação de oxihidróxido. ● As precipitações superficiais de cátions e ânions são altamente dependentes do pH. Em pH elevado, a redissolução de hidróxidos de metal ocorre.

Fonte: Adaptado de Malik, Jain e Yadav (2018).



Fonte: Adaptado de MALIK; JAIN; YADAV (2018).

Figura 3: Ilustração esquemática dos processos envolvidos na adsorção de íons de metais.

3.4.2 Adsorventes

De acordo com Pino e Torem (2011), a escolha do adsorvente deve atender à alguns requisitos como capacidade de adsorção, alta seletividade, baixo custo, fácil dessorção e regeneração, lixiviação insignificante em sistemas aquosos e fácil disponibilidade para que seja viável seu uso.

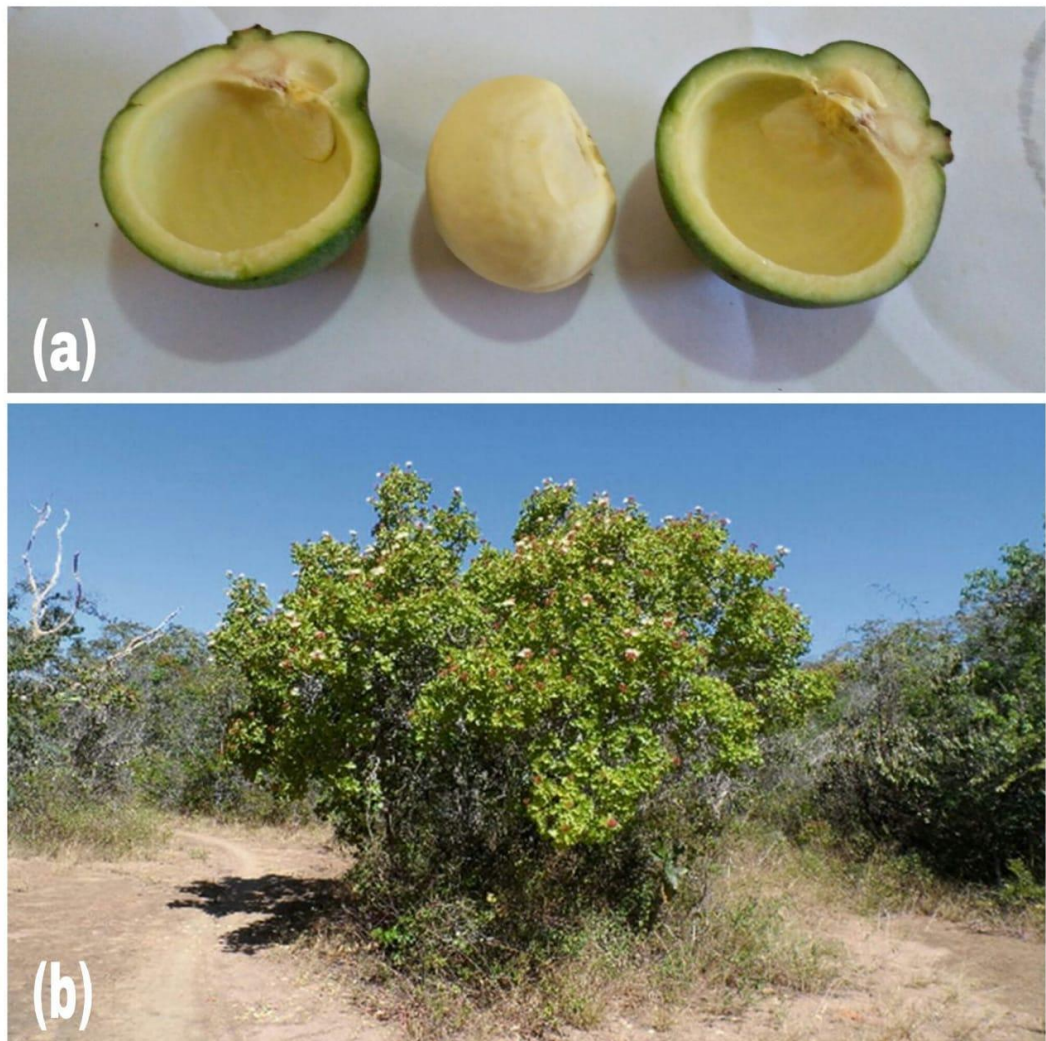
Na literatura são encontrados diversos tipos de biosorventes estudados, como exemplos listados na Tabela 5.

Tabela 5: Variedade de Biosorventes utilizados na literatura.

BIOSORVENTE	REFERÊNCIA
CASCA DE CASTANHA-DO-BRASIL (<i>BERTHOLLETIA EXCELSA</i> H.B.K.) E SERRAGEM DA MADEIRA CEDRINHO (<i>ERISMA UNCINATUM</i>)	(SCHNEIDER et al., 2018)
FOLHAS DO CAJUEIRO (<i>ANACARDIUM OCCIDENTALE</i> L.) E DA CARNAÚBA (<i>COPERNICIA PRUNIFERA</i>)	(PEREIRA, 2017)
VAGENS DE <i>DIMORPHANDRA GARDNERIANA TULASNE</i> (FAVA D'ANTA)	(SANTANA, 2018)
PERICARPO DE COCO VERDE (<i>COCOS NUCIFERA</i> L. - <i>ARECACEAE</i>)	(DE MAGALHÃES; NEVES, 2011)
BORRA DE CAFÉ INDUSTRIALIZADO E FOLHAS DE <i>CORYMBIA CITRIODORA</i> (EUCALIPTO LIMÃO)	(RAMOS et al., 2017)
ALGAS MARINHAS	HACKBARTH (2014); MOREIRA (2007); SCHNEIDER (1955)
DIVERSOS TIPOS DE MICROORGANISMOS	ARAÚJO (2011); BARROS et al. (2006); CONICELLI (2018); POLICARPO (2015)

3.4.2.1 *Pequi*

De acordo com Costa; Pinto e Soares (2017), o pequi (Figura 4 a), , é produzido pelo pequizeiro (Figura 4 b), árvore perene, explorada de forma extrativista, pertencente ao gênero *Caryocar* e família Caryocaraceae típica da região do Cerrado brasileiro.



Fonte: (a) Autor; (b) De Aquino Saraiva et al. (2018).

Figura 4: (a) Pequi descascado; (b) Pequizeiro.

Segundo Oliveira et al. (2008) e Oliveir (2010), a palavra pequi vem da língua indígena tupi, onde “PY” significa pele e “qui” espinhos, por causa dos pequenos espinhos no caroço. Além da denominação de pequi, este também é conhecido pelos nomes de piqui ou

piquiá, sendo muito apreciado e utilizado na culinária da Região Centro-Oeste, Norte e parte do Nordeste do Brasil.

Almeida (2014) e Pereira et al. (2014), ressaltam que na região nordeste do Brasil é encontrado o pequizeiro da espécie *Caryocar coriaceum* Wittm, que exerce importante papel socioeconômico na região do Cariri cearense, como também em outras áreas do Piauí e Pernambuco, devido, além do seu uso culinário, também por ser extraído óleo da amêndoa para fabricação de cosméticos e pela geração de empregos com a coleta de seus frutos, apanhados diretamente no solo, sendo que sua safra ocorre, segundo Souza et al. (2013), entre os meses de janeiro e março.

Conforme abordado por Moraes et al. (2016), o pequi é composto por casca, polpa e semente, sendo que, quando maduro, a polpa representa 10% do seu peso total, a semente 6% e a casca do fruto representa cerca de 84% do peso, sendo que por não serem consumidas, estas são descartadas nos centros urbanos, causando poluição ambiental.

3.4.3 Fatores que influenciam ao Processo Adsorativo

Vários fatores podem influenciar no processo adsorativo, como a natureza do adsorvente, do adsorvato e das condições operacionais.

Conforme exposto por Nascimento et al. (2020), as características do adsorvente incluem: área superficial, tamanho do poro, densidade, grupos funcionais presentes na superfície e hidrofobicidade do material. Quanto a natureza do adsorvato, depende da polaridade, do tamanho da molécula, da solubilidade e da acidez ou basicidade. As condições operacionais incluem, principalmente, temperatura, pH e natureza do solvente.

Na Tabela 6, são apresentados alguns fatores que influenciam na capacidade de bioadsorção de um adsorvente, bem como o seu efeito.

Tabela 6: Fatores que podem afetar a capacidade de bioadsorção.

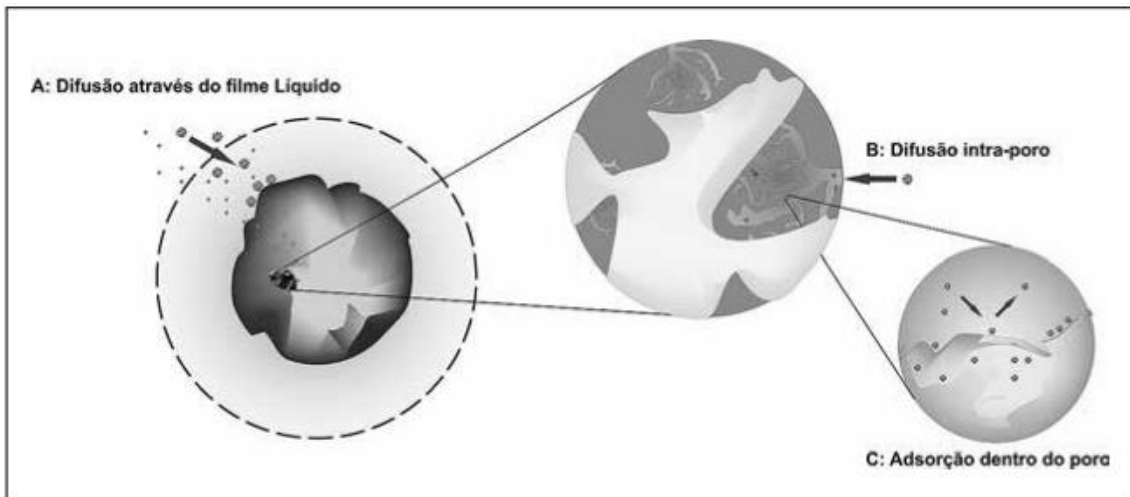
PARÂMETRO	EFEITO
TEMPERATURA	Influência na difusão do adsorvato no meio e na ligação entre o adsorvato-adsorvente.
PH	Solubilidade do metal
NATUREZA DO BIOSORVENTE	Maior disponibilização de sítios de adsorção
ÁREA SUPERFICIAL DO BIOSORVENTE	Maior/menor contato com o biosorvato
CONCENTRAÇÃO DE BIOMASSA	Diretamente proporcional ao consumo do metal
CONCENTRAÇÃO INICIAL DO ÍON DO METAL	A quantidade crescente de metal adsorvido pela biomassa será aumentada com a concentração inicial de metais
AFINIDADE DO METAL COM O BIOSORVENTE	O pré-tratamento físico/químico afeta a permeabilidade e as cargas de superfície da biomassa e torna os grupos de ligação de metal acessíveis para a ligação.

Fonte: Adaptado de Al-Qodah; Yahya e Al-Shannag, (2017) e Shamim (2018).

3.5. CINÉTICA DE ADSORÇÃO

Nascimento et al. (2020), expressa a cinética de adsorção como a taxa de remoção do adsorvato na fase fluida em relação ao tempo, envolvendo a transferência de massa de um ou mais componentes contidos em uma massa líquida externa para o interior da partícula do adsorvente, os quais deverão migrar através dos macroporos até as regiões mais interiores desta partícula.

O autor ainda informa que a cinética poderá ocorrer por diferentes processos, onde são apresentados e descritos na Tabela 7 e ilustrados na Figura 5.



Fonte: Pereira et al. (2014).

Figura 5: Etapas da Cinética de Adsorção.

Tabela 7: Processos ocorridos na cinética de adsorção.

PROCESSO	DESCRIÇÃO
TRANSFERÊNCIA DE MASSA EXTERNA	Transferência de moléculas da fase fluida para superfície externa da partícula adsorvente, por intermédio de uma camada de fluido que envolve a partícula.
DIFUSÃO NO PORO	Ocasionada pela difusão de moléculas no fluido para o interior dos poros.
DIFUSÃO NA SUPERFÍCIE	Difusão das moléculas totalmente adsorvidas ao longo da superfície do poro.

Fonte: Adaptado de Nascimento et al. (2020).

Santana (2018) e Teixeira (2015), relatam a importância de se realizar um estudo cinético para os processos de bioadsorção. Os autores destacam que a cinética permite elucidar mecanismos envolvidos nos processos adsorptivos e que a determinação de parâmetros, tais como: tempo de equilíbrio, taxa de adsorção inicial e taxas de dessorção, configuram-se como importantes informações do ponto de vista de definição para melhores condições de operação dos reatores, possibilitando otimizar o tempo de operação e por consequência minimizar os custos operacionais.

De acordo com Wang e Guo (2020), a cinética da bioadsorção pode ser representada por diversos modelos de adsorção, sendo que os dois mais utilizados na literatura para descrever

o comportamento da bioadsorção ao longo do tempo são o de pseudo-primeira ordem e o de pseudo-segunda ordem.

3.5.1. Modelo de Pseudo-primeira Ordem

Duarte- Neto et al. (2014) e Policarpo (2015), relatam que a equação de pseudo-primeira ordem, ou equação de Lagergren (1898), é uma das mais utilizadas para avaliar os processos de adsorção do soluto de uma solução líquida, e está baseada na capacidade de adsorção do sólido. Neste modelo considera-se que a taxa de ocupação dos sítios de adsorção é proporcional ao número de sítios desocupados e que a força motriz é linear.

De acordo com Ighalo et al. (2020), as equações do modelo de pseudo-primeira ordem e sua forma linearizada, são apresentados na Tabela 8.

Tabela 8: Equações de pseudo-primeira ordem.

Forma de apresentação	Equação	Número da Equação	Parâmetros
Não linearizada	$\frac{dQ_t}{dt} = k_1 \times (q_e - q_t)$	1	dQ_t : Grau de bioadsorção em um tempo qualquer (mg/g); Q_{eq} : Capacidade de bioadsorção no equilíbrio (mg metal / g biomassa); q_e e q_t : são as quantidades adsorvidas por grama de adsorvente no equilíbrio e no tempo t, respectivamente (mg.g ⁻¹);
Linearizada	$\ln(Q_{Eq} - Q_t) = \ln(Q_{Eq}) - K_1 t$	2	k_1 : Constante de velocidade de reação de pseudo-primeira ordem (min ⁻¹).

Fonte: adaptado de Ighalo et al. (2020)

Os valores de Q_{eq} e k_1 pode ser determinados através dos coeficientes angular e linear, obtidos a partir da regressão linear do gráfico de $\ln (q_e - q_t)$ versus t (TAVANA; PAHLAVANZADEH; ZAREI, 2020).

Ho e Mckay (1999), constataram que o modelo de pseudo-primeira ordem há uma limitação para o intervalo completo do tempo de contato da biossorção e mostrou-se aplicável somente para os primeiros 20 minutos do processo nos casos estudados.

3.5.2. Modelo de Pseudo-segunda Ordem

Segundo Duarte- Neto et al. (2014), o modelo cinético de pseudo-segunda ordem, assim como o modelo cinético de primeira ordem, é baseado na capacidade de adsorção da fase sólida por tratar do comportamento do processo em toda a faixa de tempo de contato, dos tempos curtos aos longos.

De acordo com Ighalo et al. (2020), o modelo de pseudo-segunda ordem assume que o processo de adsorção é dependente da quantidade de adsorbato presente no solução, bem como de locais de adsorção livres na superfície do adsorvente. Este, ao contrário do de pseudo-primeira ordem, mostra-se aplicável ao intervalo completo da biossorção para todos os sistemas analisados por Ho; Mckay (1999).

De acordo com Tavana, Pahlavanzadeh e Zarei (2020), as equações do modelo de pseudo-segunda ordem e sua forma linearizada, são apresentados na tabela 9.

Tabela 9: Equações de pseudo-segunda ordem.

Forma de apresentação	Equação	Número da Equação	Parâmetros
Não linearizada	$\frac{dQ_t}{dt} = K_2(Q_{eq} - Q_t)^2$	3	dQ_t : Grau de bioadsorção em um tempo qualquer (mg/g); Q_{eq} : Capacidade de bioadsorção no equilíbrio (mg metal / g biomassa);
Linearizada	$\frac{t}{Q_t} = \frac{1}{K_2 Q_{Eq}^2} + \frac{1}{Q_{Eq}} t$	4	Q_t : são as quantidades adsorvidas por grama de adsorvente no tempo t, respectivamente (mg.g ⁻¹); K_2 : constante de velocidade de reação de pseudo-segunda ordem (g / (mg.min)).

Fonte: adaptado de Tavana, Pahlavanzadeh e Zarei (2020) e (IGHALO et al., 2020a)

3.5.3. Modelo Cinético de Elovich

Segundo Elovich e Larinov (1962) e Low (1960), o modelo de Elovich é adequado para sistemas cujas superfícies de adsorção são heterogêneas e propõe que a adsorção é definida pela quimissorção entre o adsorvato e a superfície heterogênea do adsorvente.

De acordo com Nascimento et al. (2020), o modelo de Elovich é representado pela Equação 5 e após linearizada, pela Equação 6.

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

$$q_t = \frac{1}{\beta} \ln\left(\frac{\alpha}{\beta}\right) + \frac{1}{\beta} \ln(t) \quad (6)$$

Onde:

α : é a taxa de adsorção inicial ($\text{mg.g}^{-1}.\text{min}^{-1}$);

β : constante de dessorção (mg.g^{-1});

q_t : são as quantidades adsorvidas por grama de adsorvente no tempo t,

t: tempo.

3.6. MODELOS DE DIFUSÃO

3.6.1 Modelo de Weber e Morris

Se a difusão intrapartícula é o fator determinante da velocidade, a remoção do adsorvato varia com a raiz quadrada do tempo (BOPARAI; JOSEPH; O'CARROLL, 2011; GUGUSHE et al., 2021; WEBER; MORRIS, 1963). Assim, o coeficiente de difusão intrapartícula (K_d) pode ser definido pela Equação 7.

$$q_t = K_d * t^{0,5} + C \quad (7)$$

Onde:

q_t : quantidade de adsorvato adsorvida na fase sólida (mg g^{-1}) em um tempo t (min);

K_d : Coeficiente de difusão intrapartícula ($\text{mg.g}^{-1}.\text{min}^{-0.5}$);

C: Constante relacionada com a resistência à difusão (mg.g^{-1}).

De acordo com Nascimento et al. (2020) e Wang e Guo (2020) K_d e C podem ser estimados através dos valores de coeficiente angular e linear, respectivamente, obtidos pela

regressão linear de um gráfico $qt \times t^{0.5}$ e ainda afirmam que a linha do gráfico corta os eixos x e y na origem (0,0), quando a difusão intrapartícula controla o processo de adsorção, caso contrário, a adsorção será controlada por processos intrafilme.

3.6.2 Modelo de Boyd

Outro modelo de difusão utilizado é o de Boyd (BOYD; SCHUBERT; ADAMSON, 1947). Este modelo confirma o de Weber e Morris, na elucidação dos mecanismos difusivos predominantes no processo de adsorção. Se a difusão no interior dos poros é a etapa limitante do processo de adsorção, então o resultado pode ser expresso pela Equação 8:

$$F = 1 - \left(\frac{6}{\pi^2}\right) \sum_{n=1}^{\infty} \left(\frac{1}{n^2}\right) e^{(-\pi^2 Bt)} \quad (8)$$

O valor de F é obtido pela Equação 9 e a partir deste valor determina-se B_t utilizando as Equações 10 ou 11, desenvolvidas por Reichenberg (1953), sendo que para valores de F variando de 0 à 0,85, é utilizada a equação 10, enquanto que para valores de F entre 0,85 à 1, a equação 11. As equações estão apresentadas na tabela 10.

Tabela 10: Equações de Boyd.

VALORES DE F	EQUAÇÃO	NÚMERO DA EQUAÇÃO	PARÂMETROS
---	$F = \frac{q_t}{q_e}$	9	F: Alcance fracionário do equilíbrio
$0,85 > F > 0$	$F = \frac{6}{\pi^{3/2}}\sqrt{Bt} - \frac{3}{\pi^2}(Bt)$ <p style="text-align: center;">Ou</p> $Bt = 2\pi - \frac{\pi^2 F}{3} - 2\pi \left(1 - \frac{\pi F}{3}\right)^{1/2}$	10	q_e : Quantidade de adsorvato adsorvido em um tempo infinito ($\text{mg}\cdot\text{g}^{-1}$);
$1 > F > 0,85$	$F = 1 - \frac{\pi^2}{6}e^{-Bt}$ <p style="text-align: center;">Ou</p> $Bt = -\ln \frac{\pi^2}{6}(1 - F)$	11	q_t : quantidade de adsorvato adsorvido em um tempo t; Bt : Constante (Função matemática de F).

Segundo Wang e Guo (2020), Os valores resultantes de Bt são traçados contra t (gráfico de Boyd) e se o gráfico gerar uma reta que atravessa a origem é possível concluir que o processo de difusão intraporo é a etapa limitante do processo de adsorção para a faixa de tempo especificada. Nascimento et al. (2020) afirma que o valor de B_d (constante de Boyd) pode ser determinado através do coeficiente linear do gráfico $Bt \times t$, e com ele pode-se obter o coeficiente de difusão (D) ($\text{cm}^2\cdot\text{min}^{-1}$) que está relacionado a constante de Boyd através da Equação 12.

$$B_d = \left(\frac{\pi^2 D}{d^2}\right) \quad (12)$$

Onde:

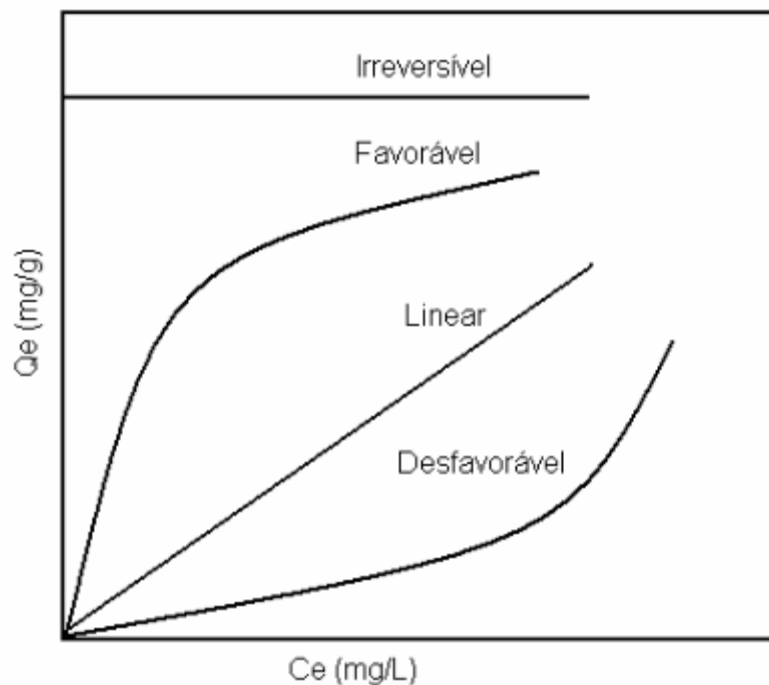
D: Coeficiente de difusão ($\text{cm}^2 \cdot \text{min}^{-1}$)

d: Diâmetro médio das partículas (cm)

B_d : Constante de Boyd

3.7. ISOTERMAS DE ADSORÇÃO

O conceito fundamental em ciência da adsorção é o que chamamos de isoterma de adsorção e conforme Abdi e Kazemi (2015), o desempenho da sorção de um bioadsorvente deve ser levado em consideração, para se observar a cinética de bioadsorção de qualquer metal tóxicos, com isso, uma isoterma de bioadsorção deve ser estudada (Figura 6). Nesta isoterma, gera-se um gráfico de capacidade adsorviva em equilíbrio (q_e) versus concentração de soluto em equilíbrio na solução (C_e), onde são mantidos constantes os parâmetros de temperatura, pH, força iônica e pressão, enquanto se varia apenas a concentração de metal.



Fonte: MOREIRA (2008).

Figura 6: Diferentes comportamentos dos isotermas de adsorção.

Na Tabela 11 são destacados os tipos de comportamento das isotermas, bem como descrita algumas de suas características.

Azari et al. (2020) afirmam que os modelos de isotermas de adsorção apresentam informações valiosas como a distribuição de sítios ativos disponíveis na superfície do adsorvente, sua capacidade máxima de adsorção de adsorbato, a interação entre o adsorvente e o adsorbato e as características do sistema de adsorção.

Vários são os modelos de isotermas utilizados pela literatura para descrever o equilíbrio da adsorção, porém os mais conhecidos e utilizados para prever comportamentos no processo de adsorção são os modelos de Langmuir, Freundlich, Temkin, Dubinin–Radushkevich (COSTA; SILVA; VIEIRA, 2020).

Tabela 11: Tipos de Comportamento da isoterma e descrição.

COMPORTAMENTO DA ISOTERMA	DESCRIÇÃO
ISOTERMA LINEAR	<ul style="list-style-type: none"> • Adsorção proporcional à concentração em equilíbrio; • Não mostra um limite máximo para a capacidade do adsorvente.
ISOTERMA EXTREMAMENTE FAVORÁVEL	<ul style="list-style-type: none"> • capacidade de remoção relativamente alta, mesmo em condições de baixa concentração de adsorbato na solução.
ISOTERMA IRREVERSÍVEL	<ul style="list-style-type: none"> • Comportamento constante independente da concentração.
ISOTERMA NÃO FAVORÁVEL	<ul style="list-style-type: none"> • Capacidade de remoção só é satisfatória em condições de alta concentração de adsorbato.

Fonte: Adaptado de Duarte- Neto et al. (2014).

3.7.1. Modelo de Langmuir

Shamim (2018) e Teixeira (2015), relatam que o modelo de Langmuir trata-se do modelo mais utilizado para descrever fenômenos de adsorção e foi desenvolvido em 1918, para demonstrar a adsorção de gás ou líquido em material sólido.

Segundo Araújo (2011), o modelo de Langmuir é baseado na adsorção ocorrendo em sítios uniformes com recobrimento em monocamadas e afinidade iônica independente da quantidade de material adsorvido, considerando que:

- O sistema é ideal;
- No equilíbrio, as velocidades de adsorção e dessorção são iguais;
- As moléculas são adsorvidas e aderem na superfície do adsorvente em sítios ativos definidos e localizados;
- Cada sítio ativo pode acomodar uma única espécie adsorvida (monocamada);
- A energia da entidade adsorvida é a mesma em todos os sítios da superfície, apresentando interação desprezível entre as moléculas adsorvidas.

O modelo de Langmuir é ser expresso pela Equação 13, em sua forma não linearizada. Para possível aplicação do método de regressão linear, torna-se necessário o uso de equações lineares, sendo apresentada na Equação 14, sua forma linear. As equações 14 e 15 são apresentadas na Tabela 12:

Tabela 12: Equações Lineares e não lineares para a isoterma de Langmuir.

Forma de apresentação	Equação	Número da equação	Parâmetros
Não linearizada	$Q = \frac{q_{m\acute{a}x} \times K_L \times C_e}{1 \pm (K_L \times C_e)}$	13	<p>Q: Quantidade de metal adsorvido por unidade de massa de adsorvente ($\text{mg}\cdot\text{g}^{-1}$);</p> <p>$C_e$: Concentração do íon na solução em equilíbrio ($\text{mg}\cdot\text{L}^{-1}$);</p> <p>$K_L$: Constante de equilíbrio ($\text{L}\cdot\text{g}^{-1}$);</p> <p>$q_{m\acute{a}x}$: capacidade máxima de adsorção do adsorvente ($\text{mg}\cdot\text{g}^{-1}$).</p>
Linearizada	$\frac{C_e}{q_e} = \frac{1}{q_{max}} C_e + \frac{1}{q_{max} \times K_L}$	14	

Fonte: Adaptado de (ABDI; KAZEMI, 2015; COSTA; SILVA; VIEIRA, 2020; TEIXEIRA, 2015).

Escudero-Oñate e Villaescusa, (2018) afirmam que a partir deste modelo é possível obter a capacidade máxima de adsorção do adsorvente, q_{max} ($\text{mol}\cdot\text{g}^{-1}$), e a constante de Langmuir (K_L) ($\text{L}\cdot\text{mol}^{-1}$), que é relacionada à energia de adsorção e reflete a afinidade entre o adsorvente e o adsorbato.

3.7.2. Modelo de Freundlich

Gholamiyan, Hamzehloo e Farrokhnia, (2020) relatam que a isoterma de Freundlich considera um mecanismo de adsorção multimolecular e é uma equação prática baseada na adsorção em uma superfície heterogênea com sítios de dependência variada, que geralmente é usada para determinar a intensidade de adsorção de superfícies de adsorbato com distribuição desigual de energia.

Segundo Silva et al. (2014), a isoterma de Freundlich é frequentemente recomendada devido à sua exatidão, onde pode-se obter resultados mais exatos do que os da

isoterma de Langmuir, para uma larga variedade de sistemas heterogêneos de adsorção, porém apresenta a desvantagem da convergência para a lei de Henry, falhando na descrição do equilíbrio quando q_e tender a 0, o que é termodinamicamente inconsistente, entretanto, a extrapolação dos dados quando a concentração é zero pode superar este problema.

As equações matemáticas que representam o modelo de Freundlich em suas formas linearizadas e não linearizadas são apresentadas na Tabela 13:

De acordo com Gholamiyan; Hamzehloo; Farrokhnia (2020) e Nascimento et al., (2020), uma adsorção favorável apresenta valor de n entre 1 e 10, logo, quanto maior o valor de n , menor será $1/n$, e mais forte será a interação entre o adsorvato e o adsorvente, por outro lado, para o valor $1/n$ igual a 1, indica uma adsorção linear, ou seja, as energias são idênticas para todos os sítios de adsorção, e para valor de $1/n$ maior do que 1, o adsorvente tem maior afinidade pelo solvente, sugerindo que há uma forte atração intermolecular entre os dois.

Tabela 13: Equações Lineares e não lineares para a isoterma de Freundlich.

FORMA DE APRESENTAÇÃO	EQUAÇÃO	NÚMERO DA EQUAÇÃO	PARÂMETROS
NÃO LINEARIZADA	$q_e = K_F \times (C_e)^{\frac{1}{n}}$	15	q_e : Quantidade de soluto adsorvido (mg.g^{-1}); C_e : Concentração do íon na solução em equilíbrio (mg.L^{-1});
LINEARIZADA	$\text{Ln}(q_e) = \text{Ln}(K_F) + \frac{1}{n}\text{Ln}(C_e)$	16	$\frac{1}{n}$: Constante relacionada à heterogeneidade da superfície; K_F : Constante de capacidade de adsorção de Freundlich ($(\text{mg.g}^{-1})(\text{L.mg}^{-1})^{1/n}$).

Fonte: Adaptado de (HIKMAT; QASSIM; KHETHI, 2014).

3.7.3. Modelo de Temkin

Para Kheddo et al. (2020), a isoterma de Temkin determina o potencial de adsorção do adsorvente para adsorbatos e prevê uma distribuição consistente das energias de ligação sobre os locais de adsorção de ligação à superfície, dependendo da densidade e alocação de grupos funcionais nas superfícies adsorvente e adsorbato.

Mondal e Majumder (2019) afirmam que o modelo de Temkin representa as interações moleculares, levando-se em consideração algumas suposições, sendo elas:

- Com o aumento da cobertura da superfície o calor de adsorção diminui linearmente;
- A energia de ligação dos locais de adsorção são uniformemente distribuídas.

De acordo com Rasoulpoor; Poursattar Marjani e Nozad (2020), o modelo de Temkin pode ser dado pela equação 17.

$$q_e = \frac{RT}{b} \ln(k_t C_e) \quad (17)$$

Onde:

b_T : Constante de Temkin ($J \cdot mol^{-1}$);

K_t : Constante Isotérmica de Temkin ($L \cdot g^{-1}$);

R : Constante universal dos gases ($J \cdot mol^{-1} K^{-1}$)

T : temperatura (K)

Estudos como os de Avdeev, Luchkin e Kuznetsov, (2020), Biswas, Saha e Ghosh, (2007) e Li et al. (2020) indicam que os dados que apresentam bom enquadramento ao modelo isotérmico de Temkin, configuram-se por apresentar comportamento de quimissorção.

3.7.4. Modelo de Dubinin-Radushkevich

Boparai, Joseph e O'carroll, (2011) e Mondal e Majumder (2019) apontam que o modelo isotérmico de Dubinin-Radushkevich (D – R) é amplamente utilizado para examinar os processos de adsorção nas superfícies heterogêneas, onde os potenciais de adsorção são variáveis e apresenta uma equação semiempírica em que a adsorção segue um mecanismo de preenchimento de poros. Neste modelo a adsorção tem caráter de camada múltipla, envolve forças de Van der Waals e é aplicável para processos de adsorção física.

De acordo com (KHEDDO et al., 2020), o modelo D-R pode ser aplicado através das equações 18 e 19.

$$\ln q_e = \ln(q_d) - \beta * \varepsilon^2 \quad (18)$$

$$\varepsilon = R * T * \ln\left(1 + \frac{1}{c_e}\right) \quad (19)$$

Onde:

q_e : Capacidade de adsorção do adsorbato por unidade de massa de adsorvente (mg.g^{-1});

q_d : Constante de D - R (mg.g^{-1});

β : Constante relacionada à energia livre;

ε : Potencial de Polanyi.

C_e : Concentração do adsorbato em equilíbrio na solução

R : Constante universal dos gases ($\text{J.mol}^{-1}\text{K}^{-1}$)

T : temperatura (K)

Os valores de q_d e β podem ser determinados através da regressão linear de um gráfico $\ln(q_e) \times \varepsilon^2$, utilizando-se os coeficientes linear e angular, respectivamente. De posse do valor de β pode-se determinar de energia livre (E), em KJ.mol^{-1} , pela equação 20.

$$E = \sqrt{\frac{1}{2\beta}} \quad (20)$$

3.8. TERMODINÂMICA DE ADSORÇÃO

Os parâmetros termodinâmicos da adsorção, como as variações da energia livre de Gibbs (ΔG°), de entalpia (ΔH) e de entropia (ΔS°), são de grande importância a serem estudados, pois a partir destes, muitas informações acerca do processo de adsorção podem ser entendidas, como é o caso da viabilidade e espontaneidade do processo, o tipo de adsorção envolvida (fisissorção ou quimissorção), e a respeito da heterogeneidade da superfície do adsorvente (COSTA; SILVA; VIEIRA, 2020; HIKMAT; QASSIM; KHETHI, 2014; KADIRI et al., 2019; YADAV; TIWARI; BHAGAT, 2020).

Para verificação da espontaneidade do processo, segundo (FENG et al., 2011), faz-se uso da ΔG° , obtida a partir da diferença entre os valores do estado inicial (soluto livre) e do estado final equilibrado (composto adsorvido), sendo valores ΔG° negativos indicativos de que o processo é espontâneo, enquanto que para valores positivos, o processo não será espontâneo.

A natureza do processo de bioadsorção pode ser identificada fazendo-se uso da ΔH do sistema. Segundo Escudero-Oñate e Villaescusa (2018) e Hikmat, Qassim e Khethi (2014), valores para ΔH entre 2,1 e 20,9 kJ.mol^{-1} , podem ser indicativos de uma adsorção física, também chamada de fisissorção, maiores valores de ΔH , em torno de 20 - 800 kJ.mol^{-1} , a adsorção pode ser classificada como quimissorção. O valor da mudança de entalpia $\Delta H < 0$ ou $\Delta H > 0$ também sugere o caráter exotérmico ou endotérmico do processo, respectivamente.

A variação de entropia (ΔS°) reflete essencialmente a variação na desordem de um sistema ao longo de um processo, sendo $\Delta S^\circ > 0$ indicativo de maior aleatoriedade na interface sólido/solução, possibilitando algumas mudanças na estrutura do sorvente e do sorbato, além de implicar em um aumento no grau de liberdade das espécies adsorvidas, ou seja, indica uma forte afinidade entre o adsorvente e o adsorbato. Já para $\Delta S^\circ < 0$, o processo de adsorção

envolve um mecanismo associativo e implica em redução da desordem na interface sorvente/solução durante o processo de sorção, fazendo com que as espécies de sorbato escapassem da fase sólida para a fase de solução, indicando baixa afinidade entre o adsorvente e o adsorbato (COSTA; SILVA; VIEIRA, 2020; ESCUDERO-OÑATE; VILLAESCUSA, 2018).

Nascimento et al. (2020), afirmam que os parâmetros termodinâmicos podem ser determinados por métodos gráficos, após obtido o valor da constante de adsorção (K_0), pela equação 21, porém quando o modelo de Langmuir se ajusta bem aos dados experimentais, a constante de adsorção de Langmuir pode ser convenientemente empregada para os cálculos dos parâmetros termodinâmicos. Com isso, para determinação da ΔG° (kJ mol^{-1}) pode-se utilizar a Equação 22 ou 23, enquanto que para determinar a ΔH° (kJ mol^{-1}) e a ΔS ($\text{Jmol}^{-1} \text{K}^{-1}$), plota-se um gráfico $\text{Ln}(K_0) \times 1/T$ e aplica-se a regressão linear; tendo os valores do coeficiente angular e linear, respectivamente, e fazendo-se uso da equação 24, determinam-se tais parâmetros.

$$K_0 = \frac{q_e}{q_{max} - q_e} * \frac{1}{q_e} \quad (21)$$

$$\Delta G^\circ = -RT \ln K_0 \quad (22)$$

$$\Delta G^\circ = \Delta H - T\Delta S \quad (22)$$

$$\ln K_0 = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (23)$$

Onde:

q_e : Capacidade de adsorção do adsorbato por unidade de massa de adsorvente ($\text{mg}\cdot\text{g}^{-1}$);

q_{max} : Capacidade máxima de adsorção do adsorbato por unidade de massa de adsorvente ($\text{mg}\cdot\text{g}^{-1}$);

R : Constante universal dos gases ($8,314 \text{ J mol}\cdot\text{K}^{-1}$);

T: Temperatura em Kelvin.

REFERÊNCIAS

- ABDI, O.; KAZEMI, M. A review study of biosorption of heavy metals and comparison between different biosorbents. **Journal of Materials and Environmental Science**, v. 6, n. 5, p. 1386–1399, 2015.
- ABDIĆ et al. Adsorptive removal of eight heavy metals from aqueous solution by unmodified and modified agricultural waste: tangerine peel. **International Journal of Environmental Science and Technology**, v. 15, n. 12, p. 2511–2518, 2018.
- ACHARYA, J.; KUMAR, U.; RAFI, P. M. Removal of Heavy Metal Ions from Wastewater by Chemically Modified Agricultural Waste Material as Potential Adsorbent-A Review. **International Journal of Current Engineering and Technology**, v. 8, n. 3, p. 526–530, 2018.
- AHAYLA, N.; RAMACHANDRA, T. V. Biosorption of heavy metals. **Biotechnology progress**, v. 11, n. 3, p. 235–50, 1995.
- AL-QODAH, Z.; YAHYA, M. A.; AL-SHANNAG, M. On the performance of bioadsorption processes for heavy metal ions removal by low-cost agricultural and natural by-products bioadsorbent: a review. **Desalination and Water Treatment**, v. 85, n. August, p. 339–357, 2017.
- ALMEIDA, A. Avaliação ecológica do extrativismo do pequi (*Caryocar coriaceum* Wittm.) na Floresta Nacional do Araripe, Ceará: informações para um plano de uso sustentável. **Tese de Doutorado**, p. 164, 2014.
- AMIN, M. T.; ALAZBA, A. A.; AMIN, M. N. Absorption behaviours of copper, lead, and arsenic in aqueous solution using date palm fibres and orange peel: Kinetics and thermodynamics. **Polish Journal of Environmental Studies**, v. 26, n. 2, p. 543–557, 2017.
- AMORIM, D. J. et al. Characterization of Pequi (*Caryocar brasiliense*) Shells and Evaluation of Their Potential for the Adsorption of PbII Ions in Aqueous Systems. **Journal of the Brazilian Chemical Society**, v. 27, n. 3, p. 616–623, 2016.
- ARAÚJO, R. R. D. L. **MODELAGEM DO PROCESSO DE BIOSSORÇÃO DE CHUMBO UTILIZA?DO A MACRÓFITA AQUÁTICA *Eichhornia crassipes***. Curitiba - PR: UFPR, 2011.
- ARSLANOĞLU, E. et al. Fabrication, characterization, and adsorption applications of low-cost hybride activated carbons from peanut shell-vinasse mixtures by one-step pyrolysis. **Biomass Conversion and Biorefinery**, 2021.
- ATKINS, P.; JONES, L.; LAVERMAN, L. **Princípios de Química, questionando a vida**
-

moderna e o meio ambiente. 7^a ed. Porto Alegre: [s.n.].

ATKINS, P.; JONES, L.; LAVERMAN, L. **Princípios de Química, questionando a vida moderna e o meio ambiente.** 7^a ed. Porto Alegre: 2018.

AVDEEV, Y. G.; LUCHKIN, A. Y.; KUZNETSOV, Y. I. Adsorption of IFKhAN-92 Inhibitor on Low Carbon Steel from Sulfuric Acid Solution. **Protection of Metals and Physical Chemistry of Surfaces**, v. 56, n. 7, p. 1244–1248, 2020.

AWUAL, M. R. Mesoporous composite material for efficient lead(II) detection and removal from aqueous media. **Journal of Environmental Chemical Engineering**, v. 7, n. 3, p. 103124, 2019a.

AWUAL, M. R. et al. Introducing an alternate conjugated material for enhanced lead(II) capturing from wastewater. **Journal of Cleaner Production**, v. 224, p. 920–929, 2019.

AWUAL, M. R. Innovative composite material for efficient and highly selective Pb(II) ion capturing from wastewater. **Journal of Molecular Liquids**, v. 284, p. 502–510, 2019b.

AWUAL, M. R. et al. Naked-eye lead(II) capturing from contaminated water using innovative large-pore facial composite materials. **Microchemical Journal**, v. 154, n. November 2019, p. 104585, 2020.

AWUAL, M. R.; HASAN, M. M. Novel conjugate adsorbent for visual detection and removal of toxic lead(II) ions from water. **Microporous and Mesoporous Materials**, v. 196, p. 261–269, 2014.

AWUAL, M. R.; HASAN, M. M. A ligand based innovative composite material for selective lead(II) capturing from wastewater. **Journal of Molecular Liquids**, v. 294, p. 111679, 2019.

AZARI, A. et al. Comprehensive systematic review and meta-analysis of dyes adsorption by carbon-based adsorbent materials: Classification and analysis of last decade studies. **Chemosphere**, v. 250, n. 5, p. 126238, 2020.

AZOULAY, K. et al. Comparative study between static and dynamic adsorption efficiency of dyes by the mixture of palm waste using the central composite design. **Chemical Data Collections**, v. 27, 2020.

BANERJEE, M. et al. Removal of Cr(VI) from Its Aqueous Solution Using Green Adsorbent Pistachio Shell: a Fixed Bed Column Study and GA-ANN Modeling. **Water Conservation Science and Engineering**, v. 3, n. 1, p. 19–31, 2018.

BARROS, A. J. M. et al. ESTUDO TERMOGRAVIMÉTRICO DO PROCESSO DE SORÇÃO DE METAIS PESADOS POR RESÍDUOS SÓLIDOS ORGÂNICOS. **Engenharia Sanitaria e Ambiental**, v. 11, p. 184–190, 2006.

BARROS, A. J. M. **Estudo da Formação de Complexos Pelo Processo de Biossorção.** Joao Pessoa: UFPB, 2006.

- BISWAS, K.; SAHA, S. K.; GHOSH, U. C. Adsorption of fluoride from aqueous solution by a synthetic iron(III)-aluminum(III) mixed oxide. **Industrial and Engineering Chemistry Research**, v. 46, n. 16, p. 5346–5356, 2007.
- BLAGOJEV, N. et al. A new approach for modelling and optimization of Cu(II) biosorption from aqueous solutions using sugar beet shreds in a fixed-bed column. **Journal of Hazardous Materials**, v. 363, n. June 2018, p. 366–375, 2019.
- BOEHM, H. P. Surface oxides on carbon and their analysis: A critical assessment. **Carbon**, v. 40, n. 2, p. 145–149, 2002.
- BOPARAI, H. K.; JOSEPH, M.; O’CARROLL, D. M. Kinetics and thermodynamics of cadmium ion removal by adsorption onto nano zerovalent iron particles. **Journal of Hazardous Materials**, v. 186, n. 1, p. 458–465, 2011.
- BOYD, G. E.; SCHUBERT, J.; ADAMSON, A. W. The Exchange Adsorption of Ions from Aqueous Solutions by Organic Zeolites. Ion-exchange Equilibria. **Journal of the American Chemical Society**, v. 69, n. 11, p. 2818–2829, 1947.
- BREDA, C. A. et al. Processing and Characterization of Chitosan Films with Incorporation of Ethanolic Extract from “Pequi” Peels. **Macromolecular Research**, 2017.
- BURAKOV, A. E. et al. Adsorption of heavy metals on conventional and nanostructured materials for wastewater treatment purposes: A review. **Ecotoxicology and Environmental Safety**, v. 148, n. August 2017, p. 702–712, 2018.
- CAO, M. LI et al. Functionalized graphene nanosheets as absorbent for copper (II) removal from water. **Ecotoxicology and Environmental Safety**, v. 173, n. September 2018, p. 28–36, 2019.
- CONAMA. Resolução CONAMA 430/2011. **Diário Oficial da União**, p. 9, 2011.
- CONICELLI, B. P. **BIOSSORÇÃO DE CHUMBO E MERCÚRIO PELAS LINHAGENS SELVAGEM E RECOMBINANTE DE C. metallidurans EM MEIO AQUOSO**. [s.l.] USP, 2018.
- CORDEIRO, M. W. S. et al. PHYSICAL CHARACTERISTICS, CHEMICAL-NUTRITIONAL COMPOSITION AND ESSENTIAL OILS OF Caryocar brasiliense NATIVE FROM THE STATE OF MATO GROSSO (In Portuguese). **Revista Brasileira de Fruticultura**, v. 35, n. 4, p. 1127–1139, 2013.
- CORDEIRO, R. D. M. **AS AGLOMERAÇÕES PRODUTIVAS DE CALÇADOS, FOLHEADOS E DE JOIAS DO CRAJUBAR (CE): FORMAÇÃO, PRODUÇÃO, TRABALHO, IMPLICAÇÕES SOCIOESPACIAIS**. [s.l.] Unesp, 2015.
- COSTA, D. A.; MENDONÇA, R. H.; WYSARD JUNIOR, M. M. Evaluation of removal of chromium (III) by composite porous adsorbents materials of PE-g-MA, coconut fiber and
-

- chitosan using experimental design (In Portuguese). **Engenharia Sanitaria e Ambiental**, v. 22, n. 6, p. 1203–1213, 2017.
- COSTA, A. P. F. DA; PINTO, E. G.; SOARES, D. S. B. Obtenção de farinha do mesocarpo de pequi. **Revista Agrarian**, p. 113–119, 2017.
- COSTA, T. B. DA; SILVA, M. G. C. DA; VIEIRA, M. G. A. Recovery of rare-earth metals from aqueous solutions by bio/adsorption using non-conventional materials: a review with recent studies and promising approaches in column applications. **Journal of Rare Earths**, v. 38, n. 4, p. 339–355, 2020.
- COSTA, W. D. et al. Removal of copper(II) ions and lead(II) from aqueous solutions using seeds of *Azadirachta indica* A. Juss as bioadsorbent. **Environmental Research**, v. 183, n. June 2019, p. 109213, 2020.
- CRINI, G. et al. Conventional and non-conventional adsorbents for wastewater treatment. **Environmental Chemistry Letters**, n. 0123456789, 2018.
- CUI, H. et al. Dry-wet and freeze-thaw aging activate endogenous copper and cadmium in biochar. **Journal of Cleaner Production**, v. 288, p. 125605, 2021.
- DADA, A. O.; ADEKOLA, F. A.; ODEBUNMI, E. O. A novel zerovalent manganese for removal of copper ions : synthesis , characterization and adsorption studies. **Applied Water Science**, 2015.
- DE AQUINO SARAIVA, R. et al. Caryocar coriaceum Wittm. **Medicinal and Aromatic Plants of South America**, v. 5, p. 153–162, 2018.
- DE MAGALHÃES, V. H. P.; NEVES, M. A. F. E S. UTILIZAÇÃO DO PERICARPO DE COCO VERDE (*Cocos nucifera* L . - ARECACEAE) PARA A REMOÇÃO DE RESÍDUOS DE ÍONS CROMO (VI) EM SOLUÇÕES AQUOSAS. **Perspectivas da Ciência e Tecnologia**, v. 3, p. 10–16, 2011.
- DE OLIVEIRA, M. N. S. et al. Estádio de maturação dos frutos e fatores relacionados aos aspectos nutritivos e de textura da polpa de pequi (*Caryocar brasiliense* Camb.). **Revista Brasileira de Fruticultura**, v. 28, n. 3, p. 380–386, 2006.
- DELBIANCO, G. A. B. **Estudo de Rejeitos de Galvanoplastia e a sua Aplicação na Fabricação de Peças Cerâmicas Rústicas para Fins Decorativos**. [s.l.] UNESP, 2008.
- DENG, J. et al. Competitive adsorption of Pb(II), Cd(II) and Cu(II) onto chitosan-pyromellitic dianhydride modified biochar. **Journal of Colloid and Interface Science**, v. 506, p. 355–364, 2017.
- DUARTE- NETO, J. F. et al. Processos de adsorção de corantes em argilas esmectíticas: uma revisão. **Revista Eletrônica de Materiais e Processos**, v. 9, p. 51–59, 2014.
- EL-ARABY, H. A. et al. Sesame Husk as Adsorbent for Copper(II) Ions Removal from
-

- Aqueous Solution. **Journal of Geoscience and Environment Protection**, v. 05, n. 07, p. 109–152, 2017.
- ELOVICH, S. Y.; LARINOV, O. G. Theory of adsorption from solutions of non electrolytes on solid (I) equation adsorption from solutions and the analysis of its simplest form,(II) verification of the equation of adsorption isotherm from solutions. **Izvestiya Akademii Nauk**, v. 2, n. 2, p. 209–216, 1962.
- ESCUADERO-OÑATE, C.; VILLAESCUSA, I. The Thermodynamics of Heavy Metal Sorption onto Lignocellulosic Biomass. **Heavy Metals**, 2018.
- FALAKI, Z.; BASHIRI, H. Preparing an adsorbent from the unused solid waste of Rosewater extraction for high efficient removal of Crystal Violet. **Journal of the Iranian Chemical Society**, v. 18, n. 10, p. 2689–2702, 2021.
- FEI, Q.; BEI, W. Single- and multi-component adsorption of Pb, Cu, and Cd on peat. **Bulletin of Environmental Contamination and Toxicology**, v. 78, n. 3–4, p. 265–269, 2007.
- FENG, N. et al. Biosorption of heavy metals from aqueous solutions by chemically modified orange peel. **Journal of Hazardous Materials**, v. 185, n. 1, p. 49–54, 2011.
- FUTALAN, C. M. et al. Comparative and competitive adsorption of copper, lead, and nickel using chitosan immobilized on bentonite. **Carbohydrate Polymers**, v. 83, n. 2, p. 528–536, 2011.
- GEÓCZE, K. C. **Exploratory analysis of carotenoids, essential oils and triacylglycerides of pequi (Caryocar brasiliense Camb.) from brazilian districts located in the cerrado biome (In Portugues)**. [s.l.] Universidade Federal de Viçosa, 2011.
- GHOLAMIYAN, S.; HAMZEHLOO, M.; FARROKHANIA, A. RSM optimized adsorptive removal of erythromycin using magnetic activated carbon: Adsorption isotherm, kinetic modeling and thermodynamic studies. **Sustainable Chemistry and Pharmacy**, v. 17, n. May, p. 100309, 2020.
- GIRALDO, L.; MORENO-PIRAJÁN, J. C. Pb²⁺ adsorption from aqueous solutions on activated carbons obtained from lignocellulosic residues. **Brazilian Journal of Chemical Engineering**, v. 25, n. 1, p. 143–151, 2008.
- GUGUSHE, A. S. et al. Adsorptive removal of cd, cu, ni and mn from environmental samples using fe₃o₄-zro₂@aps nanocomposite: Kinetic and equilibrium isotherm studies. **Molecules**, v. 26, n. 11, 2021.
- HACKBARTH, F. V. **REMOÇÃO DE METAIS DE EFLUENTES PETROQUÍMICOS UTILIZANDO BIOMASSA DE MACROALGA MARINHA PELVETIA CANALICULATA COMO ADSORVENTE**. Florianópolis: UFSC, 2014.
- HIKMAT, N. A.; QASSIM, B. B.; KHETHI, M. T. Thermodynamic and Kinetic Studies of
-

- Lead Adsorption from Aqueous Solution onto Petiole and Fiber of Palm Tree. **American Journal of Chemistry**, v. 4, n. 4, p. 116–124, 2014.
- HO, Y. S.; MCKAY, G. Pseudo-second order model for sorption processes. **Process Biochemistry**, v. 34, n. 5, p. 451–465, 1999.
- HOSSAIN, A. et al. Biosorption of Cu(II) From Water by Banana Peel Based Biosorbent: Experiments and Models of Adsorption and Desorption. n. January 2012, 2012.
- HUSSAIN, A. et al. Synthesis and Application of Modified Orchard Waste Biochar for Efficient Scavenging of Copper from Aqueous Solutions. **Arabian Journal for Science and Engineering**, n. 0123456789, 2021.
- IBGE. **Pesquisa nacional de saneamento básico 2017: abastecimento de água e esgotamento sanitário**. [s.l.: s.n.].
- IGHALO, J. O. et al. Mitigation of clofibric acid pollution by adsorption: A review of recent developments. **Journal of Environmental Chemical Engineering**, v. 8, n. 5, 2020a.
- IGHALO, J. O. et al. Competitive adsorption of Pb(II), Cu(II), Fe(II) and Zn(II) from aqueous media using biochar from oil palm (*Elaeis guineensis*) fibers: a kinetic and equilibrium study. **Indian Chemical Engineer**, v. 0, n. 0, p. 1–11, 30 jun. 2020b.
- IRAVANI MOHAMMADABADI, S.; JAVANBAKHT, V. Fabrication of dual cross-linked spherical treated waste biomass/alginate adsorbent and its potential for efficient removal of lead ions from aqueous solutions. **Industrial Crops and Products**, v. 168, n. April, p. 113575, 2021.
- JUMINA et al. Synthesis of C-4-hydroxy-3-methoxyphenylcalix[4]resorcinarene and its application as adsorbent for lead(II), copper(II) and chromium(III). **Bulletin of the Chemical Society of Japan**, v. 92, n. 4, p. 825–831, 2019.
- JUMINA et al. Simultaneous removal of lead(II), chromium(III), and copper(II) heavy metal ions through an adsorption process using C-phenylcalix[4]pyrogallolarene material. **Journal of Environmental Chemical Engineering**, v. 8, n. 4, p. 103971, 2020.
- KADIRI, L. et al. Mathematical modeling and thermodynamic study of copper (II) removal from aqueous solution by *Coriandrum Sativum* seeds. **Mediterranean Journal of Chemistry**, v. 7, n. 6, p. 478–490, 2019.
- KAMARI, A. et al. Biosorptive removal of Cu(II), Ni(II) and Pb(II) ions from aqueous solutions using coconut dregs residue: Adsorption and characterisation studies. **Journal of Environmental Chemical Engineering**, v. 2, n. 4, p. 1912–1919, 2014.
- KHEDDO, A. et al. Adsorption of synthetic dyed wastewater using activated carbon from rice husk. **SN Applied Sciences**, v. 2, n. 12, p. 1–14, 2020.
- KOVÁCS, E. et al. Investigation into the mechanism of stimulation by low-concentration
-

- stressors in barley seedlings. **Journal of Plant Physiology**, v. 166, n. 1, p. 72–79, 2009.
- LAGERGREN, S. Zur Theorie der Sogenannten Adsorption Gelöster Stoffe, Kungliga Svenska Vetenskapsakademiens. **Handlingar**, v. 24, n. 4, p. 1–39, 1898.
- LI, C. et al. Facile synthesis of low-cost magnetic biosorbent from peach gum polysaccharide for selective and efficient removal of cationic dyes. **International Journal of Biological Macromolecules**, v. 107, p. 1871–1878, 2018.
- LI, H. et al. Modified carbon spheres as universal materials for adsorption of cationic harmful substances (paraquat and dyes) in water. **Microporous and Mesoporous Materials**, v. 297, n. June 2019, p. 110040, 2020.
- LI, W. C.; LAW, F. Y.; CHAN, Y. H. M. Biosorption studies on copper (II) and cadmium (II) using pretreated rice straw and rice husk. **Environmental Science and Pollution Research**, v. 24, n. 10, p. 8903–8915, 2017.
- LIMA, V. F.; MERÇON, F. Metais Pesados no Ensino de Química. **Química Nova Na Escola**, v. 33, n. 4, p. 199–205, 2011.
- LIU, R.; LIAN, B. Non-competitive and competitive adsorption of Cd²⁺, Ni²⁺, and Cu²⁺ by biogenic vaterite. **Science of the Total Environment**, v. 659, n. 1, p. 122–130, 2019.
- LIU, X. et al. Competitive adsorption of heavy metal ions from aqueous solutions onto activated carbon and agricultural waste materials. **Polish Journal of Environmental Studies**, v. 29, n. 1, p. 749–761, 2020.
- LONG, Y. et al. Packed bed column studies on lead(II) removal from industrial wastewater by modified *Agaricus bisporus*. **Bioresource Technology**, v. 152, p. 457–463, 2014.
- LOPES, P. S. N. et al. **Frutas Nativas da Região Centro-Oeste do Brasil**. 1^a edição ed. Planaltina - DF: [s.n.].
- LOULIDI, I. et al. Adsorption of Crystal Violet onto an Agricultural Waste Residue: Kinetics, Isotherm, Thermodynamics, and Mechanism of Adsorption. **Scientific World Journal**, v. 2020, 2020.
- LOW, M. J. D. Kinetics of chemisorption of gases on solids. **Chemical Reviews**, v. 60, n. 3, p. 267–312, 1960.
- MAALOUL, N. et al. Synthesis and characterization of eco-friendly cellulose beads for copper (II) removal from aqueous solutions. **Environmental Science and Pollution Research**, v. 27, n. 19, p. 23447–23463, 2020.
- MACIEL, T. C. M. et al. SUBSTRATO À BASE DE PEQUI (*Caryocar coriaceum*) NA PRODUÇÃO DE MUDAS DE TOMATE E PIMENTÃO. **Revista De Agricultura Neotropical**, v. 4, n. 2, p. 9–16, 2017.
- MADALA, S. et al. Equilibrium, kinetics and thermodynamics of Cadmium (II) biosorption
-

- on to composite chitosan biosorbent. **Arabian Journal of Chemistry**, v. 10, p. S1883–S1893, 2017.
- MAHDI, Z.; YU, Q. J.; EL HANANDEH, A. Competitive adsorption of heavy metal ions (Pb^{2+} , Cu^{2+} , and Ni^{2+}) onto date seed biochar: batch and fixed bed experiments. **Separation Science and Technology (Philadelphia)**, v. 54, n. 6, p. 888–901, 2019.
- MALIK, D. S.; JAIN, C. K.; YADAV, A. K. Heavy Metal Removal by Fixed-Bed Column – A Review. **ChemBioEng Rev**, v. 5, n. 3, p. 173–179, 2018.
- MENEZES, J. M. C. et al. Equilibrium, kinetics and thermodynamics of lead (II) adsorption in bioadsorbent composed by Caryocar coriaceum Wittm barks. **Chemosphere**, v. 261, 2020.
- MINISTÉRIO DA SAÚDE. Portaria MS N°2914/2011. **Dou 14/12/2011**, 2011.
- MOHAMMAD, S. G.; AHMED, S. M.; EL-SAYED, M. M. H. Removal of copper (II) ions by eco-friendly raw eggshells and nano-sized eggshells: a comparative study. **Chemical Engineering Communications**, v. 0, n. 0, p. 1–13, 2020.
- MONDAL, S.; MAJUMDER, S. K. **Honeycomb-like porous activated carbon for efficient copper (II) adsorption synthesized from natural source: Kinetic study and equilibrium isotherm analysis**. [s.l.] Elsevier Ltd, 2019. v. 7
- MORAIS, M. J. DE et al. CARACTERIZAÇÃO DA CASCA DE PEQUI (Caryocar Brasiliense Camb.) PARA SUA UTILIZAÇÃO COMO BIOMASSA. **III Congresso de Ensino, Pesquisa e Extensão da UEG**, v. 2, n. 1c, p. 17, 2016.
- MOREIRA, A. DA S. **BIOSSORÇÃO UTILIZANDO ALGA MARINHA (SARGASSUMsp.) APLICADA EM MEIO ORGÂNICO**. [s.l.] UFRN, 2007.
- MOREIRA, S. D. A. **ADSORÇÃO DE ÍONS METÁLICOS DE EFLUENTE AQUOSO USANDO BAGAÇO DO PEDÚNCULO DE CAJU: ESTUDO DE BATELADA E COLUNA DE LEITO FIXO**. [s.l.] UFC, 2008.
- MORENO-BENAVIDES, J. A.; PEÑA-SALAMANCA, E. J.; BENÍTEZ-CAMPO, N. Reducing Cr^{6+} in electroplating wastewater with Bacillus cereus strain B 1. **Universitas Scientiarum**, v. 24, n. 1, p. 73–89, 2019.
- MORIN-CRINI, N. et al. Hemp-based adsorbents for sequestration of metals: a review. **Environmental Chemistry Letters**, 2018.
- NASCIMENTO, R. F. DO et al. **ADSORÇÃO: Aspectos teóricos e aplicações ambientais**. 2ª ed. Fortaleza - Ce: Imprensa Universitária UFC, 2020.
- NERIS, J. B. et al. Evaluation of adsorption processes of metal ions in multi-element aqueous systems by lignocellulosic adsorbents applying different isotherms: A critical review. **Chemical Engineering Journal**, v. 357, n. April 2018, p. 404–420, 2019.
- OLIVEIRA, M. E. B. DE et al. Aspectos Agronômicos e de Qualidade do Pequi. **Embrapa**, v.
-

113, p. 33, 2008.

OLIVEIRA, S. A. DE. **ESTUDO DE ADSORÇÃO DE METAIS PESADOS EM ZEÓLITAS PARA FINS DE USO EM BARREIRA REATIVA**. [s.l.] UFRJ, 2011.

OLIVEIRA, W. L. DE. **Boas Práticas de Manejo para p Extrativismo Sustentável do Pequi**. Brasília: [s.n.].

PEREIRA, F. D. A. et al. ANÁLISE DA ATIVIDADE EXTRATIVISTA DO PEQUI (*Caryocar coriaceum* Wittm) EM COMUNIDADES DA CHAPADA DO ARARIPE NA REGIÃO DO CARIRI CEARENSE. **Conexões Ciência e Tecnologia**, v. 8, p. 59–66, 2014.

PEREIRA, J. E. S. **Biossorção de cobre em solução aquosa utilizando os pós das folhas do cajueiro (*Anacardium occidentale* L.) e da carnaúba (*Copernicia prunifera*)**. [s.l.] UFRN, 2017.

PEREZ, I. C.; CORRÊA, R. G.; PIRES, J. L. *Gestão Ambiental - Galvanoplastia, orientações para o controle ambiental*. p. 48, 2014.

PINO, G. A. H. **Biossorção de Metais Pesados Utilizando Pó da Casca de Coco Verde (*Cocos nucifera*)**. [s.l.] PUC - Rio de Janeiro, 2005.

PINO, G. H.; TOREM, M. L. ASPECTOS FUNDAMENTAIS DA BISSORÇÃO DE METAIS NÃO FERROSOS ESTUDO DE CASO. **Tecnologia em Metalurgia e Materiais**, 2011.

POLICARPO, L. M. **ESTUDO DE EQUILÍBRIO E CINÉTICA DA BISSORÇÃO DE COBRE (II) POR RHIZOPUS MICROSPORUS**. São Paulo - SP: USP, 2015.

RAMOS, K. M. C.; SOUZA, V. A. B. DE. Características físicas e químico-nutricionais de frutos de pequi (*Caryocar coriaceum* Wittm.) em populações naturais da região meio-norte do Brasil. **Revista Brasileira de Fruticultura**, v. 33, n. 2, p. 500–508, 2011.

RAGAVENDRAN, P. et al. FUNCTIONAL GROUP ANALYSIS OF VARIOUS EXTRACTS OF *Aerva lanata* (L.,) BY FTIR SPECTRUM. **Pharmacologyonline**, v. 364, p. 358–364, 2011.

RAMOS, K. M. C.; SOUZA, V. A. B. DE. Características físicas e químico-nutricionais de frutos de pequi (*Caryocar coriaceum* Wittm.) em populações naturais da região meio-norte do Brasil. **Revista Brasileira de Fruticultura**, v. 33, n. 2, p. 500–508, 2011.

RAMOS, R. et al. Produção de adsorventes a base de borra de café industrializado e folhas de *Corymbia citriodora* (eucalipto limão). **Dissertar Produção**, v. 1, n. 28–29, p. 17–22, 2017.

RASOULPOOR, K.; POURSATTAR MARJANI, A.; NOZAD, E. Competitive chemisorption and physisorption processes of a walnut shell based semi-IPN bio-composite adsorbent for lead ion removal from water: Equilibrium, Kinetic and Thermodynamic studies. **Environmental Technology and Innovation**, v. 20, p. 101133, 2020.

- RAY, S.; MISHRA, A. K.; KALAMDHAD, A. S. Adsorption and Hydraulic Conductivity Studies on Bentonite in Presence of Copper Solution. **Journal of Hazardous, Toxic, and Radioactive Waste**, v. 25, n. 2, p. 06020007, 2021.
- REGALBUTO, J. R.; ROBLES, JAIME O. **The Engineering of Pt / Carbon Catalyst Preparation For application on Proton Exchange Fuel Cell Membrane (PEFCM)**. Chicago: [s.n.].
- REICHENBERG, D. Properties of Ion-Exchange Resins in Relation to their Structure. III. Kinetics of Exchange. **Journal of the American Chemical Society**, v. 75, n. 3, p. 589–597, 1953.
- RENGEL, Z. Aluminium cycling in the soil-plant-animal-human continuum. **BioMetals**, v. 17, n. 6, p. 669–689, 2004.
- RODRIGUES, R. F. et al. HEAVY METALS SORPTION ON TREATED WOOD SAWDUST (In Portuguese). **Quimica Nova**, 2007.
- RUTHVEN, D. M. **Principles of adsorption and adsorption processes**. New York: John Wiley&Sons, 1984. v. 4
- ŠABANOVI, E. et al. Simultaneous adsorption of heavy metals from water by novel lemon-peel based biomaterial. **Polish Journal of Chemical Technology**, v. 22, n. 1, p. 46–53, 2020.
- ŠABANOVIĆ, E. et al. Pulverized Banana Peel as an Economical Sorbent for the Preconcentration of Metals. **Analytical Letters**, v. 48, n. 3, p. 442–452, 2015.
- SABELA, M. I. et al. Removal of copper (II) from wastewater using green vegetable waste derived activated carbon: An approach to equilibrium and kinetic study. **Arabian Journal of Chemistry**, v. 12, n. 8, p. 4331–4339, 2019.
- SAHA, U. K.; TANIGUCHI, S.; SAKURAI, K. Simultaneous Adsorption of Cadmium, Zinc, and Lead on Hydroxyaluminum- and Hydroxyaluminosilicate-Montmorillonite Complexes. **Soil Science Society of America Journal**, v. 66, n. 1, p. 117–128, 2002.
- SAHMOUNE, M. N. Evaluation of thermodynamic parameters for adsorption of heavy metals by green adsorbents. **Environmental Chemistry Letters**, v. 17, n. 2, p. 697–704, 2019.
- SALAME, I. I.; BANDOSZ, T. J. Surface chemistry of activated carbons: Combining the results of temperature-programmed desorption, Boehm, and potentiometric titrations. **Journal of Colloid and Interface Science**, v. 240, n. 1, p. 252–258, 2001.
- SALIHI, I. U. et al. Adsorption of copper using modified and unmodified sugarcane bagasse. **International Journal of Applied Engineering Research**, v. 10, n. 19, p. 40434–40438, 2015.
- SANTANA, A. H. **REMOÇÃO DE ÍONS COBRE E CHUMBO DE ÁGUAS**
-

RESIDUAIS UTILIZANDO VAGENS DE *Dimorphandra gardneriana* Tulasne (FAVA D'ANTA). [s.l.] URCA, 2018.

SANTANA, A. H. et al. Copper and lead ion removal from wastewater using fava d'anta fodder (*Dimorphandra gardneriana* Tulasne). **Environmental Geochemistry and Health**, v. 0123456789, 2020.

SANTHOSH, A.; DAWN, S. S. Synthesis of zinc chloride activated eco-friendly nano-adsorbent (activated carbon) from food waste for removal of pollutant from biodiesel wash water. **Water Science and Technology**, v. 00, n. 0, p. 1–12, 2021.

SCHNEIDER, I. A. H. **Biossorção de Metais Pesados com a Biomassa de Macrófitos Aquáticos.** [s.l.] UFRGS, 1955.

SCHNEIDER, R. M. et al. **BIOMASSAS PARA A ADSORÇÃO DO METAL CROMO III DE EFLUENTE.** Gramado - RS: [s.n.].

ŠĆIBAN, M.; KLAŠNJA, M.; ŠKRBIĆ, B. Modified softwood sawdust as adsorbent of heavy metal ions from water. **Journal of Hazardous Materials**, v. 136, n. 2, p. 266–271, 2006.

ŠĆIBAN, M.; KLAŠNJA, M.; ŠKRBIĆ, B. Adsorption of copper ions from water by modified agricultural by-products. **Desalination**, v. 229, n. 1–3, p. 170–180, 2008.

SEBRAE. Lapidando a imagem da jóia brasileira. 2007.

SEBRAE. Indústria da Moda: Gemas e Joias. **Estudo de Mercado**, 2017.

SEMACE. Resolução COEMA nº02, de 02 de fevereiro de 2017. p. 56–61, 2017.

ŞENEL, G. U. Adsorption of Copper (II) from Aqueous Solution by Using Carbonized Peanut Hull: Determination of the Equilibrium, Kinetic and Thermodynamic Parameters. **Journal of Anatolian Environmental and Animal Sciences**, v. 90, n. 533, 2020.

SENTHIL KUMAR, P. et al. Adsorption of metal ions onto the chemically modified agricultural waste. **Clean - Soil, Air, Water**, v. 40, n. 2, p. 188–197, 2012.

SHAHAT, A. et al. Novel hierarchical composite adsorbent for selective lead(II) ions capturing from wastewater samples. **Chemical Engineering Journal**, v. 332, n. September 2017, p. 377–386, 2018.

SHAMIM, S. Biosorption of Heavy Metals. **Biosorption**, 2018.

SIQUEIRA, B. DOS S. et al. PECTINA EXTRAÍDA DE CASCA DE PEQUI E APLICAÇÃO EM GELEIA LIGHT DE MANGA. **revista brasileira fruticultura**, v. 34, n. 2, p. 560–567, 2012.

SOETAREDJO, F. E. et al. Incorporation of selectivity factor in modeling binary component adsorption isotherms for heavy metals-biomass system. **Chemical Engineering Journal**, v. 219, p. 137–148, 2013.

- SOUSA NETO, V. O. et al. Use of coconut bagasse as alternative adsorbent for separation of copper (II) ions from aqueous solutions: Isotherms, kinetics, and thermodynamic studies. **BioResources**, v. 6, n. 3, p. 3376–3395, 2011.
- SOUZA, J. P. DE et al. PEQUI (*Caryocar coriaceum* Wittm) PRODUCT STABILITY UNDER FREEZING IN DIFFERENT TYPES OF PACKAGING (In Portuguese). **Revista Brasileira de Fruticultura**, v. 35, n. 4, p. 971–976, 2013.
- TANG, X. et al. Extremely efficient and rapidly adsorb methylene blue using porous adsorbent prepared from waste paper: Kinetics and equilibrium studies. **Journal of Hazardous Materials**, v. 402, n. July 2020, p. 123579, 2021.
- TARIBA LOVAKOVIĆ, B. Cadmium, arsenic, and lead: elements affecting male reproductive health. **Current Opinion in Toxicology**, v. 19, n. Figure 1, p. 7–14, 2020.
- TARLEY, C. R. T.; ARRUDA, M. A. Z. Biosorption of heavy metals using rice milling by-products. Characterisation and application for removal of metals from aqueous effluents. **Chemosphere**, v. 54, n. 7, p. 987–995, 2004.
- TAŞAR, Ş.; ÖZER, A. A thermodynamic and kinetic evaluation of the adsorption of pb(II) ions using peanut (*arachis hypogaea*) shell-based biochar from aqueous media. **Polish Journal of Environmental Studies**, v. 29, n. 1, p. 293–305, 2020.
- TAVANA, M.; PAHLAVANZADEH, H.; ZAREI, M. J. The novel usage of dead biomass of green algae of *Schizomeris leibleinii* for biosorption of copper(II) from aqueous solutions: Equilibrium, kinetics and thermodynamics. **Journal of Environmental Chemical Engineering**, v. 8, n. 5, p. 104272, 2020.
- TEIXEIRA, R. N. P. **REMOÇÃO DE Cu(II), Ni(II), Cd(II) E Pb(II) DE EFLUENTES DE INDÚSTRIAS DE GALVANOPLASTIA USANDO O SISTEMA HÍBRIDO ADSORÇÃO- ELETRO-FLOTAÇÃO-COAGULAÇÃO**. [s.l.] UFC, 2015.
- TOUIHRI, M. et al. Single and simultaneous adsorption of Cr(VI) and Cu (II) on a novel Fe₃O₄/pine cones gel beads nanocomposite: Experiments, characterization and isotherms modeling. **Chemical Engineering Journal**, v. 416, n. February, 2021.
- USLU, G.; TANYOL, M. Equilibrium and thermodynamic parameters of single and binary mixture biosorption of lead (II) and copper (II) ions onto *Pseudomonas putida*: Effect of temperature. **Journal of Hazardous Materials**, v. 135, n. 1–3, p. 87–93, 2006.
- VERÍSSIMO, L. S.; CAVALCANTE, I. N. AS ÁGUAS SUBTERRÂNEAS DO CRAJUBAR, REGIÃO DO CARIRI - ESTADO DO CEARÁ - BRASIL. **1st Joint World Congress on GroundWaterr**, n. 85, p. 1–17, 2000.
- WANG, J.; GUO, X. Adsorption kinetic models: Physical meanings, applications, and solving methods. **Journal of Hazardous Materials**, v. 390, n. November 2019, p. 122156, 2020.
-

- WEBER, W. J.; MORRIS, J. C. Kinetics of adsorption on carbon from solution. **Journal of the Sanitary Engineering Division**, v. 89, p. 31–60, 1963.
- WONG, K. K. et al. Removal of Cu and Pb from electroplating wastewater using tartaric acid modified rice husk. **Process Biochemistry**, v. 39, n. 4, p. 437–445, 2003.
- YADAV, V.; BHAGAT, M. Isotherm , kinetics and thermodynamic parameters study of arsenic (III) and copper (II) adsorption onto Limonia acidissima shell carbon. **Desalination and Water Treatment**, v. 184, n. April, p. 214–224, 2020.
- YADAV, V.; TIWARI, D. P.; BHAGAT, M. Isotherm, kinetic and thermodynamic parameters study of arsenic (III) and copper (II) adsorption onto Limonia acidissima shell carbon. **Desalination and Water Treatment**, v. 184, n. April, p. 214–224, 2020.
- ZHU, Y.; HU, J.; WANG, J. Competitive adsorption of Pb(II), Cu(II) and Zn(II) onto xanthate-modified magnetic chitosan. **Journal of Hazardous Materials**, v. 221–222, p. 155–161, 2012.
- ZOU, W.; BAI, H.; GAO, S. Competitive adsorption of neutral red and Cu²⁺ onto pyrolytic char: Isotherm and kinetic study. **Journal of Chemical and Engineering Data**, v. 57, n. 10, p. 2792–2801, 2012.
-

Artigo 1 – Equilibrium, kinetics and thermodynamics of lead (ii) adsorption in bioadsorbent composed by *Caryocar Coriaceum* WITTM barks

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Situação: Publicado

Resumo do artigo em português:

O descarte inadequado de resíduos contendo metais tóxicos promove sérios problemas ambientais. A bioadsorção destaca-se como uma técnica poderosa na remoção de metais tóxicos de soluções aquosas, tornando-se uma técnica eficiente e de baixo custo, pois utiliza materiais abundantes e de origem natural. Este trabalho teve como objetivo estudar a aplicação da casca de *Caryocar coriaceum* Wittm, como possível bioabsorvente para a remoção do Chumbo (II) presente em soluções aquosas, para isso, os resíduos deste material foram coletados em um mercado público, onde foram lavados e secos, depois triturados, peneirados (32mesh) e lavados novamente, para então serem utilizados nos testes cinéticos, isotérmicos e termodinâmicos de adsorção de íons chumbo (II). Após os experimentos, verificou-se que o aumento da temperatura desfavoreceu a taxa de adsorção de chumbo (II), variando de 15,6 a 13,5 mg.L⁻¹, para temperaturas de 5 °C e 35 °C, respectivamente. O modelo cinético de pseudo-segunda ordem caracteriza melhor a velocidade de adsorção obtendo um coeficiente de regressão linear de 0,9997, enquanto o modelo de pseudo-primeira ordem obteve um valor de 0,7117. A adsorção ocorreu por quimissorção, com difusão intrafilme. O modelo isotérmico que melhor representou a adsorção foi o de Langmuir (R² 0,99). Concluiu-se que a casca de *Caryocar coriaceum* Wittm é uma boa alternativa para ser utilizada como bioabsorvente para soluções contendo chumbo dissolvido (II).

Palavras-chave Bioadsorção, Metal Tóxico, Biorremediação, Casca de Pequi.

Artigo 2 – Kinetic and thermodynamic study of copper (II) IONS biosorption by *Caryocar Coriaceum* Wittm bark.

Autores: Jorge Marcell Coelho Menezes, Amanda Maria da Silva Bento, Francisco José de Paula Filho, José Galberto Martins da Costa , Henrique Douglas Melo Coutinho Raimundo Nonato Pereira Teixeira

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Resumo do artigo em português

O descarte inadequado de resíduos contendo metais tóxicos é um grande problema de poluição ambiental. Dentre as diferentes metodologias para lidar com este problema, a biossorção é considerada um dos processos mais eficientes para a remoção de metais tóxicos de soluções aquosas. A utilização de adsorventes naturais, como os resíduos vegetais, em um processo conhecido como biossorção, destaca-se ainda mais por combinar a remediação de águas poluídas com a redução da quantidade de resíduos sólidos. Este trabalho teve como objetivo estudar o uso da casca de *Caryocar Coriaceum* Wittm, fruto conhecido como pequi, como possível bioadsorvente para remoção de cobre (II) de soluções aquosas. Para tanto, a casca do pequi foi coletada em um mercado público da cidade, lavada, seca e triturada. O material obtido foi então peneirado e a fração de 32 mesh foi recolhida, lavada e seca novamente. O material resultante foi então submetido a ensaios cinéticos, isotérmicos e termodinâmicos para biossorção de cobre (II). Verificamos que a capacidade de biossorção do cobre (II) é favorecida pelo aumento das temperaturas, variando de 16,8 a 20,4 mg.L⁻¹ a 5°C e 35°C, respectivamente. O modelo cinético que melhor se ajustou ao processo de biossorção foi o modelo de pseudo-segunda ordem, que produziu um coeficiente de regressão linear de 0,999, enquanto o modelo de pseudo-primeira ordem produziu um valor de 0,695. O processo de bioadsorção foi caracterizado por quimissorção com difusão intrafilme. O modelo isotérmico que melhor representou a biossorção foi o de Langmuir (R² = 0,99). Diante dos resultados obtidos, concluímos que a casca de *Caryocar Coriaceum* Wittm é uma boa alternativa bioadsorvente para soluções contendo cobre dissolvido (II).

Palavras-chave: Biossorção, Metais Tóxicos, Íons Cu(II), Biorremediação, *Cariocar Coriaceum* Wittm, Casca de Pequi.

Artigo 3 – Competitive bioadsorption of Pb^{+2} and Cu^{+2} ions by *Caryocar Coriaceum* WITTM barks

Autores: Jorge Marcell Coelho Menezes, Francisco José de Paula Filho; José Galberto M. da Costa; Henrique Douglas M. Coutinho; Raimundo Nonato Pereira Teixeira.

Revista / link / Qualis: International Biodeterioration and Biodegradation,

<https://www.sciencedirect.com/journal/international-biodeterioration-and-biodegradation>, IF: 4,907 (Qualis A1).

Situação: Submetido

Resumo do artigo em português

A deterioração do meio ambiente e os danos à saúde dos seres vivos são características do descarte inadequado de resíduos contendo metais tóxicos como íons cobre e chumbo. Dentre várias técnicas, a bioadsorção se destaca por ser uma técnica barata e de fácil operação para remoção de contaminantes, como metais tóxicos, em ambientes aquosos. A adsorção de espécies químicas em sistemas multielementares é caracterizada por sua competição por sítios ativos presentes na superfície bioadsorvente. Este trabalho teve como objetivo avaliar o uso de resíduos descartados da casca de *Caryocar Coriaceum* WITTM como um possível bioabsorvente para a remoção de íons Pb^{+2} e Cu^{+2} em sistemas mono e multielementares, apresentados em soluções aquosas. Técnicas de caracterização como SEM-EDS, XRD, FTIR e pH_{PZC} foram utilizadas para estudar o bioadsorvente. Os resultados mostraram que todos os sistemas seguem o modelo de pseudo segunda ordem, o processo de difusão foi a quimissorção associada à mudança de íons. O modelo de Langmuir apresentou melhor ajuste que o modelo de Freundlich. A capacidade adsorptiva máxima ($mg.g^{-1}$) obtida foi de 47,6 para Pb^{+2} e 20,4 para Cu^{+2} . Verificou-se que houve um efeito inibitório entre Cu^{+2} e Pb^{+2} , o que resultou em uma redução dos valores de q_{max} em aproximadamente 37%, para Cu^{+2} , e 55%, para Pb^{+2} . Como conclusão, verificou-se que a casca de *Caryocar Coriaceum* Wittm pode ser utilizada como bioadsorvente para soluções contendo Pb^{+2} e Cu^{+2} dissolvidos, tanto para sistemas mono quanto multielementares.

Palavras-chave: Bioadsorção Competitiva; Metais Tóxicos; Tratamento de Água Residuarias; Reutilização de Resíduos Agrícolas.

**CAPÍTULO I: PRIMEIRO ARTIGO TÉCNICO PUBLICADO EM PERIÓDICO
CIENTÍFICO**

**PRIMEIRO ARTIGO TÉCNICO PUBLICADO EM PERIÓDICO CIENTÍFICO
EQUILIBRIUM, KINETICS AND THERMODYNAMICS OF LEAD (II)
ADSORPTION IN BIOADSORVENT COMPOSED BY *Caryocar coriaceum* Wittm
BARKS**

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ABSTRACT

The improper disposal of waste containing toxic metals promotes serious environmental problems. Biosorption stands out as a powerful technique in removing toxic metals from aqueous solutions, making it an efficient and low-cost technique, since it makes use of abundant materials and of natural origins. This work aimed to study the application of the bark of *Caryocar coriaceum* Wittm, as a possible bioabsorbent for the removal of Lead (II) present in aqueous solutions, for this, residues of this material were collected in a public market, where they were washed and dried, then crushed, sieved (32mesh) and washed again, to then be used in the kinetic, isotherm and thermodynamic tests of lead (II) ions adsorption. After the experiments, it was found that the increase of the temperature disfavored the rate of lead (II) adsorption, ranging from 15.6 to 13.5 mg.L⁻¹, for temperatures of 5 °C and 35 °C, respectively. The pseudo-second order kinetic model best characterizes the adsorption velocity obtaining a linear regression coefficient of 0.9997, while the pseudo-first order obtained a value of 0.7117. Adsorption occurred by chemisorption, with intra-film diffusion. The isothermal model that best represented the adsorption was Langmuir's (R² 0.99). It was concluded that the bark of *Caryocar coriaceum* Wittm is a good alternative to be used as a bioabsorbent for solutions containing dissolved lead (II).

Keywords Bioadsorption, Toxic Metal, Bioremediation, Pequi's Bark.

HIGHLIGHTS

- *Caryocar coriaceum* Wittm bark is a good bioadsorbent for solutions with Pb(II) ions.
- *Caryocar coriaceum* Wittm bark has high adsorptive capacity compared to other natural unmodified adsorbents.
- *The use of Caryocar coriaceum* Wittm bark tailings, as adsorbent, can minimize the amount of waste being sent to landfills.
- *Caryocar coriaceum* Wittm bark is an abundant and low-cost material to be used as an adsorbent.

INTRODUCTION

Lead (Pb(II)) is associated with several human productive activities, due to its unique chemical and physical properties, considering high malleability, low melting point, ductility and corrosion resistance. Mining, galena, storage batteries, alloys, cable sheaths, solder, industrial products for use in plastics, paints, automobiles, ceramics X-ray equipment and radiation shielding, are some of the applications of this metal (AWUAL et al., 2020; SHAHAT et al., 2018).

When incorrectly disposed or accumulated in groundwater and on the soil surface, as a waste of several industrial processes, the toxic metals, such as the Lead, tend to produce serious environmental problems, as they present difficult degradation, affect the self-cleaning processes of the environment and are still bioaccumulated in the chain of living beings, promoting toxicity to living organisms, damaging human brain, liver, kidneys and reproductive system (AWUAL, 2019a; SAHMOUNE, 2019; TARIBA LOVAKOVIĆ, 2020).

In order to avoid such environmental and human health problems, residues containing toxic metals must be treated prior to their disposal, minimizing the concentration of these components in order to establish the relevant legislation.

Techniques such as chemical precipitation, electrochemical treatment, oxidoreduction processes, ion exchange, reverse osmosis, phytoremediation, among others, are possible processes for removing toxic metals present in aquatic environments, however, these have disadvantages such as: expensive, inefficient, labor intensive or the treatment process has no selectivity (ESCUADERO-OÑATE; VILLAESCUSA, 2018)

Recently, the biosorption process has been highlighted as a promising treatment technique for removing toxic metals from liquid effluents, due this process makes use of natural materials of biological origin that have metal sequestering properties, promoting to the reduce

ion concentrations of toxic metals from mg.L^{-1} to $\mu\text{g.L}^{-1}$ (AL-QODAH; YAHYA; AL-SHANNAG, 2017), in addition to being an easy to operate, profitable, simple process, environmental friendliness and presenting the possibility of efficient regeneration and reuse from the stand point of cost-effective (AWUAL et al., 2019; AWUAL; HASAN, 2019; BURAKOV et al., 2018).

The use of agricultural by-products as bioadsorbents has been widely explored with a view to verifying their efficiency in removing toxic metals. The materials used involve the most diverse types, such as seeds of *Azadirachta indica* A. Juss (COSTA et al., 2020), fava d'anta fodder (SANTANA et al., 2020), banana peel (HOSSAIN et al., 2012), coconut bagasse (SOUSA NETO et al., 2011), Palm Fibres and Orange peel (AMIN; ALAZBA; AMIN, 2017), sugarcane bagasse (GIRALDO; MORENO-PIRAJÁN, 2008), Sesame Husk (EL-ARABY et al., 2017), among others.

Some advantages of the agricultural bioadsorbents are, present a cell wall rich in polysaccharides, especially cellulosic pectin compounds, which being treated with alkalizing agents, it produces negative charges that can bind to toxic metals; another important point is the ease of preparation and availability, since these materials are basically obtained from agricultural by-products and industrial waste; another advantage is the fact that, when saturated, the metal can be separated from organic materials by incineration and be reused in other applications (AL-QODAH; YAHYA; AL-SHANNAG, 2017).

Thus, based on the adsorptive capacity of agricultural materials, the objective of this work was to study the application of the bark of *Caryocar coriaceum* Wittm (CCB), as a possible bioadsorbent for lead (II) metal ions, performing kinetic, isotherm and thermodynamic adsorptions for the removal of that metals in synthetic monoelement solutions.

MATERIALS AND METHODS

ABSORBENT COLLECTION AND PREPARATION

The CCB tailings were collected in the public market in the city of Crato, Ceará state, located in the northeast region of Brazil, with coordinates -7.228705, -39.407761, and taken to the Analytical Center of the Federal University of Cariri (UFCA).

After collected, the tailings were washed with water to remove coarse impurities, being subjected to the peeling process, using a vegetable peeler to obtain the skin epidermis, the

exocarp. Subsequently, they were exposed to natural drying, by exposure to the sun, for a period of 3 days, with an exposure time of 8 hours per day, resulting in a total of 24 hours.

The dried barks were then crushed, in a conventional blender, until a fine-looking material was obtained. From this material, the 32 mesh particle size fraction was collected through sieving using an electromagnetic agitator for round sieves of the Bertel brand, performed at the UFCA soil laboratory, for a period of 10 minutes with vibration 10. This The material was then washed with reverse osmosis purified water and then oven dried at 60 °C for a period of 24 hours.

MATERIAL CHARACTERIZATION

Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra were obtained in transmittance mode using a PerkinElmer spectrophotometer, model spectrum two. The samples were prepared in the form of KBr pellets and the spectra recorded in the range of 4000 to 450 cm^{-1} , using 48 scans and 4 cm^{-1} resolution.

Boehm Titration

Oxygen-containing functional groups present on the surface of the adsorbent material were determined by Boehm titration (BOEHM, 2002; SALAME; BANDOSZ, 2001). 0.5 grams of the adsorbents, before and after the adsorption process, were weighed in the erlenmeyers flasks, then 10 mL of NaOH (0.1M), Na_2CO_3 (0.05M) and NaHCO_3 (0.05M) solutions were transferred to the erlenmeyers flasks, that containing the weighed samples. These were sealed and stirred for 24h at 150 rpm and finally filtered. 2 mL of the filtrate was pipetted and excess base was titrated with 0.1M HCl standard solution. The whole test was performed in duplicate.

In this test, it is assumed that the carboxylic groups are neutralized with the NaHCO_3 solution, the carboxylic and lactonic groups by the Na_2CO_3 solution, and finally the carboxylic, lactonic and phenolic groups by the NaOH solution, being determined the isolated concentrations, through the difference between them.

Thermogravimetric Analysis (TGA)

Through TGA, it can determine material stability over different temperature ranges, identifying possible mass or component losses through temperature action. The test was

performed using a Shimadzu thermogravimetric analyzer, model TGA - 50. Approximately 10 mg of sample was weighed in a platinum tray and the temperature range studied was 25 to 500 °C, with a heating rate of 10 °C.min⁻¹, in nitrogen atmosphere.

Point of Zero Charge Test (PZC)

The PZC was determined based on the methodology described by Regalbuto and Robles (2004). Eleven solutions were prepared within the pH range of 1 to 11 (initial pH). A volume of 10 mL of these solutions was transferred to an erlenmeyer containing approximately 10 mg of adsorbent, previously weighed. These were subjected to agitation at 150 rpm for a period of 2 h on a shaking table of the brand Nova Ética, model 109. After this contact time, the pH of the solution (final pH) was measured.

To determine the pH_{PZC} , a graph was plotted between the initial and final pH data, and it was possible to observe a pH region that has a strong buffering effect on the final pH value. The pH_{PZC} was then determined by averaging the initial pH values present in this region.

ADSORPTION EXPERIMENTS

Adsorption Kinetics

The adsorption kinetics assay was carried out in the facilities of the UFCA Analytical Center Lab, Juazeiro do Norte, Ceará, Brazil.

The experiment was carried out at room temperature (22 °C) and in duplicate, consisting of weighing approximately 50 mg of the adsorbent material in 150 mL erlenmeyers flasks. Subsequently, 10 mL of pH 5.5 buffered copper solution (acetate buffer) was added to these. The adsorbents with the metallic solutions were agitated, with rotation of 150 rpm, in a shake table of the brand Nova Ética, model 109.

The times studied in kinetics ranged from 1 minute to 4 hours, in order to determine the minimum time required for adsorption equilibrium. After reaching the established contact time, the samples were filtered, on filter paper, and analyzed by Flame Atomic Absorption Spectroscopy (FAAS), also performed at the UFCA analytical center Lab, using a Varian spectrometer, model SpectrAA 50B.

Adsorption Isotherm

In the adsorption isotherm, the initial concentrations of the metal solutions were altered, which ranged from approximately 20 mg.L⁻¹ to 600 mg.L⁻¹, and the adsorption time fixed to that determined in the kinetics test.

As in kinetics, after reaching the established contact time, the samples were filtered and analyzed by FAAS.

Adsorption Thermodynamics

The temperatures studied in the adsorption thermodynamics test were 5, 10, 25 and 35 °C. In this test, 10 mL of 100 mg.L⁻¹ metal solution, previously submitted to the study temperature, was transferred to an erlenmeyer containing 50 mg of adsorbent. This set was agitated for 2 hours under room temperature control, using a Novatécnica shaker incubator, Model NT 715, from the Natural Products Research Laboratory (LPPN) of the Regional University of Cariri (URCA). All tests were performed in duplicate.

Analysis of Experimental Data

All metal adsorption results in this study were analyzed in terms of adsorptive capacity (q), determined by equation 1.

$$q = \frac{(C_0 - C_t) \times V}{m_{ads}} \quad (1)$$

Where: C₀: Initial concentration of the metal solution (mg.L⁻¹); C_t: Concentration of the metal solution after a time t (mg.L⁻¹); V: Volume of the solution (L); m_{ads}: Adsorbent mass (g).

Kinetic and diffusion models

In order to obtain better knowledge about the adsorptive process from lead (II) to CCB adsorbent, the experimental data were applied in well-established and widespread models. The models used in this study are shown in table 1.

Table 1: Adsorption kinetic models used in this paper.

Kinetic Model	Linearized form of equations	Parameters

		Q_t : Biosorption capacity in a t time (mg.g ⁻¹);
Pseudo-first order equation	$\ln(Q_{Eq} - Q_t) = \ln(Q_{Eq}) - K_1 t$	Q_{eq} : Equilibrium biosorption capacity (mg.g ⁻¹) k_1 : Pseudo-first order reaction speed constant (min ⁻¹). t : Time (min)
Pseudo-second order equation	$\frac{t}{Q_t} = \frac{1}{K_2 Q_{Eq}^2} + \frac{1}{Q_{Eq}} t$	K_2 : pseudo-second order reaction speed constant (g.mg ⁻¹ .min ⁻¹)
Elovich's Kinetic Model	$t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t)$	α : The initial adsorption rate (mg.g ⁻¹ .min ⁻¹). β : the desorption constants (g.mg ⁻¹). q_t : Amount of metal adsorbed on the solid phase (mg.g ⁻¹) at time t (min);
Intraparticle diffusion model	$q_t = K_d * t^{0.5} + C$	K_d : Intraparticle diffusion coefficient (mg.g ⁻¹ .min ^{-0.5}), obtained from the slope and the C value of the intersection of the graph curve qt versus t ^{0.5} ; C: Constant related to resistance to diffusion (mg.g ⁻¹).

Source: (BOPARAI; JOSEPH; O'CARROLL, 2011; DUARTE- NETO et al., 2014; HO; MCKAY, 1999; WEBER; MORRIS, 1963)

Adsorption isotherms

The relationship between the metal ions present in the solution and those adsorbed to the adsorbent, when both are in equilibrium, is investigated through the study of the adsorption isotherm (AWUAL; HASAN, 2014).

This study provides the knowledge of certain parameters that assist in the design of adsorptive systems, as well as in the nature and mechanisms involved in the adsorption process. The studied isothermal models were Langmuir, Freundlich, Temkin and Dubinin-Radushkevich (D-R), shown in table 2.

Table 2: Adsorption isotherm models used in this paper

Isotherm Model	Linearized form of equations	Parameters
Langmuir Isotherm	$\frac{C_e}{q_e} = \frac{1}{q_{max}} C_e + \frac{1}{q_{max} \times K_L}$	q_e : Amount of metal adsorbed per unit mass of adsorbent (mg.g ⁻¹); C_e : Ion concentration in equilibrium solution (mg.L ⁻¹); K_L : Equilibrium constant (L.g ⁻¹); q_{max} : Adsorbent's maximum adsorption capacity (mg.g ⁻¹).
Freundlich Isotherm	$\ln(q_e) = \ln(K_F) + \frac{1}{n} \ln(C_e)$	q_e : Amount of adsorbed solute (mg.g ⁻¹); C_e : Ion concentration in equilibrium solution (mg.L ⁻¹); K_F : Adsorption capacity constant ((mg.g ⁻¹)(L.mg ⁻¹) ^{1/n}). $1/n$: Adsorption Intensity Constant
Temkin Isotherm	$q_e = \frac{RT}{b} \ln K_t + \frac{RT}{b} \ln C_e$	b : Temkin constant (J.mol ⁻¹) K_t : Temkin's Isothermal Constant (L.g ⁻¹) R: Universal gas constant (J.mol ⁻¹ K ⁻¹) T: Temperature (K)
Dubini–Radushkevich (D-R) Isotherm	$\ln q_e = \ln q_d - \beta * \varepsilon^2$ $\varepsilon = RT \ln \left[1 + \frac{1}{C_e} \right]$	q_d : D – R Constant (mg.g ⁻¹) β : Constant related to free energy ε : Polanyi potential

Source: (ABDI; KAZEMI, 2015; DADA; ADEKOLA; ODEBUNMI, 2015; FENG et al., 2011; TAŞAR; ÖZER, 2020)

Adsorption thermodynamics

The study of the thermodynamic behavior of the adsorption processes of toxic metals in solutions, provides important information for understanding the type of mechanism involved and the spontaneity of the adsorptive process (SAHMOUNE, 2019).

The studied thermodynamic parameters were Gibbs free energy (ΔG°), the enthalpy (ΔH°) and the entropy (ΔS°). The values of ΔH° e ΔS° , corresponded to the slope and intercept, respectively, of a graph plotted between the data of $\ln(K)$ vs $1/T$. The ΔG° values were obtained using the equations presented in table 3.

Table 3: Thermodynamic equations used in this study.

Name of the equations	Equations	Parameters
Gibbs free energy	$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$	ΔG° : Gibbs free energy ($\text{J}\cdot\text{mol}^{-1}$); ΔH° : Enthalpy ($\text{kJ}\cdot\text{mol}^{-1}$); ΔS° : Entropy ($\text{kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$);
Equation for graphically determining the values of ΔH° and ΔS° .	$\Delta G^\circ = -RT\ln(K)$ $\ln(K) = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$	K: reaction speed constant; R: Gas Constante ($8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$); T: Temperature (K).

Source: (SAHMOUNE, 2019)

RESULTS AND DISCUSSION

MATERIAL CHARACTERIZATION

Infrared Spectroscopy Analysis (FTIR)

Figure 1 shows the FTIR spectrum obtained for the CCB, where the presence of a wide band centered at 3390 cm^{-1} , referring to the axial stretching of OH and NH of proteins, fatty acids, carbohydrates and lignin, present in plants, two smaller peaks with frequency 2919 and 2850 cm^{-1} for the asymmetric C-H vibration of the carbonyl and the -OH stretch of carboxylic acids, respectively. Stretch C = O (1700 cm^{-1}) indicative of carboxylic acids, CO vibration in 1625 cm^{-1} referring to amino acids, vibration $-(\text{CH}_2)_n-$ (1451 cm^{-1}). A peak at 1337 cm^{-1} is probably related to the CH_2 angular strain of CH_3 groups. Axial vibration C-O-C in 1198, 1164 and 1057 cm^{-1} , associated with glycoside groups, and finally a peak in 757 cm^{-1} regarding the presence of polysaccharides (AMORIM et al., 2016; BREDA et al., 2017; RAGAVENDRAN et al., 2011).

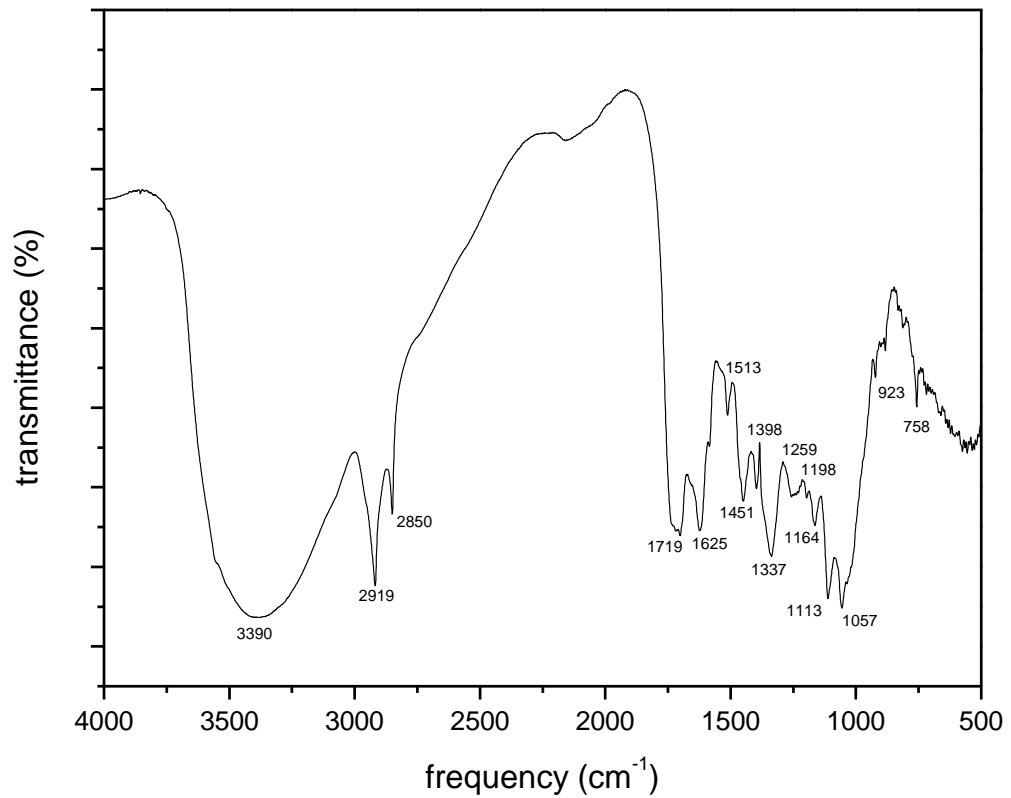


Figure 1: FTIR of CCB adsorbent material.

The CCB has a large amount of fibers in its composition, and several polysaccharides can be found, such as pectin, starch, cellulose, hemicelluloses and lignin (DE OLIVEIRA et al., 2006; LIMA; MERÇON, 2011; SIQUEIRA et al., 2012), which possibly represent the components responsible for providing the functional groups indicated in figure 1.

Boehm Titration

Table 4: Boehm titration

Sample	Total acid Sites (mmol.g ⁻¹)	Phenolic Groups (mmol.g ⁻¹)	Carboxylic Groups (mmol.g ⁻¹)	Lactonics Groups (mmol.g ⁻¹)
CCB	1.899	1.275	0.125	0.499

The presence of phenolic, carboxylic and laconic groups, indicated in the FTIR assay, is reinforced by Boehm titration (Table 4). As stated above, such groups may provide active sites favorable for the adsorption of lead (II) present in the aqueous solution.

Thermal analysis

There were 3 mass loss events for the analyzed adsorbent (figure 2), one approximately at 69 °C, characterized by water evaporation and dehydration of hydroxyl and amino groups (BREDA et al., 2017). Another around 265 °C, related to the evaporation of some volatile oils and certain fatty acids such as palmitic acid, found in large quantities in *Caryocar coriaceum* WITTM (CORDEIRO et al., 2013), evidenced by the generation of environmentally friendly odors, and finally, a third at 351 °C, related to the oxidation and decomposition of organic substances.

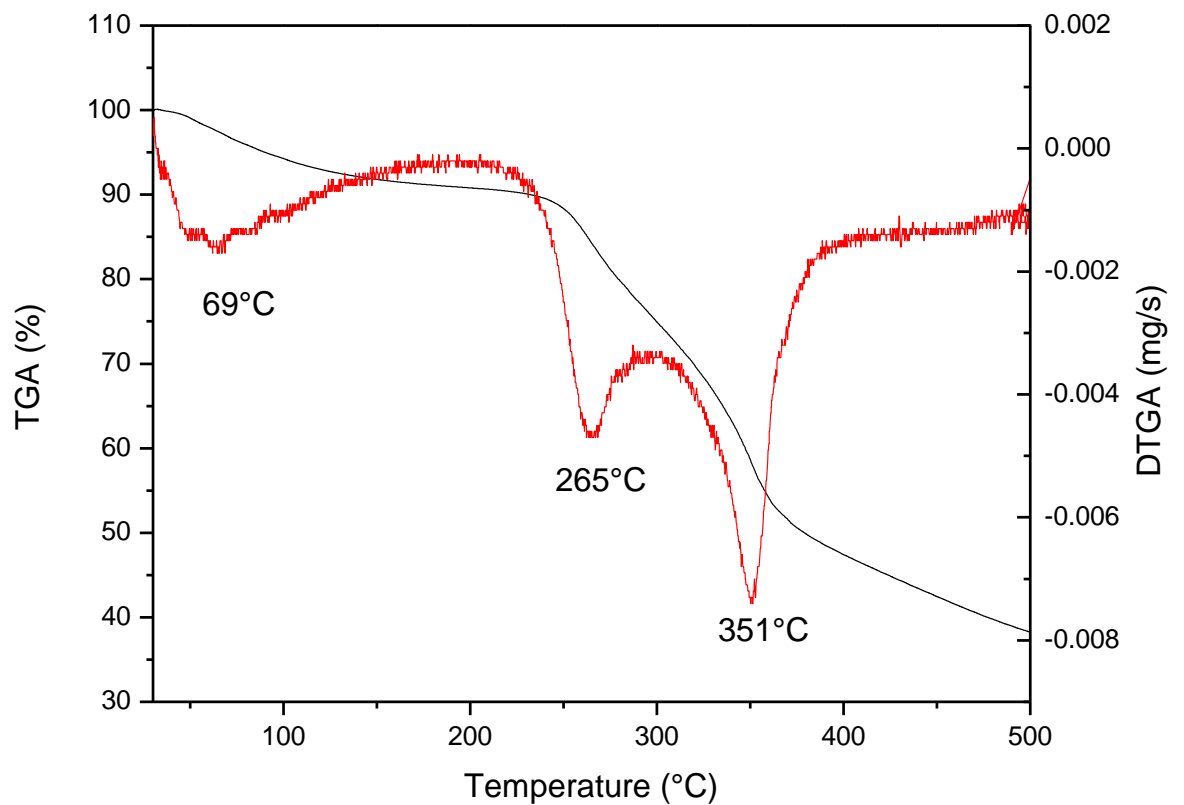


Figure 2: Thermal Analysis of CCB Adsorbent

PZC Test

Table 5, as well as figure 3, show the results obtained after performing the pzc test.

Table 5: PZC Test Results

Initial pH	1.21	1.91	3	3.95	5.05	5.96	6.92	7.94	8.98	10.01	10.99
Final pH (2 h contact)	1.3	2.0	3.1	3.5	4	4	4.2	4.7	5.1	6.3	7.6

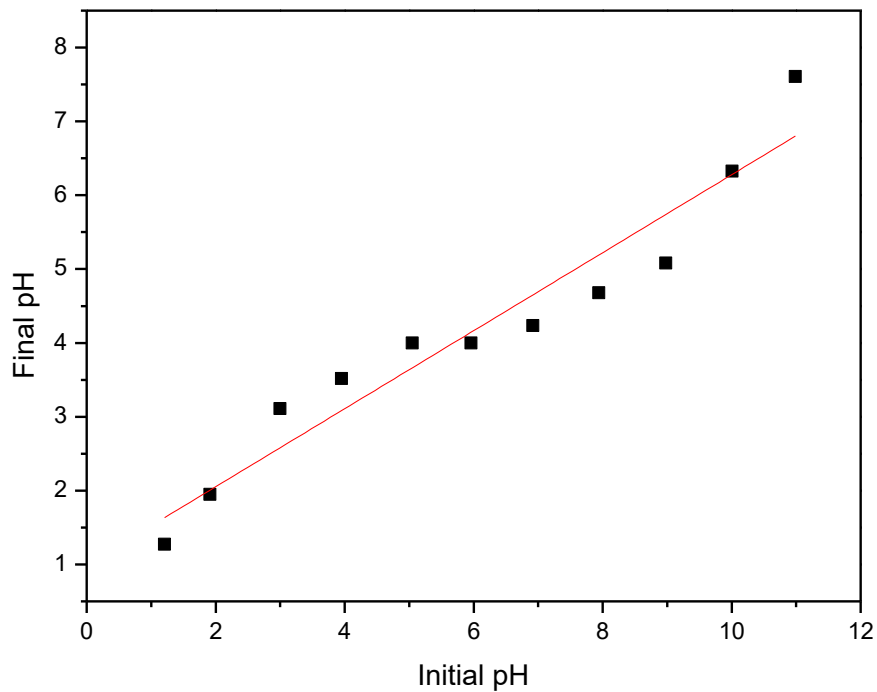


Figure 3: PZC Test

After analyzing the data presented in Table 5 and Figure 3, it can be seen that there was a strong buffering effect in the pH range between 5 and 8, where the final pH of the solution showed an average value of 4.1, with an average standard deviation 0.229, this value being considered the pH_{pzc} value.

Such determination is important, because it defines a north to determine the best pH range for the adsorption of the material of interest. In this case, for the adsorption of lead (II) using CCB as adsorbent, solutions with pH values below 4.1 will generate unfavorable conditions for adsorption of positively charged species, since there is great availability of

hydronium ions, which promotes the protonation effect of the donor atoms of the active sites of the adsorbent, impairing the adsorption of the Pb (II) ion. On the other hand, values above pH_{pzc} will favor the adsorption of these species, since there was a deprotonation of the adsorbent surface. (AWUAL, 2019b)

Therefore, a pH value of 5.5 was established for the solutions to be used in the adsorption tests, since it has a value greater than pH_{pzc} , favoring their adsorption, and it is a pH in which the metallic ions compounds are still soluble, as well as reducing the costs of neutralizing the effluents generated after the adsorption process.

RESULTS AFTER ADSORPTION TEST

FTIR

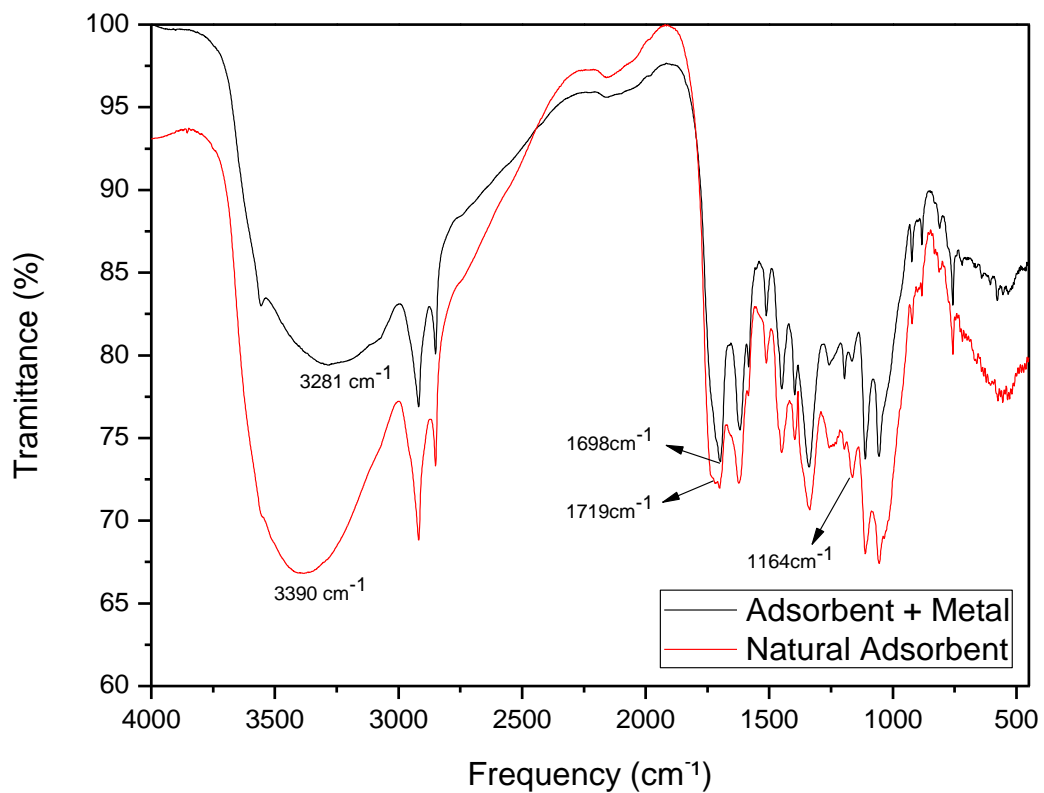


Figure 4: Comparison between the FTIR spectra of the adsorbent before and after adsorption.

When observing the FTIR spectra shown in figure 4, it can be seen that the main changes between the two spectra were the reduction of the signal centered at 3390 cm^{-1} and a small shift in its frequency to the value of 3281 cm^{-1} . It was also observed that the signal shifted from 1719

cm^{-1} to 1698 cm^{-1} (O-H and N-H axial stretching) and the signal decreased by 1164 cm^{-1} (C-O-C axial vibration associated with glycoside groups and C = O stretching Carboxylic acids). Such behaviors demonstrate that the coordination of Lead (II) to the functional groups present on the surface of the CCB in some cases inactivated certain functional groups and in others it required greater energy needs to promote the vibrations of the aforementioned connections.

Pectin, starch, cellulose, hemicelluloses and lignin, presents in the composition of the CCB, possibly has a great relationship with the coordination of lead (II) ions, possibly providing the aforementioned functional groups responsible for coordinating this metal.

Adsorption kinetics:

Figure 5 presents the results for the adsorption kinetics test, studying adsorption times ranging from 1 minute to 240 minutes, for a solution with an initial concentration of 188 mg.L^{-1} of Lead (II).

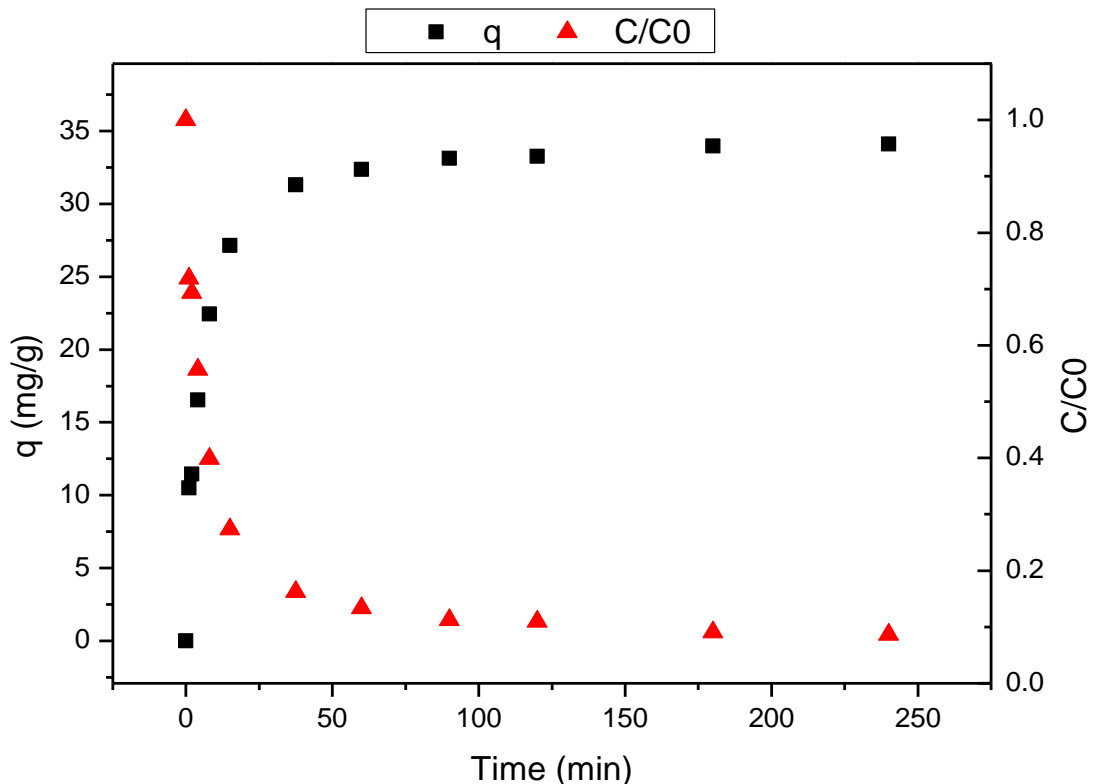


Figure 5: Study of the adsorption equilibrium time for lead metal.

From Figure 5, it is evident that there was a logarithmic growth of the adsorptive capacity (q), reaching equilibrium in the time of 120 minutes, with a value of 33.26 mg.g^{-1} and reducing the metal concentration of the solution to 20.6 mg.L^{-1} , which corresponded to a removal of approximately 89% of the metal present in the solution.

The data obtained by the kinetics were applied to the Lagergren and Ho models, in order to determine which kinetic model best fits the experimental data obtained for this adsorption. The application of data to the linearized models can be seen in figure 6 (a) and (b), while the data obtained by the models, referring to the adjustments of the linear regression are shown in table 6.

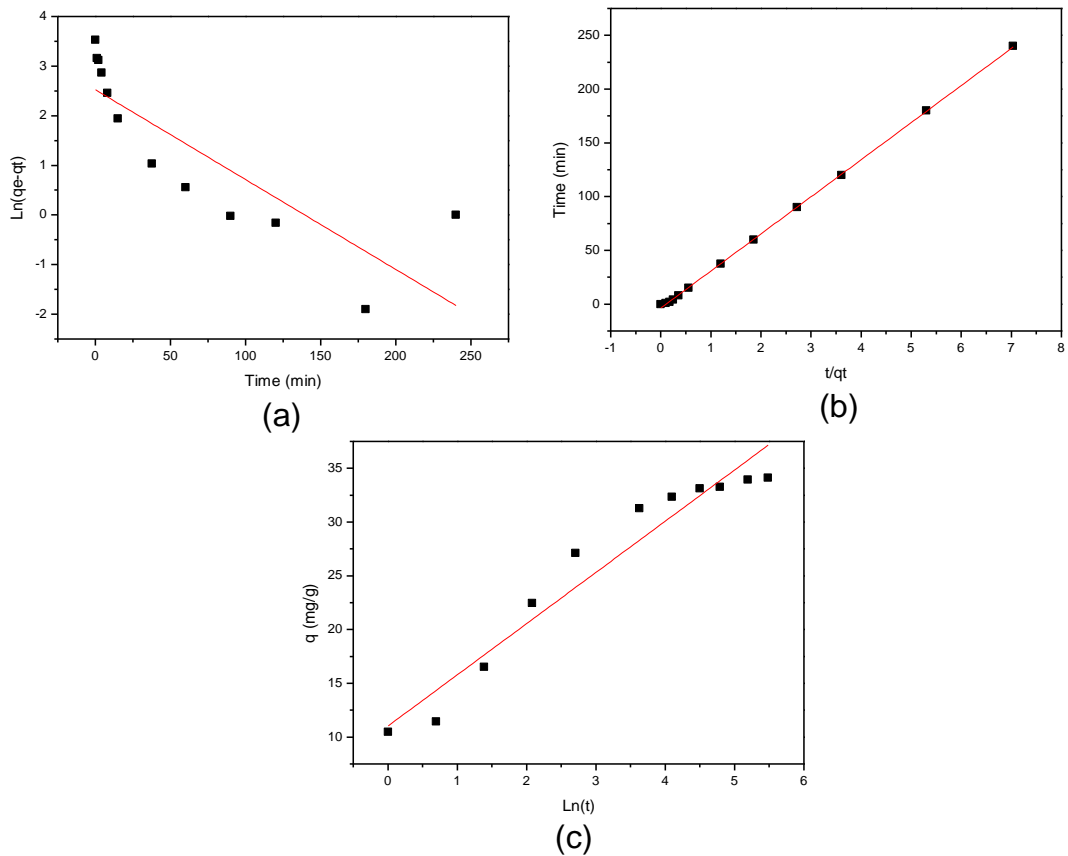


Figure 6: Application of experimental data to kinetic models: (a) pseudo-first order; (b) pseudo-second order; (c) Elovich.

Table 6: Kinetic model data.

Kinetic model	Parameters		
	Experimental	$Q_e \text{ exp. (mg.g}^{-1}\text{)}$	
Pseudo-first order	K_1	$q_{e, \text{cal}} \text{ (mg.g}^{-1}\text{)}$	R_1^2
	-0.0181	12.51	0.7117

Pseudo-second order	K_2	$q_{e, cal} (mg \cdot g^{-1})$	R^2
	$(g \cdot mg^{-1} \cdot h^{-1})$		
	8.29×10^{-5}	34.48	0.9997
Elovich	A $(mg \cdot g^{-1} \cdot h^{-1})$	B $(g \cdot mg^{-1})$	R^2

Observing figures 6 (a), (b) and (c) and the data presented in table 6, it can be concluded that the adsorption for this case is a pseudo-second order reaction, since the data fit the Ho model, obtaining a determination coefficient (R^2) = 0.9999, resulting in a theoretical q_e value of $34.48 \text{ mg} \cdot \text{g}^{-1}$ and a K_2 of $8.29 \times 10^{-5} \text{ g} \cdot \text{mg}^{-1} \cdot \text{h}^{-1}$. The experimental data did not show linear behavior for the Lagergren model, as evidenced by the low R^2 value of 0.7117. For the Elovich model, the data showed a good correlation, with R^2 of 0.9442, indicating that the adsorptive process is based on chemisorption, involving valence forces through the exchange of electrons between the adsorbent and the adsorbate (MADALA et al., 2017).

Diffusion Model

Figure 7 shows the application of the experimental data to the Weber-Morris diffusion model and Table 7, the data obtained with the analysis of the model.

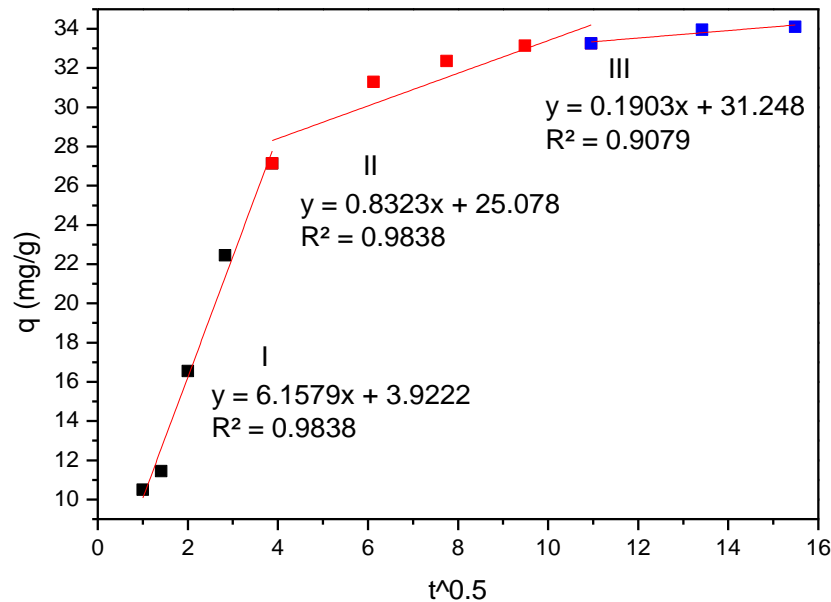


Figure 7: Experimental data applied to the Weber-Morris Model.

Table 7: Data obtained in the Weber-Morris model.

Stage	Slope	Intercept	R^2

	Kd (mg.g⁻¹.h^{0,5})	(C)	
I	6.1579	3.9222	0.9838
II	0.8323	25.078	0.8355
III	0.1903	31.248	0.9079

After analyzing figure 7 and the data presented in table 7, it is possible to verify the presence of three stages in the studied adsorption process. Analyzing the first stage, it is possible to verify that it does not present a linear coefficient (C) equal to zero, according to the Weber-Morris model, this suggests that the process that controls adsorption may be an intra-film diffusion and that the film thickness corresponds to the value of C, in the case of 3.9222 mg.g⁻¹. It can also be observed that with the increase in the contact time between the adsorbent and the adsorbent, the C value increases, indicating an increase in the thickness of the film, from 25.078 to 31.248 mg.g⁻¹, in stages II and III. Another information obtained with this model is in relation to the slope, which corresponds to the intraparticle diffusion coefficient (Kd), it can be verified that there is a reduction in this value, with the increase in time, which can be justified due to the increase in the thickness of the film hinders the diffusion of the adsorbent to the adsorbent, decreasing from the value of 6.1579 mg.g⁻¹.min^{-0,5}, in stages I, for 0.1903 mg.g⁻¹.min^{-0,5}, in stages III.

Adsorption isotherms.

Lead (II) adsorption in CCB adsorbent was modeled using the Langmuir, Freundlich, Temkin and Dubinin – Radushkevich (D – R) isotherms, and the adequacy of the data to the model was assessed using the determination coefficient (R²). The modeling is presented in figures 7 a, b, c and d, and the data obtained with the linear regression of these are presented in table 8.

Table 8: Data obtained by the models of Langmuir, Freundlich, Temkin and D - R.

Isotherm	Parameter		
Langmuir	Q_{\max} (mg.g ⁻¹)	K_L (L.mg ⁻¹)	R^2
	106.38	0.00125	0.9910
Freundlich	Parameter		
	K_f	n	R^2
	7.52	1.4760	0.9470
Temkin	Parameter		
	K_t	B	R^2
	1.3563	130.529	0.9312
D - R	Parameter		
	Q_d	B_d	R^2
	1.3675	4.00E-07	0.8332

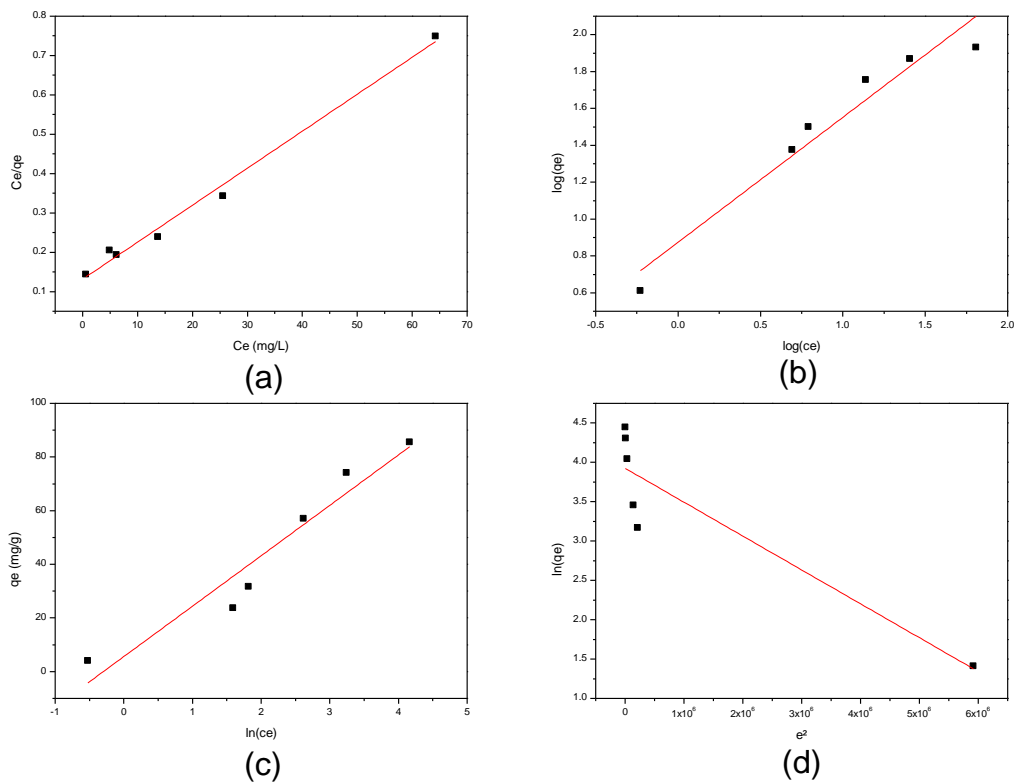


Figure 8: Linearized Modeling of Experimental Data in Models a) Langmuir; b) Freundlich; (c) Temkin; (d) D-R.

From the data presented in figure 8 and table 8, it can be seen that the experimental results showed good suitability for all models, with R^2 above 0.93, except for the D - R model, which presented a value from 0.8332. This suggests that the lead (II) adsorption, in this study,

is a chemisorption, since chemical adsorption processes are adapted to the Temkin model (BISWAS; SAHA; GHOSH, 2007), while the D - R model is suitable for physical monitoring processes. With the Langmuir model, the q_{max} value of 106.38 mg.g^{-1} can be determined, result superior to some unmodified natural adsorbents found in the literature, being highlighted in table 9.

Table 8Table 14: Comparison of the maximum adsorptive capacities of several unmodified adsorbents for Lead.

Adsorbent	Q (mg.g⁻¹)	Reference
Tangerina peel	1.5	(Abdić et al., 2018)
Banana peel	1.7	(Šabanović et al., 2015)
Wheat straw	3.9	(Zulfiqar Ali et al., 2017)
Orange peel	7.7	(Annadurai et al., 2003)
Almond shell	8.08	(Pehlivan et al., 2009)
Sugarcane Bagasse	9.73	(Salihi et al., 2015)
Crude Neem	17.96	(Costa et al., 2020)
Hazelnut shell	28.18	(Pehlivan et al., 2009)
Tea leaves	78.87	(Tee and Khan, 1988)
Lignin	102.4	(Guo et al., 2008)
CCB	106.38	This study.
Apple residue	112.1	(Heraldly et al., 2018)
Waste maize bran	142.86	(Singh et al., 2006)
Tomato waste	152	(Heraldly et al., 2018)

Regarding the Freundlich model, a value of n greater than 1 was obtained, which indicates that there is a great affinity between the adsorbent and the adsorbate (BOPARAI; JOSEPH; O'CARROLL, 2011), suggesting a chemical adsorption, which reinforces the fact that the D - R model is not suitable for this study. As for the K_f value, a value of 7.52 was presented, this indicates the adsorption capacity of the adsorbent, that is, the higher, the more favorable the ability to adsorb the Pb present in the solution.

Thermodynamic Study

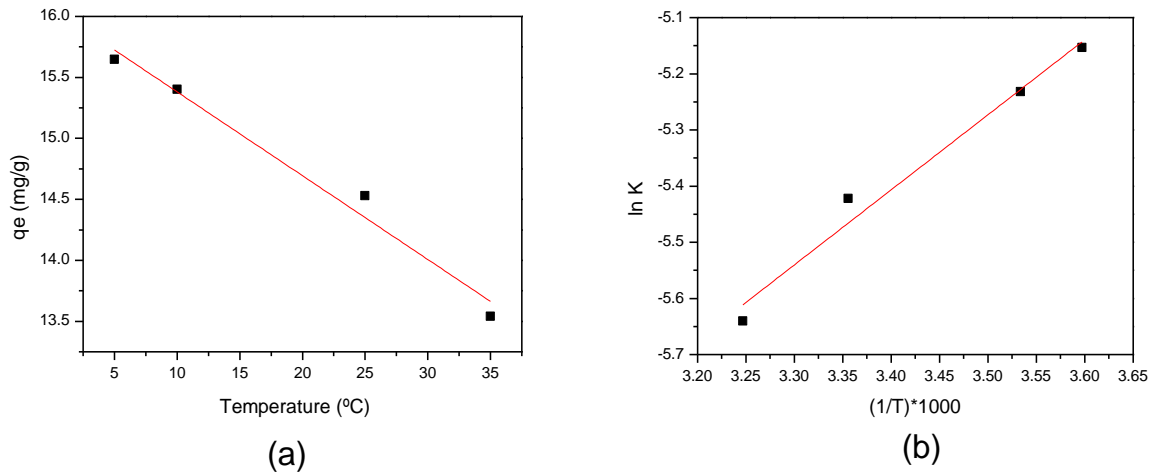


Figure. 9: Thermodynamic study (a) $q_e \times T$ curve; (b) modeling to determine ΔG° , ΔH° and ΔS .

The Pb adsorption capacity present in the solution was reduced as the system temperature increased (Figure 9a), dropping from 15.6 mg.g^{-1} (5°C) to 13.5 mg.g^{-1} (35°C). As a result, there was an increase in Gibbs free energy values (ΔG°) (table 10), with increasing temperature, indicating that the spontaneity of the process is reduced with increasing temperature, being an exothermic process.

The enthalpy (ΔH°) and entropy (ΔS) values, shown in table 10, were determined using the values of slope and intercept, respectively, obtained with the linear regression analysis of Figure 9 (b).

Negative entropy values for adsorption of metal ions in adsorbents indicate that the adsorbed species is more ordered on the surface of the adsorbent (HIKMAT; QASSIM; KHETHI, 2014).

The nature of the process can also be determined using the enthalpy value, where negative values will indicate that the process is exothermic (SENTHIL KUMAR et al., 2012).

Table 15: Thermodynamic parameters obtained.

Temperature ($^\circ\text{C}$)	ΔG° (kJ.mol^{-1})	ΔH° (kJ.mol^{-1})	ΔS ($\text{kJ.mol}^{-1}.\text{K}^{-1}$)
5	10.80		
10	12.20		
25	13.60	-28,13	-0,14
35	15.00		

CONCLUSIONS

The study suggests that the removal of lead (II), present in synthetic effluent solutions, by the adsorption process using the bark of *Caryocar coriaceum* WITTM as a bioadsorbent consists of a selective, sensitive and low-cost technique, presenting the maximum adsorption capacity of lead (II) of 106.38 mg.g⁻¹. The adsorptive process of lead (II), using *Caryocar coriaceum* Wittm bark as an adsorbent, is favored at low temperatures, since values of 15.6 mg.g⁻¹ (5 °C) and 13.5 mg.g⁻¹ (35 °C) were obtained, configuring a reduction of approximately 13.5%. The kinetic model that best represented adsorption in this study was the pseudo-second order, presenting a linear regression value of 0.9997. The adsorptive mechanism indicated by the results was Chemisorption and the process that controls adsorption is the intra-film diffusion.

It is noteworthy that the results obtained were for the raw material, which minimizes the expenses with the use of chemical modifiers.

The studied material is a rejection of a natural food, easily found in the environment during its harvest, therefore its use as an adsorbent for Lead (II) ions, diverts its original waste route, decontaminating public environments, to a new possibility application, allowing the economical treatment of wastewater containing such contaminants, and allowing industrial reincorporation of the adsorbed metal, after performing a recovery step of the adsorbed metal, as incineration.

ACKNOWLEDGMENT

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REFERENCES

- ABDI, O.; KAZEMI, M. A review study of biosorption of heavy metals and comparison between different biosorbents. **Journal of Materials and Environmental Science**, v. 6, n. 5, p. 1386–1399, 2015.
- ABDIĆ et al. Adsorptive removal of eight heavy metals from aqueous solution by unmodified and modified agricultural waste: tangerine peel. **International Journal of Environmental Science and Technology**, v. 15, n. 12, p. 2511–2518, 2018.
- ACHARYA, J.; KUMAR, U.; RAFI, P. M. Removal of Heavy Metal Ions from Wastewater by Chemically Modified Agricultural Waste Material as Potential Adsorbent-A Review. **International Journal of Current Engineering and Technology**, v. 8, n. 3, p. 526–530, 2018.
- AHAYLA, N.; RAMACHANDRA, T. V. Biosorption of heavy metals. **Biotechnology progress**, v. 11, n. 3, p. 235–50, 1995.
- AL-QODAH, Z.; YAHYA, M. A.; AL-SHANNAG, M. On the performance of bioadsorption processes for heavy metal ions removal by low-cost agricultural and natural by-products bioadsorbent: a review. **Desalination and Water Treatment**, v. 85, n. August, p. 339–357, 2017.
- ALMEIDA, A. Avaliação ecológica do extrativismo do pequi (*Caryocar coriaceum* Wittm.) na Floresta Nacional do Araripe, Ceará: informações para um plano de uso sustentável. **Tese de Doutorado**, p. 164, 2014.
- AMIN, M. T.; ALAZBA, A. A.; AMIN, M. N. Absorption behaviours of copper, lead, and arsenic in aqueous solution using date palm fibres and orange peel: Kinetics and thermodynamics. **Polish Journal of Environmental Studies**, v. 26, n. 2, p. 543–557, 2017.
- AMORIM, D. J. et al. Characterization of Pequi (*Caryocar brasiliense*) Shells and Evaluation of Their Potential for the Adsorption of PbII Ions in Aqueous Systems. **Journal of the Brazilian Chemical Society**, v. 27, n. 3, p. 616–623, 2016.
- ARAÚJO, R. R. D. L. **MODELAGEM DO PROCESSO DE BIOSSORÇÃO DE CHUMBO UTILIZA?DO A MACRÓFITA AQUÁTICA *Eichhornia crassipes***. Curitiba - PR: UFPR, 2011.
- ARSLANOĞLU, E. et al. Fabrication, characterization, and adsorption applications of low-cost hybride activated carbons from peanut shell-vinasse mixtures by one-step pyrolysis. **Biomass Conversion and Biorefinery**, 2021.
- ATKINS, P.; JONES, L.; LAVERMAN, L. **Princípios de Química, questionando a vida moderna e o meio ambiente**. 7ª ed. Porto Alegre: [s.n.].
-

- AVDEEV, Y. G.; LUCHKIN, A. Y.; KUZNETSOV, Y. I. Adsorption of IFKhAN-92 Inhibitor on Low Carbon Steel from Sulfuric Acid Solution. **Protection of Metals and Physical Chemistry of Surfaces**, v. 56, n. 7, p. 1244–1248, 2020.
- AWUAL, M. R. Mesoporous composite material for efficient lead(II) detection and removal from aqueous media. **Journal of Environmental Chemical Engineering**, v. 7, n. 3, p. 103124, 2019a.
- AWUAL, M. R. et al. Introducing an alternate conjugated material for enhanced lead(II) capturing from wastewater. **Journal of Cleaner Production**, v. 224, p. 920–929, 2019.
- AWUAL, M. R. Innovative composite material for efficient and highly selective Pb(II) ion capturing from wastewater. **Journal of Molecular Liquids**, v. 284, p. 502–510, 2019b.
- AWUAL, M. R. et al. Naked-eye lead(II) capturing from contaminated water using innovative large-pore facial composite materials. **Microchemical Journal**, v. 154, n. November 2019, p. 104585, 2020.
- AWUAL, M. R.; HASAN, M. M. Novel conjugate adsorbent for visual detection and removal of toxic lead(II) ions from water. **Microporous and Mesoporous Materials**, v. 196, p. 261–269, 2014.
- AWUAL, M. R.; HASAN, M. M. A ligand based innovative composite material for selective lead(II) capturing from wastewater. **Journal of Molecular Liquids**, v. 294, p. 111679, 2019.
- AZARI, A. et al. Comprehensive systematic review and meta-analysis of dyes adsorption by carbon-based adsorbent materials: Classification and analysis of last decade studies. **Chemosphere**, v. 250, n. 5, p. 126238, 2020.
- AZOULAY, K. et al. Comparative study between static and dynamic adsorption efficiency of dyes by the mixture of palm waste using the central composite design. **Chemical Data Collections**, v. 27, 2020.
- BANERJEE, M. et al. Removal of Cr(VI) from Its Aqueous Solution Using Green Adsorbent Pistachio Shell: a Fixed Bed Column Study and GA-ANN Modeling. **Water Conservation Science and Engineering**, v. 3, n. 1, p. 19–31, 2018.
- BARROS, A. J. M. et al. ESTUDO TERMOGRAVIMÉTRICO DO PROCESSO DE SORÇÃO DE METAIS PESADOS POR RESÍDUOS SÓLIDOS ORGÂNICOS. **Engenharia Sanitaria e Ambiental**, v. 11, p. 184–190, 2006.
- BARROS, A. J. M. **Estudo da Formação de Complexos Pelo Processo de Biossorção**. Joao Pessoa: UFPB, 2006.
- BISWAS, K.; SAHA, S. K.; GHOSH, U. C. Adsorption of fluoride from aqueous solution by a synthetic iron(III)-aluminum(III) mixed oxide. **Industrial and Engineering Chemistry Research**, v. 46, n. 16, p. 5346–5356, 2007.
-

- BLAGOJEV, N. et al. A new approach for modelling and optimization of Cu(II) biosorption from aqueous solutions using sugar beet shreds in a fixed-bed column. **Journal of Hazardous Materials**, v. 363, n. June 2018, p. 366–375, 2019.
- BOEHM, H. P. Surface oxides on carbon and their analysis: A critical assessment. **Carbon**, v. 40, n. 2, p. 145–149, 2002.
- BOPARAI, H. K.; JOSEPH, M.; O’CARROLL, D. M. Kinetics and thermodynamics of cadmium ion removal by adsorption onto nano zerovalent iron particles. **Journal of Hazardous Materials**, v. 186, n. 1, p. 458–465, 2011.
- BOYD, G. E.; SCHUBERT, J.; ADAMSON, A. W. The Exchange Adsorption of Ions from Aqueous Solutions by Organic Zeolites. Ion-exchange Equilibria. **Journal of the American Chemical Society**, v. 69, n. 11, p. 2818–2829, 1947.
- BREDA, C. A. et al. Processing and Characterization of Chitosan Films with Incorporation of Ethanolic Extract from “Pequi” Peels. **Macromolecular Research**, 2017.
- BURAKOV, A. E. et al. Adsorption of heavy metals on conventional and nanostructured materials for wastewater treatment purposes: A review. **Ecotoxicology and Environmental Safety**, v. 148, n. August 2017, p. 702–712, 2018.
- CAO, M. LI et al. Functionalized graphene nanosheets as absorbent for copper (II) removal from water. **Ecotoxicology and Environmental Safety**, v. 173, n. September 2018, p. 28–36, 2019.
- CONAMA. Resolução CONAMA 430/2011. **Diário Oficial da União**, p. 9, 2011.
- CONICELLI, B. P. **BIOSSORÇÃO DE CHUMBO E MERCÚRIO PELAS LINHAGENS SELVAGEM E RECOMBINANTE DE C. metallidurans EM MEIO AQUOSO**. [s.l.] USP, 2018.
- CORDEIRO, M. W. S. et al. PHYSICAL CHARACTERISTICS, CHEMICAL-NUTRITIONAL COMPOSITION AND ESSENTIAL OILS OF *Caryocar brasiliense* NATIVE FROM THE STATE OF MATO GROSSO (In Portuguese). **Revista Brasileira de Fruticultura**, v. 35, n. 4, p. 1127–1139, 2013.
- CORDEIRO, R. D. M. **AS AGLOMERAÇÕES PRODUTIVAS DE CALÇADOS, FOLHEADOS E DE JOIAS DO CRAJUBAR (CE): FORMAÇÃO, PRODUÇÃO, TRABALHO, IMPLICAÇÕES SOCIOESPACIAIS**. [s.l.] Unesp, 2015.
- COSTA, D. A.; MENDONÇA, R. H.; WYSARD JUNIOR, M. M. Evaluation of removal of chromium (III) by composite porous adsorbents materials of PE-g-MA, coconut fiber and chitosan using experimental design (In Portuguese). **Engenharia Sanitaria e Ambiental**, v. 22, n. 6, p. 1203–1213, 2017.
- COSTA, A. P. F. DA; PINTO, E. G.; SOARES, D. S. B. Obtenção de farinha do mesocarpo
-

de pequi. **Revista Agrarian**, p. 113–119, 2017.

COSTA, T. B. DA; SILVA, M. G. C. DA; VIEIRA, M. G. A. Recovery of rare-earth metals from aqueous solutions by bio/adsorption using non-conventional materials: a review with recent studies and promising approaches in column applications. **Journal of Rare Earths**, v. 38, n. 4, p. 339–355, 2020.

COSTA, W. D. et al. Removal of copper(II) ions and lead(II) from aqueous solutions using seeds of *Azadirachta indica* A. Juss as bioadsorbent. **Environmental Research**, v. 183, n. June 2019, p. 109213, 2020.

CRINI, G. et al. Conventional and non-conventional adsorbents for wastewater treatment. **Environmental Chemistry Letters**, n. 0123456789, 2018.

CUI, H. et al. Dry-wet and freeze-thaw aging activate endogenous copper and cadmium in biochar. **Journal of Cleaner Production**, v. 288, p. 125605, 2021.

DADA, A. O.; ADEKOLA, F. A.; ODEBUNMI, E. O. A novel zerovalent manganese for removal of copper ions : synthesis , characterization and adsorption studies. **Applied Water Science**, 2015.

DE AQUINO SARAIVA, R. et al. Caryocar coriaceum Wittm. **Medicinal and Aromatic Plants of South America**, v. 5, p. 153–162, 2018.

DE MAGALHÃES, V. H. P.; NEVES, M. A. F. E S. UTILIZAÇÃO DO PERICARPO DE COCO VERDE (*Cocos nucifera* L . - ARECACEAE) PARA A REMOÇÃO DE RESÍDUOS DE ÍONS CROMO (VI) EM SOLUÇÕES AQUOSAS. **Perspectivas da Ciência e Tecnologia**, v. 3, p. 10–16, 2011.

DE OLIVEIRA, M. N. S. et al. Estádio de maturação dos frutos e fatores relacionados aos aspectos nutritivos e de textura da polpa de pequi (*Caryocar brasiliense* Camb.). **Revista Brasileira de Fruticultura**, v. 28, n. 3, p. 380–386, 2006.

DELBIANCO, G. A. B. **Estudo de Rejeitos de Galvanoplastia e a sua Aplicação na Fabricação de Peças Cerâmicas Rústicas para Fins Decorativos**. [s.l.] UNESP, 2008.

DENG, J. et al. Competitive adsorption of Pb(II), Cd(II) and Cu(II) onto chitosan-pyromellitic dianhydride modified biochar. **Journal of Colloid and Interface Science**, v. 506, p. 355–364, 2017.

DUARTE- NETO, J. F. et al. Processos de adsorção de corantes em argilas esmectíticas: uma revisão. **Revista Eletrônica de Materiais e Processos**, v. 9, p. 51–59, 2014.

EL-ARABY, H. A. et al. Sesame Husk as Adsorbent for Copper(II) Ions Removal from Aqueous Solution. **Journal of Geoscience and Environment Protection**, v. 05, n. 07, p. 109–152, 2017.

ELOVICH, S. Y.; LARINOV, O. G. Theory of adsorption from solutions of non electrolytes

on solid (I) equation adsorption from solutions and the analysis of its simplest form,(II) verification of the equation of adsorption isotherm from solutions. **Izvestiya Akademii Nauk**, v. 2, n. 2, p. 209–216, 1962.

ESCUADERO-OÑATE, C.; VILLAESCUSA, I. The Thermodynamics of Heavy Metal Sorption onto Lignocellulosic Biomass. **Heavy Metals**, 2018.

FALAKI, Z.; BASHIRI, H. Preparing an adsorbent from the unused solid waste of Rosewater extraction for high efficient removal of Crystal Violet. **Journal of the Iranian Chemical Society**, v. 18, n. 10, p. 2689–2702, 2021.

FEI, Q.; BEI, W. Single- and multi-component adsorption of Pb, Cu, and Cd on peat. **Bulletin of Environmental Contamination and Toxicology**, v. 78, n. 3–4, p. 265–269, 2007.

FENG, N. et al. Biosorption of heavy metals from aqueous solutions by chemically modified orange peel. **Journal of Hazardous Materials**, v. 185, n. 1, p. 49–54, 2011.

FUTALAN, C. M. et al. Comparative and competitive adsorption of copper, lead, and nickel using chitosan immobilized on bentonite. **Carbohydrate Polymers**, v. 83, n. 2, p. 528–536, 2011.

GEÖCZE, K. C. **Exploratory analysis of carotenoids, essential oils and triacylglycerides of pequi (Caryocar brasiliense Camb.) from brazilian districts located in the cerrado biome (In Portugues)**. [s.l.] Universidade Federal de Viçosa, 2011.

GHOLAMIYAN, S.; HAMZEHLOO, M.; FARROKHANIA, A. RSM optimized adsorptive removal of erythromycin using magnetic activated carbon: Adsorption isotherm, kinetic modeling and thermodynamic studies. **Sustainable Chemistry and Pharmacy**, v. 17, n. May, p. 100309, 2020.

GIRALDO, L.; MORENO-PIRAJÁN, J. C. Pb²⁺ adsorption from aqueous solutions on activated carbons obtained from lignocellulosic residues. **Brazilian Journal of Chemical Engineering**, v. 25, n. 1, p. 143–151, 2008.

GUGUSHE, A. S. et al. Adsorptive removal of cd, cu, ni and mn from environmental samples using fe₃o₄-zro₂@aps nanocomposite: Kinetic and equilibrium isotherm studies. **Molecules**, v. 26, n. 11, 2021.

HACKBARTH, F. V. **REMOÇÃO DE METAIS DE EFLUENTES PETROQUÍMICOS UTILIZANDO BIOMASSA DE MACROALGA MARINHA PELVETIA CANALICULATA COMO ADSORVENTE**. Florianópolis: UFSC, 2014.

HIKMAT, N. A.; QASSIM, B. B.; KHETHI, M. T. Thermodynamic and Kinetic Studies of Lead Adsorption from Aqueous Solution onto Petiole and Fiber of Palm Tree. **American Journal of Chemistry**, v. 4, n. 4, p. 116–124, 2014.

HO, Y. S.; MCKAY, G. Pseudo-second order model for sorption processes. **Process**

Biochemistry, v. 34, n. 5, p. 451–465, 1999.

HOSSAIN, A. et al. Biosorption of Cu(II) From Water by Banana Peel Based Biosorbent: Experiments and Models of Adsorption and Desorption. n. January 2012, 2012.

HUSSAIN, A. et al. Synthesis and Application of Modified Orchard Waste Biochar for Efficient Scavenging of Copper from Aqueous Solutions. **Arabian Journal for Science and Engineering**, n. 0123456789, 2021.

IBGE. **Pesquisa nacional de saneamento básico 2017: abastecimento de água e esgotamento sanitário**. [s.l.: s.n.].

IGHALO, J. O. et al. Mitigation of clofibric acid pollution by adsorption: A review of recent developments. **Journal of Environmental Chemical Engineering**, v. 8, n. 5, 2020a.

IGHALO, J. O. et al. Competitive adsorption of Pb(II), Cu(II), Fe(II) and Zn(II) from aqueous media using biochar from oil palm (*Elaeis guineensis*) fibers: a kinetic and equilibrium study. **Indian Chemical Engineer**, v. 0, n. 0, p. 1–11, 30 jun. 2020b.

IRAVANI MOHAMMADABADI, S.; JAVANBAKHT, V. Fabrication of dual cross-linked spherical treated waste biomass/alginate adsorbent and its potential for efficient removal of lead ions from aqueous solutions. **Industrial Crops and Products**, v. 168, n. April, p. 113575, 2021.

JUMINA et al. Synthesis of C-4-hydroxy-3-methoxyphenylcalix[4]resorcinarene and its application as adsorbent for lead(II), copper(II) and chromium(III). **Bulletin of the Chemical Society of Japan**, v. 92, n. 4, p. 825–831, 2019.

JUMINA et al. Simultaneous removal of lead(II), chromium(III), and copper(II) heavy metal ions through an adsorption process using C-phenylcalix[4]pyrogallolarene material. **Journal of Environmental Chemical Engineering**, v. 8, n. 4, p. 103971, 2020.

KADIRI, L. et al. Mathematical modeling and thermodynamic study of copper (II) removal from aqueous solution by *Coriandrum Sativum* seeds. **Mediterranean Journal of Chemistry**, v. 7, n. 6, p. 478–490, 2019.

KAMARI, A. et al. Biosorptive removal of Cu(II), Ni(II) and Pb(II) ions from aqueous solutions using coconut dregs residue: Adsorption and characterisation studies. **Journal of Environmental Chemical Engineering**, v. 2, n. 4, p. 1912–1919, 2014.

KHEDDO, A. et al. Adsorption of synthetic dyed wastewater using activated carbon from rice husk. **SN Applied Sciences**, v. 2, n. 12, p. 1–14, 2020.

KOVÁCS, E. et al. Investigation into the mechanism of stimulation by low-concentration stressors in barley seedlings. **Journal of Plant Physiology**, v. 166, n. 1, p. 72–79, 2009.

LAGERGREN, S. Zur Theorie der Sogenannten Adsorption Gelöster Stoffe, Kungliga Svenska Vetenskapsakademiens. **Handlingar**, v. 24, n. 4, p. 1–39, 1898.

- LI, C. et al. Facile synthesis of low-cost magnetic biosorbent from peach gum polysaccharide for selective and efficient removal of cationic dyes. **International Journal of Biological Macromolecules**, v. 107, p. 1871–1878, 2018.
- LI, H. et al. Modified carbon spheres as universal materials for adsorption of cationic harmful substances (paraquat and dyes) in water. **Microporous and Mesoporous Materials**, v. 297, n. June 2019, p. 110040, 2020.
- LI, W. C.; LAW, F. Y.; CHAN, Y. H. M. Biosorption studies on copper (II) and cadmium (II) using pretreated rice straw and rice husk. **Environmental Science and Pollution Research**, v. 24, n. 10, p. 8903–8915, 2017.
- LIMA, V. F.; MERÇON, F. Metais Pesados no Ensino de Química. **Química Nova Na Escola**, v. 33, n. 4, p. 199–205, 2011.
- LIU, R.; LIAN, B. Non-competitive and competitive adsorption of Cd²⁺, Ni²⁺, and Cu²⁺ by biogenic vaterite. **Science of the Total Environment**, v. 659, n. 1, p. 122–130, 2019.
- LIU, X. et al. Competitive adsorption of heavy metal ions from aqueous solutions onto activated carbon and agricultural waste materials. **Polish Journal of Environmental Studies**, v. 29, n. 1, p. 749–761, 2020.
- LONG, Y. et al. Packed bed column studies on lead(II) removal from industrial wastewater by modified *Agaricus bisporus*. **Bioresource Technology**, v. 152, p. 457–463, 2014.
- LOPES, P. S. N. et al. **Frutas Nativas da Região Centro-Oeste do Brasil**. 1ª edição ed. Planaltina - DF: [s.n.].
- LOULIDI, I. et al. Adsorption of Crystal Violet onto an Agricultural Waste Residue: Kinetics, Isotherm, Thermodynamics, and Mechanism of Adsorption. **Scientific World Journal**, v. 2020, 2020.
- LOW, M. J. D. Kinetics of chemisorption of gases on solids. **Chemical Reviews**, v. 60, n. 3, p. 267–312, 1960.
- MAALOUL, N. et al. Synthesis and characterization of eco-friendly cellulose beads for copper (II) removal from aqueous solutions. **Environmental Science and Pollution Research**, v. 27, n. 19, p. 23447–23463, 2020.
- MACIEL, T. C. M. et al. SUBSTRATO À BASE DE PEQUI (*Caryocar coriaceum*) NA PRODUÇÃO DE MUDAS DE TOMATE E PIMENTÃO. **Revista De Agricultura Neotropical**, v. 4, n. 2, p. 9–16, 2017.
- MADALA, S. et al. Equilibrium, kinetics and thermodynamics of Cadmium (II) biosorption on to composite chitosan biosorbent. **Arabian Journal of Chemistry**, v. 10, p. S1883–S1893, 2017.
- MAHDI, Z.; YU, Q. J.; EL HANANDEH, A. Competitive adsorption of heavy metal ions (Pb
-

- 2+ , Cu 2+ , and Ni 2+) onto date seed biochar: batch and fixed bed experiments. **Separation Science and Technology (Philadelphia)**, v. 54, n. 6, p. 888–901, 2019.
- MALIK, D. S.; JAIN, C. K.; YADAV, A. K. Heavy Metal Removal by Fixed-Bed Column – A Review. **ChemBioEng Rev**, v. 5, n. 3, p. 173–179, 2018.
- MENEZES, J. M. C. et al. Equilibrium, kinetics and thermodynamics of lead (II) adsorption in bioadsorbent composed by Caryocar coriaceum Wittm barks. **Chemosphere**, v. 261, 2020.
- MINISTÉRIO DA SAÚDE. Portaria MS N°2914/2011. **Dou 14/12/2011**, 2011.
- MOHAMMAD, S. G.; AHMED, S. M.; EL-SAYED, M. M. H. Removal of copper (II) ions by eco-friendly raw eggshells and nano-sized eggshells: a comparative study. **Chemical Engineering Communications**, v. 0, n. 0, p. 1–13, 2020.
- MONDAL, S.; MAJUMDER, S. K. **Honeycomb-like porous activated carbon for efficient copper (II) adsorption synthesized from natural source: Kinetic study and equilibrium isotherm analysis**. [s.l.] Elsevier Ltd, 2019. v. 7
- MORAIS, M. J. DE et al. CARACTERIZAÇÃO DA CASCA DE PEQUI (Caryocar Brasiliense Camb.) PARA SUA UTILIZAÇÃO COMO BIOMASSA. **III Congresso de Ensino, Pesquisa e Extensão da UEG**, v. 2, n. 1c, p. 17, 2016.
- MOREIRA, A. DA S. **BIOSSORÇÃO UTILIZANDO ALGA MARINHA (SARGASSUMsp.) APLICADA EM MEIO ORGÂNICO**. [s.l.] UFRN, 2007.
- MOREIRA, S. D. A. **ADSORÇÃO DE ÍONS METÁLICOS DE EFLUENTE AQUOSO USANDO BAGAÇO DO PEDÚNCULO DE CAJU: ESTUDO DE BATELADA E COLUNA DE LEITO FIXO**. [s.l.] UFC, 2008.
- MORENO-BENAVIDES, J. A.; PEÑA-SALAMANCA, E. J.; BENÍTEZ-CAMPO, N. Reducing Cr 6+ in electroplating wastewater with Bacillus cereus strain B 1. **Universitas Scientiarum**, v. 24, n. 1, p. 73–89, 2019.
- MORIN-CRINI, N. et al. Hemp-based adsorbents for sequestration of metals: a review. **Environmental Chemistry Letters**, 2018.
- NASCIMENTO, R. F. DO et al. **ADSORÇÃO: Aspectos teóricos e aplicações ambientais**. 2ª ed. Fortaleza - Ce: Imprensa Universitária UFC, 2020.
- NERIS, J. B. et al. Evaluation of adsorption processes of metal ions in multi-element aqueous systems by lignocellulosic adsorbents applying different isotherms: A critical review. **Chemical Engineering Journal**, v. 357, n. April 2018, p. 404–420, 2019.
- OLIVEIRA, M. E. B. DE et al. Aspectos Agronômicos e de Qualidade do Pequi. **Embrapa**, v. 113, p. 33, 2008.
- OLIVEIRA, S. A. DE. **ESTUDO DE ADSORÇÃO DE METAIS PESADOS EM ZEÓLITAS PARA FINS DE USO EM BARREIRA REATIVA**. [s.l.] UFRJ, 2011.
-

- OLIVEIRA, W. L. DE. **Boas Práticas de Manejo para p Extrativismo Sustentável do Pequi**. Brasília: [s.n.].
- PEREIRA, F. D. A. et al. ANÁLISE DA ATIVIDADE EXTRATIVISTA DO PEQUI (*Caryocar coriaceum* Wittm) EM COMUNIDADES DA CHAPADA DO ARARIPE NA REGIÃO DO CARIRI CEARENSE. **Conexões Ciência e Tecnologia**, v. 8, p. 59–66, 2014.
- PEREIRA, J. E. S. **Biossorção de cobre em solução aquosa utilizando os pós das folhas do cajueiro (*Anacardium occidentale* L.) e da carnaúba (*Copernicia prunifera*)**. [s.l.] UFRN, 2017.
- PEREZ, I. C.; CORRÊA, R. G.; PIRES, J. L. Gestão Ambiental - Galvanoplastia, orientações para o controle ambiental. p. 48, 2014.
- PINO, G. A. H. **Biossorção de Metais Pesados Utilizando Pó da Casca de Coco Verde (*Cocos nucifera*)**. [s.l.] PUC - Rio de Janeiro, 2005.
- PINO, G. H.; TOREM, M. L. ASPECTOS FUNDAMENTAIS DA BISSORÇÃO DE METAIS NÃO FERROSOS ESTUDO DE CASO. **Tecnologia em Metalurgia e Materiais**, 2011.
- POLICARPO, L. M. **ESTUDO DE EQUILÍBRIO E CINÉTICA DA BISSORÇÃO DE COBRE (II) POR RHIZOPUS MICROSPORUS**. São Paulo - SP: USP, 2015.
- RAGAVENDRAN, P. et al. FUNCTIONAL GROUP ANALYSIS OF VARIOUS EXTRACTS OF *Aerva lanata* (L.,) BY FTIR SPECTRUM. **Pharmacologyonline**, v. 364, p. 358–364, 2011.
- RAMOS, K. M. C.; SOUZA, V. A. B. DE. Características físicas e químico-nutricionais de frutos de pequizeiro (*Caryocar coriaceum* Wittm.) em populações naturais da região meio-norte do Brasil. **Revista Brasileira de Fruticultura**, v. 33, n. 2, p. 500–508, 2011.
- RAMOS, R. et al. Produção de adsorventes a base de borra de café industrializado e folhas de *Corymbia citriodora* (eucalipto limão). **Dissertar Produção**, v. 1, n. 28–29, p. 17–22, 2017.
- RASOULPOOR, K.; POURSAATTAR MARJANI, A.; NOZAD, E. Competitive chemisorption and physisorption processes of a walnut shell based semi-IPN bio-composite adsorbent for lead ion removal from water: Equilibrium, Kinetic and Thermodynamic studies. **Environmental Technology and Innovation**, v. 20, p. 101133, 2020.
- RAY, S.; MISHRA, A. K.; KALAMDHAD, A. S. Adsorption and Hydraulic Conductivity Studies on Bentonite in Presence of Copper Solution. **Journal of Hazardous, Toxic, and Radioactive Waste**, v. 25, n. 2, p. 06020007, 2021.
- REGALBUTO, J. R.; ROBLES, JAIME O. **The Engineering of Pt / Carbon Catalyst Preparation For application on Proton Exchange Fuel Cell Membrane (PEFCM)**. Chicago: [s.n.].
-

- REICHENBERG, D. Properties of Ion-Exchange Resins in Relation to their Structure. III. Kinetics of Exchange. **Journal of the American Chemical Society**, v. 75, n. 3, p. 589–597, 1953.
- RENGEL, Z. Aluminium cycling in the soil-plant-animal-human continuum. **BioMetals**, v. 17, n. 6, p. 669–689, 2004.
- RODRIGUES, R. F. et al. HEAVY METALS SORPTION ON TREATED WOOD SAWDUST (In Portuguese). **Quimica Nova**, 2007.
- RUTHVEN, D. M. **Principles of adsorption and adsorption processes**. New York: John Wiley&Sons, 1984. v. 4
- ŠABANOVI, E. et al. Simultaneous adsorption of heavy metals from water by novel lemon-peel based biomaterial. **Polish Journal of Chemical Technology**, v. 22, n. 1, p. 46–53, 2020.
- ŠABANOVIĆ, E. et al. Pulverized Banana Peel as an Economical Sorbent for the Preconcentration of Metals. **Analytical Letters**, v. 48, n. 3, p. 442–452, 2015.
- SABELA, M. I. et al. Removal of copper (II) from wastewater using green vegetable waste derived activated carbon: An approach to equilibrium and kinetic study. **Arabian Journal of Chemistry**, v. 12, n. 8, p. 4331–4339, 2019.
- SAHA, U. K.; TANIGUCHI, S.; SAKURAI, K. Simultaneous Adsorption of Cadmium, Zinc, and Lead on Hydroxyaluminum- and Hydroxyaluminosilicate-Montmorillonite Complexes. **Soil Science Society of America Journal**, v. 66, n. 1, p. 117–128, 2002.
- SAHMOUNE, M. N. Evaluation of thermodynamic parameters for adsorption of heavy metals by green adsorbents. **Environmental Chemistry Letters**, v. 17, n. 2, p. 697–704, 2019.
- SALAME, I. I.; BANDOSZ, T. J. Surface chemistry of activated carbons: Combining the results of temperature-programmed desorption, Boehm, and potentiometric titrations. **Journal of Colloid and Interface Science**, v. 240, n. 1, p. 252–258, 2001.
- SALIHI, I. U. et al. Adsorption of copper using modified and unmodified sugarcane bagasse. **International Journal of Applied Engineering Research**, v. 10, n. 19, p. 40434–40438, 2015.
- SANTANA, A. H. **REMOÇÃO DE ÍONS COBRE E CHUMBO DE ÁGUAS RESIDUAIS UTILIZANDO VAGENS DE *Dimorphandra gardneriana* Tulasne (FAVA D’ANTA)**. [s.l.] URCA, 2018.
- SANTANA, A. H. et al. Copper and lead ion removal from wastewater using fava d’anta fodder (*Dimorphandra gardneriana* Tulasne). **Environmental Geochemistry and Health**, v. 0123456789, 2020.
- SANTHOSH, A.; DAWN, S. S. Synthesis of zinc chloride activated eco-friendly nano-
-

- adsorbent (activated carbon) from food waste for removal of pollutant from biodiesel wash water. **Water Science and Technology**, v. 00, n. 0, p. 1–12, 2021.
- SCHNEIDER, I. A. H. **Biossorção de Metais Pesados com a Biomassa de Macrófitos Aquáticos**. [s.l.] UFRGS, 1955.
- SCHNEIDER, R. M. et al. **BIOMASSAS PARA A ADSORÇÃO DO METAL CROMO III DE EFLUENTE**. Gramado - RS: [s.n.].
- ŠĆIBAN, M.; KLAŠNJA, M.; ŠKRBIĆ, B. Modified softwood sawdust as adsorbent of heavy metal ions from water. **Journal of Hazardous Materials**, v. 136, n. 2, p. 266–271, 2006.
- ŠĆIBAN, M.; KLAŠNJA, M.; ŠKRBIĆ, B. Adsorption of copper ions from water by modified agricultural by-products. **Desalination**, v. 229, n. 1–3, p. 170–180, 2008.
- SEBRAE. Lapidando a imagem da jóia brasileira. 2007.
- SEBRAE. Industria da Moda: Gemas e Joias. **Estudo de Mercado**, 2017.
- SEMACE. Resolução COEMA nº02, de 02 de fevereiro de 2017. p. 56–61, 2017.
- ŞENEL, G. U. Adsorption of Copper (II) from Aqueous Solution by Using Carbonized Peanut Hull: Determination of the Equilibrium, Kinetic and Thermodynamic Parameters. **Journal of Anatolian Environmental and Animal Sciences**, v. 90, n. 533, 2020.
- SENTHIL KUMAR, P. et al. Adsorption of metal ions onto the chemically modified agricultural waste. **Clean - Soil, Air, Water**, v. 40, n. 2, p. 188–197, 2012.
- SHAHAT, A. et al. Novel hierarchical composite adsorbent for selective lead(II) ions capturing from wastewater samples. **Chemical Engineering Journal**, v. 332, n. September 2017, p. 377–386, 2018.
- SHAMIM, S. Biosorption of Heavy Metals. **Biosorption**, 2018.
- SIQUEIRA, B. DOS S. et al. PECTINA EXTRAÍDA DE CASCA DE PEQUI E APLICAÇÃO EM GELEIA LIGHT DE MANGA. **revista brasileira fruticultura**, v. 34, n. 2, p. 560–567, 2012.
- SOETAREDJO, F. E. et al. Incorporation of selectivity factor in modeling binary component adsorption isotherms for heavy metals-biomass system. **Chemical Engineering Journal**, v. 219, p. 137–148, 2013.
- SOUSA NETO, V. O. et al. Use of coconut bagasse as alternative adsorbent for separation of copper (II) ions from aqueous solutions: Isotherms, kinetics, and thermodynamic studies. **BioResources**, v. 6, n. 3, p. 3376–3395, 2011.
- SOUZA, J. P. DE et al. PEQUI (*Caryocar coriaceum* Wittm) PRODUCT STABILITY UNDER FREEZING IN DIFFERENT TYPES OF PACKAGING (In Portuguese). **Revista Brasileira de Fruticultura**, v. 35, n. 4, p. 971–976, 2013.
-

- TANG, X. et al. Extremely efficient and rapidly adsorb methylene blue using porous adsorbent prepared from waste paper: Kinetics and equilibrium studies. **Journal of Hazardous Materials**, v. 402, n. July 2020, p. 123579, 2021.
- TARIBA LOVAKOVIĆ, B. Cadmium, arsenic, and lead: elements affecting male reproductive health. **Current Opinion in Toxicology**, v. 19, n. Figure 1, p. 7–14, 2020.
- TARLEY, C. R. T.; ARRUDA, M. A. Z. Biosorption of heavy metals using rice milling by-products. Characterisation and application for removal of metals from aqueous effluents. **Chemosphere**, v. 54, n. 7, p. 987–995, 2004.
- TAŞAR, Ş.; ÖZER, A. A thermodynamic and kinetic evaluation of the adsorption of pb(II) ions using peanut (*arachis hypogaea*) shell-based biochar from aqueous media. **Polish Journal of Environmental Studies**, v. 29, n. 1, p. 293–305, 2020.
- TAVANA, M.; PAHLAVANZADEH, H.; ZAREI, M. J. The novel usage of dead biomass of green algae of *Schizomeris leibleinii* for biosorption of copper(II) from aqueous solutions: Equilibrium, kinetics and thermodynamics. **Journal of Environmental Chemical Engineering**, v. 8, n. 5, p. 104272, 2020.
- TEIXEIRA, R. N. P. **REMOÇÃO DE Cu(II), Ni(II), Cd(II) E Pb(II) DE EFLUENTES DE INDÚSTRIAS DE GALVANOPLASTIA USANDO O SISTEMA HÍBRIDO ADSORÇÃO- ELETRO-FLOTAÇÃO-COAGULAÇÃO**. [s.l.] UFC, 2015.
- TOUIHRI, M. et al. Single and simultaneous adsorption of Cr(VI) and Cu (II) on a novel Fe₃O₄/pine cones gel beads nanocomposite: Experiments, characterization and isotherms modeling. **Chemical Engineering Journal**, v. 416, n. February, 2021.
- USLU, G.; TANYOL, M. Equilibrium and thermodynamic parameters of single and binary mixture biosorption of lead (II) and copper (II) ions onto *Pseudomonas putida*: Effect of temperature. **Journal of Hazardous Materials**, v. 135, n. 1–3, p. 87–93, 2006.
- VERÍSSIMO, L. S.; CAVALCANTE, I. N. AS ÁGUAS SUBTERRÂNEAS DO CRAJUBAR, REGIÃO DO CARIRI - ESTADO DO CEARÁ - BRASIL. **1st Joint World Congress on GroundWaterr**, n. 85, p. 1–17, 2000.
- WANG, J.; GUO, X. Adsorption kinetic models: Physical meanings, applications, and solving methods. **Journal of Hazardous Materials**, v. 390, n. November 2019, p. 122156, 2020.
- WEBER, W. J.; MORRIS, J. C. Kinetics of adsorption on carbon from solution. **Journal of the Sanitary Engineering Division**, v. 89, p. 31–60, 1963.
- WONG, K. K. et al. Removal of Cu and Pb from electroplating wastewater using tartaric acid modified rice husk. **Process Biochemistry**, v. 39, n. 4, p. 437–445, 2003.
- YADAV, V.; BHAGAT, M. Isotherm , kinetics and thermodynamic parameters study of arsenic (III) and copper (II) adsorption onto *Limonia acidissima* shell carbon. **Desalination**
-

and Water Treatment, v. 184, n. April, p. 214–224, 2020.

YADAV, V.; TIWARI, D. P.; BHAGAT, M. Isotherm, kinetic and thermodynamic parameters study of arsenic (III) and copper (II) adsorption onto *Limonia acidissima* shell carbon. **Desalination and Water Treatment**, v. 184, n. April, p. 214–224, 2020.

ZHU, Y.; HU, J.; WANG, J. Competitive adsorption of Pb(II), Cu(II) and Zn(II) onto xanthate-modified magnetic chitosan. **Journal of Hazardous Materials**, v. 221–222, p. 155–161, 2012.

ZOU, W.; BAI, H.; GAO, S. Competitive adsorption of neutral red and Cu²⁺ onto pyrolytic char: Isotherm and kinetic study. **Journal of Chemical and Engineering Data**, v. 57, n. 10, p. 2792–2801, 2012.

**CAPÍTULO II: SEGUNDO ARTIGO TÉCNICO PUBLICADO EM PERIÓDICO
CIENTÍFICO**

**KINETIC AND THERMODYNAMIC STUDY OF COPPER (II) IONS
BIOSORPTION BY *CARYOCAR CORIACEUM* WITTM BARK**

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ABSTRACT

The improper disposal of waste containing toxic metals is a major environmental pollution problem. Among the different methodologies to deal with this problem, biosorption is considered one of the most efficient processes for the removal of toxic metals from aqueous solutions. The use of natural adsorbents, such as vegetable waste, in a process known as biosorption, stands out even more as it combines the remediation of polluted water with a reduction in the amount of solid waste. This work aimed to study the use of the bark of *Caryocar Coriaceum* WITTM, a fruit known as pequi, as a possible bioadsorbent for the removal of copper (II) from aqueous solutions. To this end, pequi bark was collected from a public city market, washed, dried up and crushed. The obtained material was then sieved and the 32-mesh fraction was collected, washed and dried again. The resulting material was then submitted to kinetic, isothermal and thermodynamic testing for copper (II) biosorption. We found that the copper (II) biosorption capacity is favored by increasing temperatures, ranging from 16.8 to 20.4 mg.L⁻¹ at 5°C and 35°C, respectively. The kinetic model that best fits de biosorption process was the pseudo-second order model, which produced a linear regression coefficient of 0.999, while the pseudo-first order model produced a value of 0.695. The bioadsorption process was characterized by chemisorption with intra-film diffusion. The isothermal model that best represented the biosorption was Langmuir's ($R^2 = 0.99$). In sight of the obtained results, we

concluded that *Caryocar Coriaceum* WITTM bark is a good bioadsorbent alternative for solutions containing dissolved copper (II).

Keywords: Biosorption, Toxic Metals, Cu (II) ions, Bioremediation, *Cariocar Coriaceum* Wittm, Pequi bark.

Highlights:

- *Caryocar Coriaceum* WITTM bark is a good bioadsorbent for solutions with Cu (II) ions.
- *Caryocar Coriaceum* WITTM bark has a high adsorptive capacity compared to other natural bioadsorbents.
- Kinetic, equilibrium and thermodynamic tests were conducted in this study.
- Experimental data were compared with classical adsorption models.

1 Introduction

The improper disposal of industrial and domestic waste may have a significant impact on the environment, as it carries several toxic components that, more often than not, are difficult to degrade, impairing the self-purifying processes of the environment and thus leading to adverse environmental effects.

Toxic metals stand out among the different toxic compounds found in these wastes because, besides not being chemically and/or biologically degraded, they also have certain characteristics in their electronic structures that make them highly reactive, tending to form complexes and, consequently, develop an intense biochemical and physiological activity, thus causing several environmental and health effects (BURAKOV et al., 2018).

Certain metals, such as copper (Cu), are essential in small quantities for plants and animals as they participate in biosynthetic and other essential processes involving nucleic acids and carbohydrates, bone and tissue improvement in the human body, as well as in maintaining the integrity of biological membranes (RENGEL, 2004; TAVANA; PAHLAVANZADEH; ZAREI, 2020). However, an excessive intake of Cu (II) ions may have toxic effects on living organisms and can have serious effects, such as gastric pain, nausea, vomiting, severe diarrhea, bleeding, cancer in the digestive tract and lungs, as well as Menkes', Parkinson's and Alzheimer's diseases (Acharya et al., 2018; Costa et al., 2017; Kovács et al., 2009; Maaloul et al., 2020; Rodrigues et al., 2007).

Techniques such as chemical precipitation, electrochemical treatment, oxide-reduction processes, ion exchange, reverse osmosis, and phytoremediation, among others, are commonly

used in order to remove toxic metals present in aquatic environments. However, among other disadvantages they are expensive, inefficient, labor-intensive or the treatment process has no selectivity (SHAMIM, 2018).

Thus, in recent years several studies have been highlighting biosorption as a promising treatment technique for the removal of toxic metals from liquid effluents, as this process uses natural biological materials with metal-sequestering properties, able to reduce toxic metal ion concentrations from the range of mg.L^{-1} to $\mu\text{g.L}^{-1}$ (AL-QODAH; YAHYA; AL-SHANNAG, 2017). Furthermore, they are simple, easy to use and cost-effective (AWUAL et al., 2020).

Biosorption is an adsorption process using a biological substrate as adsorbent. Such a substrate is known as a bioadsorbent and can be composed of one of three sources, i.e. microbial biomass, algal biomass, or even dead biomass, the latter including specific tissues of plants, natural fibers or cotton, among others (CRINI et al., 2018; MORIN-CRINI et al., 2018).

A myriad of bioadsorbents have been tested to check for their efficiency in removing toxic metals. Different materials have been studied, such as eggshells (MOHAMMAD; AHMED; EL-SAYED, 2020), tangerine peels (ABDIĆ et al., 2018), lemon peels (ŠABANOVI et al., 2020), rice husk (WONG et al., 2003), pistachio shells (BANERJEE et al., 2018), hazelnut and almond shells (USLU; TANYOL, 2006), *Agaricus bisporus* (LONG et al., 2014), fava d'anta fodder (SANTANA et al., 2020), and seeds of *Azadirachta indica* A. Juss (COSTA et al., 2020), among others.

In Brazil, the pequi, a fruit of the *Caryocar* genus, occurs in the Cerrado region and in the states of Bahia, Piauí, São Paulo, Pará, Mato Grosso, Tocantins, Maranhão, Mato Grosso do Sul, Minas Gerais, and Ceará (LOPES et al., 2006). It plays an important socioeconomic role due to its culinary use and the extraction of almond oil for the manufacture of cosmetics. It generates jobs required for the collection of the fruits, which are picked directly from the soil, while its harvest takes place between January and March (Souza et al., 2013).

The pequi is composed of bark, pulp and seed. When ripe, the pulp accounts for 10% of its total weight, the seed for 6%, and the fruit bark for about 84%. Since the bark is not consumed, it is disposed as waste in urban centers, causing environmental pollution (Morais et al., 2016). In sight of this, the reuse of the bark would contribute to reduce its environmental impacts.

Pequi bark could be used as a bioadsorbent to treat effluents containing toxic metals, allowing not only the treatment of polluted waters but also the reduction of the quantities of discarded, currently unused solid waste.

Therefore, this work aims to study the use of *Caryocar Coriaceum* Wittm bark (CCB) as a possible bioadsorbent for Cu (II) ions dissolved in water through kinetic, isothermal and

thermodynamic tests, aiming to understand the biosorption equilibrium time, the maximum adsorption capacity, the biosorption mechanisms, and the energies involved in the thermodynamics of the system.

2 Materials and methods

2.1 Bioadsorbent collection and preparation

CCB was collected from the public market of the city of Crato, state of Ceará, northeastern Brazil (coordinates: -7.228705, -39.407761) and taken to the Central Analytical Lab of the Federal University of Cariri (UFCA).

The adsorbent was prepared according to Menezes et al. (2020), consisting in washing the material with water to remove coarse impurities. The peeling was done using a vegetable peeler to obtain the upper layers, which were dried by exposure to the sun for 3 days (8 hours per day, resulting in a total of 24 hours). The CCB was then ground and sieved, obtaining particles with a size under the 32 mesh fraction. Such particles were once again washed and then oven-dried at 60°C for 24 hours.

2.2 Material characterization

2.2.1 Fourier Transform Infrared Spectroscopy (FTIR)

A PerkinElmer Spectrum Two FTIR spectrophotometer was used in transmittance mode. The samples were prepared as KBr pellets and the recorded spectrum range was 4000 to 450 cm^{-1} , using 48 scans and a 4 cm^{-1} resolution.

2.2.2 Boehm Titration

According to Boehm (2002) and Salame and Bandosz (2001), the Boehm titration determines the oxygen-containing functional groups present on the surface of the bioadsorbent material and can reinforce part of the data obtained with the FTIR testing.

The test consisted of weighting 0.5 grams of the bioadsorbent in Erlenmeyer flasks before and after the biosorption process, and then adding 10 mL of NaOH (0.1 M), Na_2CO_3 (0.05 M) and NaHCO_3 (0.05 M) solutions to different flasks.

The flasks were then sealed, stirred for 24 hours at 150 rpm, and filtered at the end of the stirring. Subsequently, a sample of 2 mL of the filtrate was pipetted and the excess base was titrated with a 0.1 M HCl standard solution. The entire test was performed in duplicate.

It is assumed that the NaHCO_3 solution neutralizes the carboxylic groups, the Na_2CO_3 solution neutralizes the carboxylic and lactonic groups, and the NaOH solution neutralizes the

carboxylic, lactonic and phenolic groups. The isolated concentrations of each group can be then determined through the difference between them.

2.2.3 X-ray fluorescence (XRF)

The metals present on the bioadsorbent samples were determined by X-Ray Fluorescence (XRF) using a Panalytical XRF spectrometer, model Epsilon 1, on the semi-quantitative mode.

2.3 Biosorption Experiments

2.3.1 Biosorption Kinetics

The biosorption kinetics assay was carried out at the UFCA Central Analytical Lab, in the city of Juazeiro do Norte, Ceará, Brazil. All the experiments were performed in duplicate and at a temperature of 22°C. Approximately 50 mg of the bioadsorbent (CCB) were weighted in 150 mL Erlenmeyer flasks and then added 10 mL of a 5.5 pH-buffered Cu (II) solution (acetate buffer). The choice of the pH used in all the biosorption tests was determined based on the pH analysis for the Point of Zero Charge (pHpzc) according to Menezes et al. (2020). We determined that the pHpzc for CCB is 4.1.

In other words, pH values above 4.1 will favor the biosorption of cationic chemical species, such as Cu (II). The flasks with the bioadsorbents and the Cu (II) solutions were shaken on a Novatecnica (model 109) shake table at 150 rpm.

Samples were collected after contact times ranging from 1 minute to 4 hours in order to determine the minimum time required to reach the biosorption equilibrium. After reaching the respective contact time, the samples were filtered on filter paper and tested by Flame Atomic Absorption Spectroscopy (FAAS), also at the UFCA Central Analytical Lab, using a Varian SpectrAA 50B spectrometer.

2.3.2 Biosorption Isotherm

On the isotherm biosorption study, Cu (II) solutions with different concentrations, ranging from approximately 20 mg.L⁻¹ to 600 mg.L⁻¹, were used to check for the influence of the initial concentration of Cu (II) ions on the CCB bioadsorptive process. The contact time was defined according to the results obtained in the biosorption kinetic test and the pH of the Cu (II) solutions was buffered at 5.5, according to Menezes et al. (2020).

After reaching the established contact time, the samples were filtered and tested by FAAS.

2.3.3 Biosorption Thermodynamics

As in the kinetic and isotherm tests, 50 mg of CCB were weighted in Erlenmeyer flasks and added 10 mL of Cu (II) solutions. In this test, however, the initial concentration of the solutions was 100 mg.L^{-1} and the established ambient temperatures were 5, 15, 25 and 35°C .

The flasks were shaken for 2 hours under controlled temperatures using a Novatecnica shaker incubator (Model NT 715) at the Natural Products Research Laboratory (LPPN) of the Regional University of Cariri (URCA). All tests were performed in duplicate.

2.3.4 Analysis of the experimental data

The adsorptive capacity (q) was the parameter used to study all the Cu (II) biosorption results. Equation 1 was used to determine the values of q .

$$q = \frac{(C_0 - C_t) \times V}{m_{ads}} \quad (1)$$

Where: C_0 : Initial concentration of the metal solution (mg.L^{-1}); C_t : Concentration of the metal solution after a given time t (mg.L^{-1}); V : Volume of the solution (L); m_{ads} : Bioadsorbent mass (g).

2.3.5 Kinetic models

Duarte-Neto et al. (2014) reported that the pseudo-first order equation, or Lagergren equation, is one of the most commonly used to evaluate biosorption processes of a liquid solution, based on the biosorption capacity of the solid. In this model, it is assumed that the occupancy rate of the biosorption sites is proportional to the number of unoccupied sites.

The pseudo-second order model, also known as the Ho model, is based on the hypothesis that the occupancy rate of the biosorption sites is proportional to the square of the number of unoccupied sites. (BOPARAI; JOSEPH; O'CARROLL, 2011; HO; MCKAY, 1999).

The pseudo-first and the pseudo-second order models are linearly described in Table 1.

Table 1: Kinetic Models

Kinetic models	Equation	Parameters
Pseudo-first order	$\ln(Q_{Eq} - Q_t) = \ln(Q_{Eq}) - K_1 t$	Q _t : Biosorption capacity at time t (mg.g ⁻¹); Q _{eq} : Biosorption capacity at equilibrium (mg.g ⁻¹); K ₁ : Pseudo-first order reaction rate constant (min ⁻¹); K ₂ : Pseudo-second order reaction rate; t: Time (min).
Pseudo-second order	$\frac{t}{Q_t} = \frac{1}{K_2 Q_{Eq}^2} + \frac{1}{Q_{Eq}} t$	

Source (Boparai et al., 2011; Duarte- Neto et al., 2014; Ho and McKay, 1999)

2.3.6 Diffusion model

According to Weber and Morris (1963), if intraparticle diffusion is the determinant of velocity, biosorption removal varies with the square root of time. Thus, the intraparticle diffusion coefficient (K_d) can be defined by Equation 2.

$$q_t = K_d * t^{0.5} + C \quad (2)$$

Where: q_t: Amount of solid phase adsorbed (mg.g⁻¹) at a given time t (min); K_d: Intraparticle diffusion coefficient (mg.g⁻¹.min^{-0.5}), obtained from the slope and the C value at the intersection of the graph curve of q_t versus t^{0.5}; C: Constant related to diffusion resistance (mg.g⁻¹).

2.3.7 Biosorption isotherms

The Langmuir model is based on the biosorption occurring at uniform sites with a monolayer coating and ion affinity regardless of the amount of adsorbed material, so it is possible to determine the maximum biosorption capacity of the bioadsorbent (ABDI; KAZEMI, 2015; FENG et al., 2011). The q_{max} and K_L values correspond to the slope and intercept constant, respectively, obtained by the linear regression of the curve Ce/q_e versus Ce.

Freundlich's isotherm presents an empirical equation, applicable to non-ideal systems and assumes heterogeneous surfaces and a multilayer biosorption (FENG et al., 2011). By plotting Ln(q_e) vs Ln(C_e), it is possible to determine the values of K_F and 1/n by linear regression using the slope and intersection constant values.

Temkin's isotherm contains a factor that explicitly takes bioadsorbent-adsorbate interactions into account. The model assumes that the heat of biosorption (temperature function) of all molecules in the layer would decrease linearly with surface coverage due to bioadsorbent-adsorbate interactions (DADA; ADEKOLA; ODEBUNMI, 2015). Temkin's b and K_t constants can be obtained from the slope and interception values derived from the linear regression of the q_e versus $\ln C_e$ plot.

The D-R model assumes that biosorption occurs in a multilayer involving Van der Waals forces and works on processes with physisorption characteristics. The constants β and q_d can be obtained through the slope and interception values, respectively, derived from the linear regression of the $\ln(q_e)$ versus ε^2 plot.

The linearized equations of the isothermal models used in this study are presented in Table 2.

Table 2: Isotherm Models

Isotherm model	Equation	Parameters
Langmuir Model	$\frac{C_e}{q_e} = \frac{1}{q_{max}} C_e + \frac{1}{q_{max} \times K_L}$	q_e : Amount of adsorbed metal per unit of bioadsorbent mass (mg.g^{-1});
Freundlich model	$\ln(q_e) = \ln(K_F) + \frac{1}{n} \ln(C_e)$	C_e : Concentration of the ion in the equilibrium solution (mg.g^{-1}); K_L : Equilibrium constant (L.g^{-1});
Temkin model	$q_e = \frac{RT}{b} \ln K_t + \frac{RT}{b} \ln C_e$	q_{max} : Maximum biosorption capacity of the bioadsorbent (mg.g^{-1}); K_F : Biosorption capacity constant ($(\text{mg.g}^{-1}) (\text{L.mg}^{-1})^{1/n}$); $1/n$: Biosorption intensity constant; b : Temkin constant (J.mol^{-1}); K_t : Temkin isothermal constant (L.g^{-1});
Dubinin-Radushkevich (D-R) model	$\ln q_e = \ln q_d - \beta * \varepsilon^2$ $\varepsilon = RT \ln \left[1 + \frac{1}{C_e} \right]$	R : Universal gas constant ($\text{J.mol}^{-1}\text{K}^{-1}$); T : Temperature (K) q_d : D-R constant (mg.g^{-1}); β : Constant related to free energy; ε : Polanyi Potential

Source (ABDI; KAZEMI, 2015; DADA; ADEKOLA; ODEBUNMI, 2015; FENG et al., 2011; TAŞAR; ÖZER, 2020)

3 Results

3.1 Infrared spectroscopy analysis

When we compare the materials before and after the biosorption process, we can see a decreasing trend in some bands with frequencies below 2000 cm^{-1} (Figure 1).

The main alterations occurred at 1515 cm^{-1} , corresponding to the angular deformation of CH_2 , at 1342 cm^{-1} , corresponding to the C-CO-C section of the carbonyl or ketone functional groups and to the C-CHO angular deformation of aldehydes, and at 1216 and 1037 cm^{-1} , corresponding to the C-O binding stretch (Amorim et al., 2016; Breda et al., 2017; Ragavendran et al., 2011).

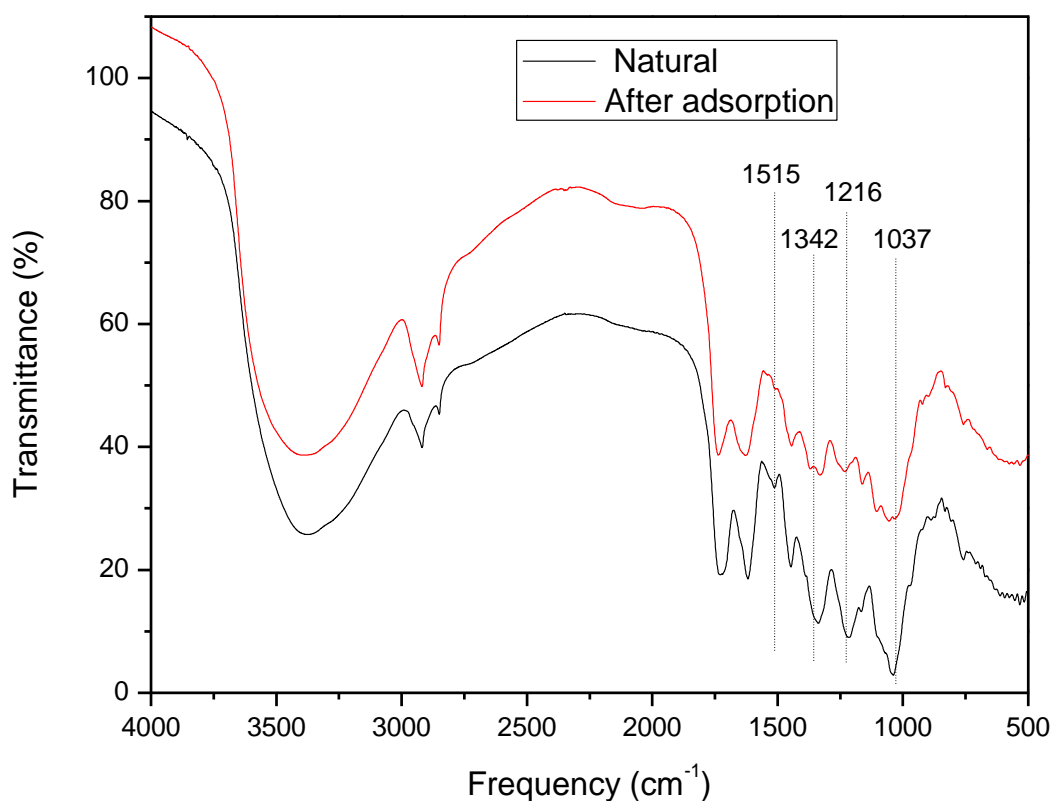


Figure 1: FTIR spectra of the bioadsorbents before and after the biosorption process

These alterations possibly indicate that Cu (II) was bound to the functional groups present in the bioadsorbent molecule, promoting the reduction of the initial signal as it probably makes the bond less susceptible to vibration.

When studying Cu biosorption in green vegetable waste with activated carbon, Sabela et al. (2019) showed changes on the FTIR spectra before and after biosorption at 3400, 2995, 2205, 1550 and 855 cm^{-1} . Zhu et al. (2012) also found changes on the FTIR spectra before and

after Cu (II) biosorption on xanthate-modified magnetic chitosan. In their study, they found such reductions at 1239 and 992 cm^{-1} , as well as a bandwidth shift at the region of 1552 cm^{-1} .

3.2 Boehm Titration

In addition to the FTIR, the Boehm titration showed the presence of phenolic, carboxylic and lactonic groups (Table 3) that may provide available active sites for the biosorption of Cu (II) ions present in an aqueous solution.

Table 3 shows the reduction in the Cu(II) concentrations of the carboxylic and lactonic groups, with a reduction rate of around 60% and 14.8%, respectively, indicating that they favored the binding of Cu(II) ions to the radicals of these groups, further strengthening the data obtained from the FTIR spectra.

Table 3: Boehm titration

CCB bioadsorbent	Total acid sites (mmol.g⁻¹)	Phenolic groups (mmol.g⁻¹)	Carboxylic groups (mmol.g⁻¹)	Lactonic groups (mmol.g⁻¹)
Before biosorption	1.899	1.275	0.125	0.499
After biosorption	1.749	1.275	0.050	0.425
Reduction (%)	7.9	0	60	14.8

3.5 XRF

Table 4 presents the concentration of some elements within the CCB substrate. After being submitted to the biosorption process with a solution containing Cu (II) ions, we found an increase in the concentration of this metal, showing that biosorption of the metal occurred on the surface of the bioadsorbent.

Even though the bioadsorbent was washed after the biosorption process, it still presented a high concentration of Cu (II) (19.47%) in its composition. Costa et al. (2020) related this phenomenon to a chemisorption process that in their study, conducted using seeds of *Azadirachta indica* A. Juss, accounted for approximately 3% of the adsorbed Cu.

Table 4: Elementary characterization of the bioadsorbent by XRF spectrometry.

CCB bioadsorbent	Concentration (%)						
	Si	P	S	Cl	K	Fe	Cu
Before biosorption	0.23	0.13	0.13	0.13	0.17	0.11	N/D
After biosorption	0.36	0.15	0.11	0.14	N/D	N/D	19.47

N/D – Not Detectable.

3.6 Biosorption kinetics

Figure 2 shows the logarithmic growth of the adsorptive capacity (q), which begins to show a constant behavior after 120 minutes of contact time between the solution and the bioadsorbent, reaching a concentration of 16.7 mg.g^{-1} and reducing the Cu (II) ions concentration ratio from 1 to 0.22. This corresponds to a concentration of 23.6 mg.L^{-1} , indicating a removal efficiency of 78% of the Cu (II) ions from the solution.

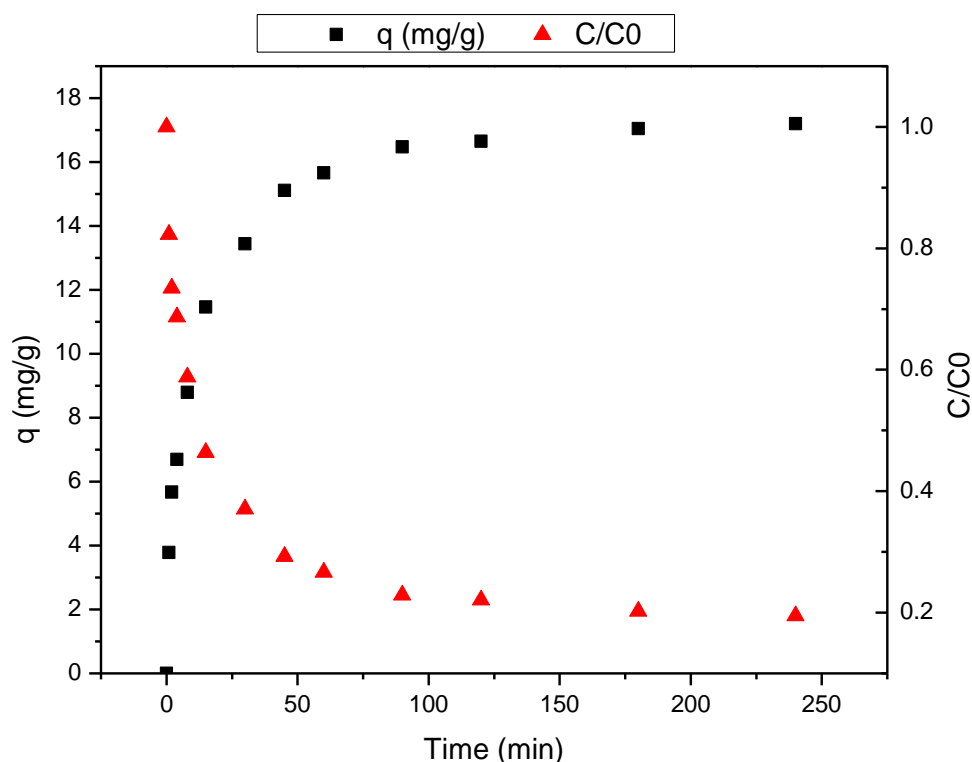


Figure 2: Biosorption kinetics for Cu (II) (Left axis) and remaining Cu (II) ions concentration ratio in the aqueous solution (Right axis). Aqueous solution with an initial concentration of 107 mg.L^{-1} Cu (II).

When we applied the kinetics data to the Lagergren and Ho models (Figures 3(a) and 3(b)), we could determine that the biosorption reaction on the CCB adsorbent is a pseudo-second order one, as the data fits the Ho model. It presented a coefficient of determination $R^2 = 0.999$, resulting in a theoretical q_e value of 17.54 mg.g^{-1} and a K_2 value of $0.0011 \text{ g.mg}^{-1}\text{h}^{-1}$ (Table 5). The experimental data failed to show the linear behavior typical of the Lagergren model, as evidenced by the low value of R^2 ($R^2 = 0.696$).

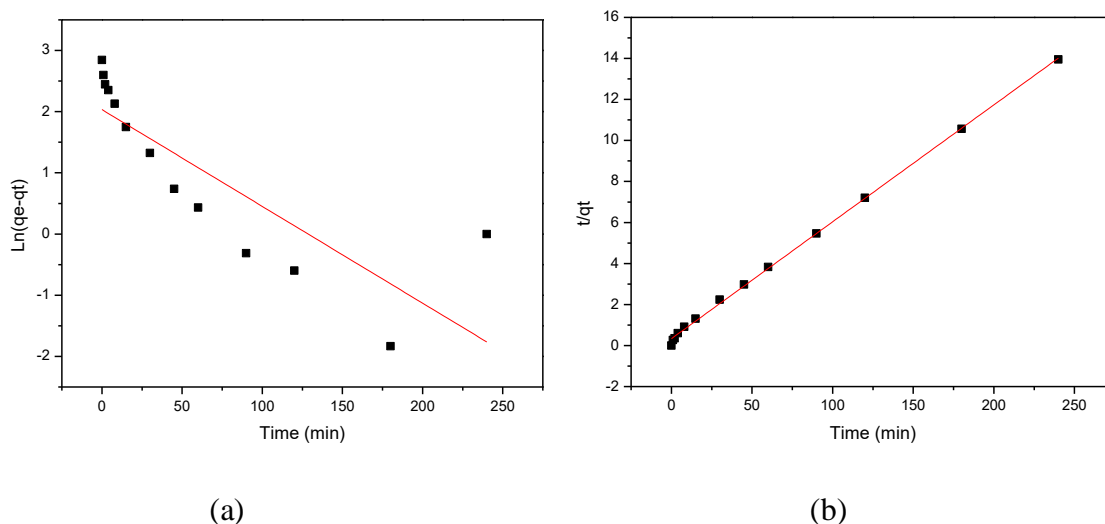


Figure 3: Application of experimental data to the kinetic models: (a) pseudo-first order; (b) pseudo-second order.

Table 5: Kinetic model data

Sample	Exp. Q_e (mg.g^{-1})	Pseudo-first order			Pseudo-second order		
		K_1	$Q_{e, \text{cal}}$ (mg.g^{-1})	R_1^2	$K_2 \times 10^{-3}$ ($\text{g mg}^{-1}\text{h}^{-1}$)	$Q_{e, \text{cal}}$ (mg.g^{-1})	R_2^2
CCB	16.7	-0.0158	7.64	0.696	0.0011	17.5	0.999

3.7 Diffusion model

Figure 4 presents the application of the experimental data to the Weber Morris diffusion model, showing that the biosorption process has three stages. The first stage is characterized by a fast biosorption. Liu et al. (2020) and Weber and Morris (1963) indicated that a large amount of heavy metals are transferred from the solution to the external layer film and adsorbed, while a linear coefficient (C) different from zero suggests for intrafilm diffusion to be the process

controlling the biosorption. The second stage corresponds to intraparticle diffusion, and the last stage to the point of equilibrium (GHOLAMIYAN; HAMZEHLOO; FARROKHANIA, 2020).

Another important point was that the thickness of the film (corresponding to the linear coefficient) was 1.5924 mg.g^{-1} for the first stage and increased with the progression of the contact time between the bioadsorbent and the solution. We saw the value of C increasing, reaching levels of 8.4071 and 15.283 mg.g^{-1} at stages II and III, respectively.

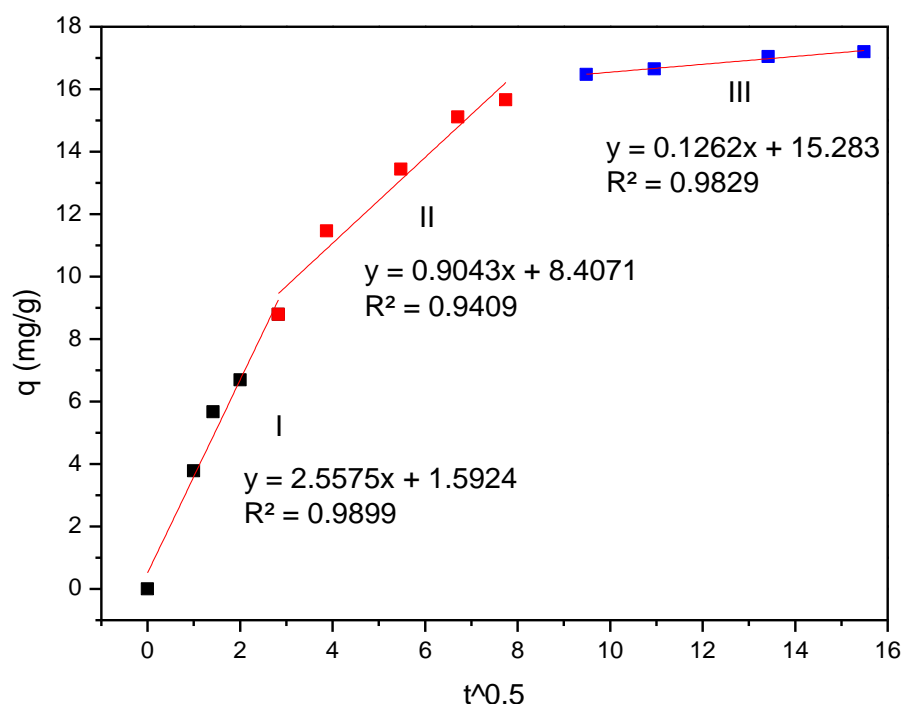


Figure 4: Experimental data applied to the Weber Morris model.

Additional information obtained with this model was related to the intraparticle diffusion coefficient (K_d). The value of this coefficient declined along the different stages, revealing an increasing film thickness and a greater difficulty in the diffusion from the solution to the bioadsorbent. K_d decreased from $2.5575 \text{ mg.g}^{-1}.\text{min}^{-0.5}$ at stage I to $0.1262 \text{ mg.g}^{-1}.\text{min}^{-0.5}$ at stage III, pointing to a weakening intraparticle diffusion and to the appearance of another mechanism (Cao et al., 2019).

3.8 Biosorption isotherms

Figure 5 presents the application of the obtained experimental data to the isothermic models of Langmuir, Freundlich, Temkin and Dubinin-Radushkevich (D-R), while Table 6 shows the information collected through those models. The experimental data fits all the

isothermal models, with an R^2 above 0.940, except for the D-R model, which had an R^2 value of 0.776.

This may suggest that there is a monolayer biosorption of Cu (II) on the surface of the bioadsorbent. However, according to Mohammad et al. (2020), multilayer biosorption can occur through capillary action in the mesopores of the bioadsorbent.

In this study, the adsorptive process was a chemisorption one, as the obtained results fit the Temkin model, while results fitting the D–R model would have indicated the occurrence of physisorption processes (Biswas et al. (2007); Boparai et al. (2011)).

A q_{\max} value of 26.9 mg.g^{-1} was obtained (Table 6) from the Langmuir model. This value is higher than that of some unmodified natural bioadsorbents found in the literature (Table 7), making CCB an efficient and low-cost alternative to be used in adsorptive processes for the removal of Cu (II) ions.

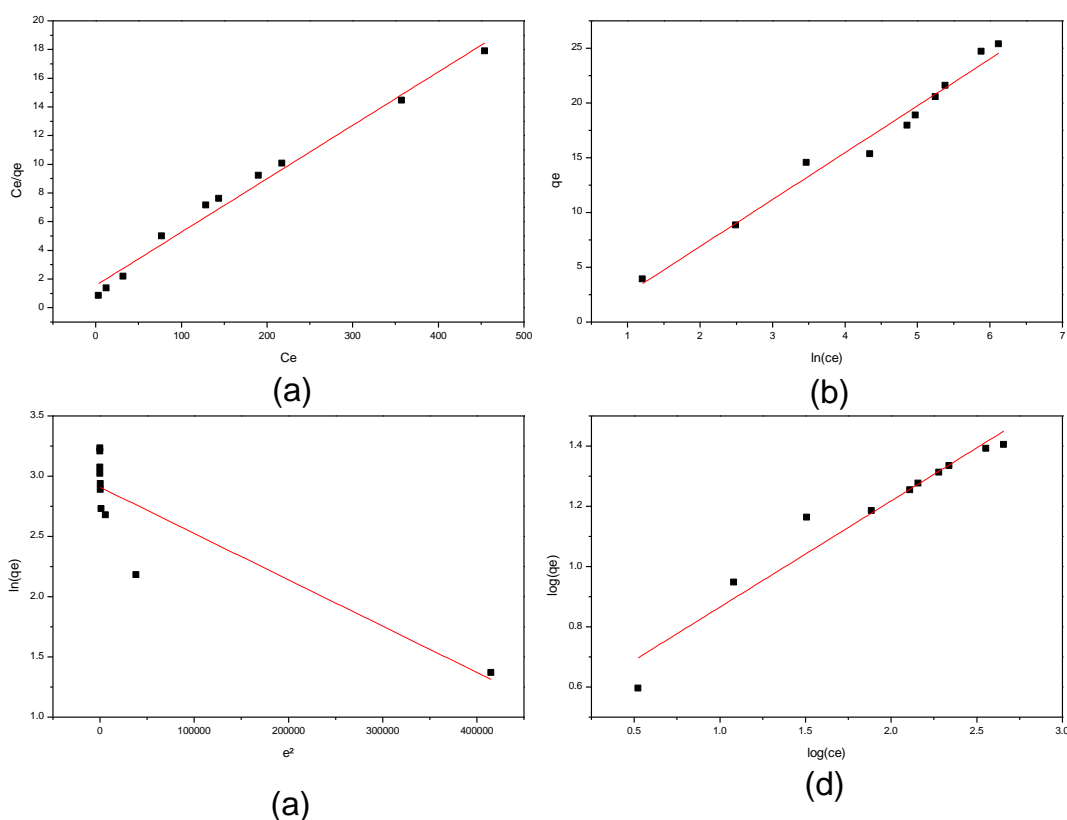


Figure 5: Application of the experimental data to the models of: a) Langmuir; b) Freundlich; (c) D-R; (d) Temkin.

Table 6: Data obtained with the Langmuir, Freundlich, Temkin and D-R models.

Isotherms	Parameter		
Langmuir	Q_{\max} (mg.g ⁻¹)	K_L (L.mg ⁻¹)	R^2
	26.9	0.0583	0.986
Freundlich	Parameter		
	K_f	n	R^2
	3.26	2.8361	0.945
Temkin	Parameter		
	K_t	B	R^2
	0.6834	573.052	0.979
D-R	Parameter		
	Q_d	B_d	R^2
	1.067	4.00E-06	0.776

Regarding the Freundlich model, Boparai et al. (2011) and Kadiri et al. (2019) proposed that a favorable biosorption condition and a high affinity between bioadsorbent and adsorbate occur when the value of n is greater than 1, thereby pointing to a chemical biosorption. This reinforces the fact that the D-R model did not fit the results of this study. We obtained a K_f value of 3.26, which indicates the biosorption capacity of the bioadsorbent material.

Table 7: Comparison of maximum adsorptive capacities of several unmodified Cu (II) bioadsorbents.

Bioadsorbents	q_{\max} (mg.g ⁻¹)	Reference
Soy straw	5.4	(ŠĆIBAN; KLAŠNJA; ŠKRBIĆ, 2008)
Cornstalk	3.7	
Oat straw	5.1	
Alamo sawdust	2.5	(ŠĆIBAN; KLAŠNJA; ŠKRBIĆ, 2006)
Fir sawdust	2.4	
Rice straw	12.23	(LI; LAW; CHAN, 2017)
Rice husk	8.89	
Sugarcane bagasse	9.73	(SALIHI et al., 2015)
Sesame shell	10.83	(EL-ARABY et al., 2017)
Tangerine peel	1.6	(ABDIĆ et al., 2018)
Seeds of Azadirachta indica A. Juss	11.54	(COSTA et al., 2020)
Raw eggshells	8.83	(MOHAMMAD; AHMED; EL-SAYED, 2020)
Fava d'anta fodder	24.45	(SANTANA et al., 2020)
CCB bark	26.9	This study

3.9 Thermodynamic study

A higher temperature favored the adsorptive process and allowed a 21.7% increase in the Cu (II) biosorption capacity, from 16.8 mg.g⁻¹ at 5°C to 20.4 mg.g⁻¹ at 35°C (Figure 6a). According to Yadav and Bhagat (2020), this behavior indicates that we are in the presence of an endothermic biosorption process.

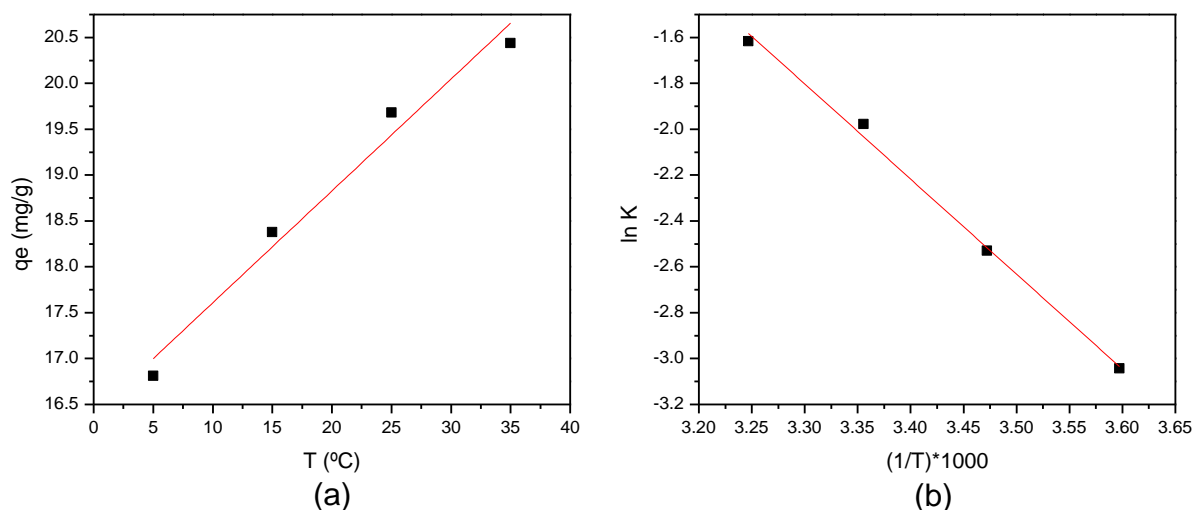


Figure 6 - Thermodynamic study (a) Curve $q_e \times T$; (b) Modeling for the determination of Gibbs Free energy (ΔG°), Enthalpy (ΔH°) and Entropy (ΔS).

Table 8 shows other parameters also pointing to the endothermic nature of the reaction. A reduction in the Gibbs Free energy (ΔG°) values from 7.01 to 4.05 KJ.mol^{-1} was obtained after increasing the system's temperature from 5°C to 35°C. Such behavior indicates that, with an increase in temperature, less energy is necessary to promote the biosorption reaction. According to Loulidi et al. (2020), the fact that the reactions become more spontaneous in such a warmer scenario indicates that the process is endothermic.

An enthalpy (ΔH°) value of 34.5 KJ.mol^{-1} was obtained. Sahmoune (2019) and Yadav and Bhagat (2020) commented that a positive ΔH° value indicates that the biosorption is an endothermic process.

Table 8: Thermodynamic parameters

Temperature (°C)	ΔG° (KJ.mol^{-1})	ΔH° (KJ.mol^{-1})	ΔS ($\text{KJ.mol}^{-1}.\text{K}^{-1}$)
5	7.01	34.5	0.10
15	6.03		
25	5.04		
35	4.05		

An entropy (ΔS) value of 0.1 $\text{KJ.mol}^{-1}.\text{K}^{-1}$ was obtained. According to Kadiri et al. (2019) and Şenel (2020), positive ΔS° values point to the affinity of Cu (II) to the sorbent and to the increasing randomness at the solid/liquid interface during the sorption of Cu (II).

The ΔH° and ΔS values, presented in Table 8, were determined using the slope and intercept values, respectively, obtained with the linear regression analysis of Figure 6 (b).

4 Conclusions

This study shows that the bark of *Caryocar Coriaceum* Wittm can be used as an efficient bioadsorbent for the removal of Cu (II) ions in a solution, with a maximum removal capacity of 26.9 mg.g⁻¹.

An increased temperature during the adsorptive process favors the Cu (II) biosorption rate using *Caryocar Coriaceum* Wittm bark as bioadsorbent. The biosorption capacity of this material increased from 16.8 mg.L⁻¹ at 5°C to 20.4 mg.L⁻¹ at 35°C.

The kinetic model that best fits the biosorption process was the pseudo-second order model, as it produced a linear regression value of 0.999. Chemisorption was the adsorptive mechanism indicated by the results, with intrafilm diffusion being the process controlling the biosorption.

We should note that the material used to prepare the bioadsorbent was a food waste that can be easily found in large quantities during the harvest of the fruit. Therefore, its use as a bioadsorbent material would not only reduce the available amounts of Cu(II), a highly dangerous contaminant, when improperly disposed of in the environment, but would also reduce the quantities of a material currently discarded as waste.

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References

- ABDI, O.; KAZEMI, M. A review study of biosorption of heavy metals and comparison between different biosorbents. **Journal of Materials and Environmental Science**, v. 6, n. 5, p. 1386–1399, 2015.
- ABDIĆ et al. Adsorptive removal of eight heavy metals from aqueous solution by unmodified and modified agricultural waste: tangerine peel. **International Journal of Environmental Science and Technology**, v. 15, n. 12, p. 2511–2518, 2018.
- ACHARYA, J.; KUMAR, U.; RAFI, P. M. Removal of Heavy Metal Ions from Wastewater by Chemically Modified Agricultural Waste Material as Potential Adsorbent-A Review. **International Journal of Current Engineering and Technology**, v. 8, n. 3, p. 526–530, 2018.
- AHAYLA, N.; RAMACHANDRA, T. V. Biosorption of heavy metals. **Biotechnology progress**, v. 11, n. 3, p. 235–50, 1995.
- AL-QODAH, Z.; YAHYA, M. A.; AL-SHANNAG, M. On the performance of bioadsorption processes for heavy metal ions removal by low-cost agricultural and natural by-products bioadsorbent: a review. **Desalination and Water Treatment**, v. 85, n. August, p. 339–357, 2017.
- ALMEIDA, A. Avaliação ecológica do extrativismo do pequi (*Caryocar coriaceum* Wittm.) na Floresta Nacional do Araripe, Ceará: informações para um plano de uso sustentável. **Tese de Doutorado**, p. 164, 2014.
- AMIN, M. T.; ALAZBA, A. A.; AMIN, M. N. Absorption behaviours of copper, lead, and arsenic in aqueous solution using date palm fibres and orange peel: Kinetics and thermodynamics. **Polish Journal of Environmental Studies**, v. 26, n. 2, p. 543–557, 2017.
- AMORIM, D. J. et al. Characterization of Pequi (*Caryocar brasiliense*) Shells and Evaluation of Their Potential for the Adsorption of PbII Ions in Aqueous Systems. **Journal of the Brazilian Chemical Society**, v. 27, n. 3, p. 616–623, 2016.
- ARAÚJO, R. R. D. L. **MODELAGEM DO PROCESSO DE BIOSSORÇÃO DE CHUMBO UTILIZA?DO A MACRÓFITA AQUÁTICA *Eichhornia crassipes***. Curitiba - PR: UFPR, 2011.
- ARSLANOĞLU, E. et al. Fabrication, characterization, and adsorption applications of low-cost hybride activated carbons from peanut shell-vinasse mixtures by one-step pyrolysis. **Biomass Conversion and Biorefinery**, 2021.
- ATKINS, P.; JONES, L.; LAVERMAN, L. **Princípios de Química, questionando a vida moderna e o meio ambiente**. 7^a ed. Porto Alegre: [s.n.].
- AVDEEV, Y. G.; LUCHKIN, A. Y.; KUZNETSOV, Y. I. Adsorption of IFKhAN-92
-

- Inhibitor on Low Carbon Steel from Sulfuric Acid Solution. **Protection of Metals and Physical Chemistry of Surfaces**, v. 56, n. 7, p. 1244–1248, 2020.
- AWUAL, M. R. Mesoporous composite material for efficient lead(II) detection and removal from aqueous media. **Journal of Environmental Chemical Engineering**, v. 7, n. 3, p. 103124, 2019a.
- AWUAL, M. R. et al. Introducing an alternate conjugated material for enhanced lead(II) capturing from wastewater. **Journal of Cleaner Production**, v. 224, p. 920–929, 2019.
- AWUAL, M. R. Innovative composite material for efficient and highly selective Pb(II) ion capturing from wastewater. **Journal of Molecular Liquids**, v. 284, p. 502–510, 2019b.
- AWUAL, M. R. et al. Naked-eye lead(II) capturing from contaminated water using innovative large-pore facial composite materials. **Microchemical Journal**, v. 154, n. November 2019, p. 104585, 2020.
- AWUAL, M. R.; HASAN, M. M. Novel conjugate adsorbent for visual detection and removal of toxic lead(II) ions from water. **Microporous and Mesoporous Materials**, v. 196, p. 261–269, 2014.
- AWUAL, M. R.; HASAN, M. M. A ligand based innovative composite material for selective lead(II) capturing from wastewater. **Journal of Molecular Liquids**, v. 294, p. 111679, 2019.
- AZARI, A. et al. Comprehensive systematic review and meta-analysis of dyes adsorption by carbon-based adsorbent materials: Classification and analysis of last decade studies. **Chemosphere**, v. 250, n. 5, p. 126238, 2020.
- AZOULAY, K. et al. Comparative study between static and dynamic adsorption efficiency of dyes by the mixture of palm waste using the central composite design. **Chemical Data Collections**, v. 27, 2020.
- BANERJEE, M. et al. Removal of Cr(VI) from Its Aqueous Solution Using Green Adsorbent Pistachio Shell: a Fixed Bed Column Study and GA-ANN Modeling. **Water Conservation Science and Engineering**, v. 3, n. 1, p. 19–31, 2018.
- BARROS, A. J. M. et al. ESTUDO TERMOGRAVIMÉTRICO DO PROCESSO DE SORÇÃO DE METAIS PESADOS POR RESÍDUOS SÓLIDOS ORGÂNICOS. **Engenharia Sanitaria e Ambiental**, v. 11, p. 184–190, 2006.
- BARROS, A. J. M. **Estudo da Formação de Complexos Pelo Processo de Bio-sorção**. Joao Pessoa: UFPB, 2006.
- BISWAS, K.; SAHA, S. K.; GHOSH, U. C. Adsorption of fluoride from aqueous solution by a synthetic iron(III)-aluminum(III) mixed oxide. **Industrial and Engineering Chemistry Research**, v. 46, n. 16, p. 5346–5356, 2007.
- BLAGOJEV, N. et al. A new approach for modelling and optimization of Cu(II) biosorption
-

- from aqueous solutions using sugar beet shreds in a fixed-bed column. **Journal of Hazardous Materials**, v. 363, n. June 2018, p. 366–375, 2019.
- BOEHM, H. P. Surface oxides on carbon and their analysis: A critical assessment. **Carbon**, v. 40, n. 2, p. 145–149, 2002.
- BOPARAI, H. K.; JOSEPH, M.; O'CARROLL, D. M. Kinetics and thermodynamics of cadmium ion removal by adsorption onto nano zerovalent iron particles. **Journal of Hazardous Materials**, v. 186, n. 1, p. 458–465, 2011.
- BOYD, G. E.; SCHUBERT, J.; ADAMSON, A. W. The Exchange Adsorption of Ions from Aqueous Solutions by Organic Zeolites. Ion-exchange Equilibria. **Journal of the American Chemical Society**, v. 69, n. 11, p. 2818–2829, 1947.
- BREDA, C. A. et al. Processing and Characterization of Chitosan Films with Incorporation of Ethanolic Extract from “Pequi” Peels. **Macromolecular Research**, 2017.
- BURAKOV, A. E. et al. Adsorption of heavy metals on conventional and nanostructured materials for wastewater treatment purposes: A review. **Ecotoxicology and Environmental Safety**, v. 148, n. August 2017, p. 702–712, 2018.
- CAO, M. LI et al. Functionalized graphene nanosheets as absorbent for copper (II) removal from water. **Ecotoxicology and Environmental Safety**, v. 173, n. September 2018, p. 28–36, 2019.
- CONAMA. Resolução CONAMA 430/2011. **Diário Oficial da União**, p. 9, 2011.
- CONICELLI, B. P. **BIOSSORÇÃO DE CHUMBO E MERCÚRIO PELAS LINHAGENS SELVAGEM E RECOMBINANTE DE C. metallidurans EM MEIO AQUOSO**. [s.l.] USP, 2018.
- CORDEIRO, M. W. S. et al. PHYSICAL CHARACTERISTICS, CHEMICAL-NUTRITIONAL COMPOSITION AND ESSENTIAL OILS OF *Caryocar brasiliense* NATIVE FROM THE STATE OF MATO GROSSO (In Portuguese). **Revista Brasileira de Fruticultura**, v. 35, n. 4, p. 1127–1139, 2013.
- CORDEIRO, R. D. M. **AS AGLOMERAÇÕES PRODUTIVAS DE CALÇADOS, FOLHEADOS E DE JOIAS DO CRAJUBAR (CE): FORMAÇÃO, PRODUÇÃO, TRABALHO, IMPLICAÇÕES SOCIOESPACIAIS**. [s.l.] Unesp, 2015.
- COSTA, D. A.; MENDONÇA, R. H.; WYSARD JUNIOR, M. M. Evaluation of removal of chromium (III) by composite porous adsorbents materials of PE-g-MA, coconut fiber and chitosan using experimental design (In Portuguese). **Engenharia Sanitaria e Ambiental**, v. 22, n. 6, p. 1203–1213, 2017.
- COSTA, A. P. F. DA; PINTO, E. G.; SOARES, D. S. B. Obtenção de farinha do mesocarpo de pequi. **Revista Agrarian**, p. 113–119, 2017.
-

- COSTA, T. B. DA; SILVA, M. G. C. DA; VIEIRA, M. G. A. Recovery of rare-earth metals from aqueous solutions by bio/adsorption using non-conventional materials: a review with recent studies and promising approaches in column applications. **Journal of Rare Earths**, v. 38, n. 4, p. 339–355, 2020.
- COSTA, W. D. et al. Removal of copper(II) ions and lead(II) from aqueous solutions using seeds of *Azadirachta indica* A. Juss as bioadsorbent. **Environmental Research**, v. 183, n. June 2019, p. 109213, 2020.
- CRINI, G. et al. Conventional and non-conventional adsorbents for wastewater treatment. **Environmental Chemistry Letters**, n. 0123456789, 2018.
- CUI, H. et al. Dry-wet and freeze-thaw aging activate endogenous copper and cadmium in biochar. **Journal of Cleaner Production**, v. 288, p. 125605, 2021.
- DADA, A. O.; ADEKOLA, F. A.; ODEBUNMI, E. O. A novel zerovalent manganese for removal of copper ions : synthesis , characterization and adsorption studies. **Applied Water Science**, 2015.
- DE AQUINO SARAIVA, R. et al. *Caryocar coriaceum* Wittm. **Medicinal and Aromatic Plants of South America**, v. 5, p. 153–162, 2018.
- DE MAGALHÃES, V. H. P.; NEVES, M. A. F. E S. UTILIZAÇÃO DO PERICARPO DE COCO VERDE (*Cocos nucifera* L . - ARECACEAE) PARA A REMOÇÃO DE RESÍDUOS DE ÍONS CROMO (VI) EM SOLUÇÕES AQUOSAS. **Perspectivas da Ciência e Tecnologia**, v. 3, p. 10–16, 2011.
- DE OLIVEIRA, M. N. S. et al. Estádio de maturação dos frutos e fatores relacionados aos aspectos nutritivos e de textura da polpa de pequi (*Caryocar brasiliense* Camb.). **Revista Brasileira de Fruticultura**, v. 28, n. 3, p. 380–386, 2006.
- DELBIANCO, G. A. B. **Estudo de Rejeitos de Galvanoplastia e a sua Aplicação na Fabricação de Peças Cerâmicas Rústicas para Fins Decorativos**. [s.l.] UNESP, 2008.
- DENG, J. et al. Competitive adsorption of Pb(II), Cd(II) and Cu(II) onto chitosan-pyromellitic dianhydride modified biochar. **Journal of Colloid and Interface Science**, v. 506, p. 355–364, 2017.
- DUARTE- NETO, J. F. et al. Processos de adsorção de corantes em argilas esmectíticas: uma revisão. **Revista Eletrônica de Materiais e Processos**, v. 9, p. 51–59, 2014.
- EL-ARABY, H. A. et al. Sesame Husk as Adsorbent for Copper(II) Ions Removal from Aqueous Solution. **Journal of Geoscience and Environment Protection**, v. 05, n. 07, p. 109–152, 2017.
- ELOVICH, S. Y.; LARINOV, O. G. Theory of adsorption from solutions of non electrolytes on solid (I) equation adsorption from solutions and the analysis of its simplest form,(II)
-

- verification of the equation of adsorption isotherm from solutions. **Izvestiya Akademii Nauk**, v. 2, n. 2, p. 209–216, 1962.
- ESCUADERO-OÑATE, C.; VILLAESCUSA, I. The Thermodynamics of Heavy Metal Sorption onto Lignocellulosic Biomass. **Heavy Metals**, 2018.
- FALAKI, Z.; BASHIRI, H. Preparing an adsorbent from the unused solid waste of Rosewater extraction for high efficient removal of Crystal Violet. **Journal of the Iranian Chemical Society**, v. 18, n. 10, p. 2689–2702, 2021.
- FEI, Q.; BEI, W. Single- and multi-component adsorption of Pb, Cu, and Cd on peat. **Bulletin of Environmental Contamination and Toxicology**, v. 78, n. 3–4, p. 265–269, 2007.
- FENG, N. et al. Biosorption of heavy metals from aqueous solutions by chemically modified orange peel. **Journal of Hazardous Materials**, v. 185, n. 1, p. 49–54, 2011.
- FUTALAN, C. M. et al. Comparative and competitive adsorption of copper, lead, and nickel using chitosan immobilized on bentonite. **Carbohydrate Polymers**, v. 83, n. 2, p. 528–536, 2011.
- GEÓCZE, K. C. **Exploratory analysis of carotenoids, essential oils and triacylglycerides of pequi (Caryocar brasiliense Camb.) from brazilian districts located in the cerrado biome (In Portugues)**. [s.l.] Universidade Federal de Viçosa, 2011.
- GHOLAMIYAN, S.; HAMZEHLOO, M.; FARROKHANIA, A. RSM optimized adsorptive removal of erythromycin using magnetic activated carbon: Adsorption isotherm, kinetic modeling and thermodynamic studies. **Sustainable Chemistry and Pharmacy**, v. 17, n. May, p. 100309, 2020.
- GIRALDO, L.; MORENO-PIRAJÁN, J. C. Pb²⁺ adsorption from aqueous solutions on activated carbons obtained from lignocellulosic residues. **Brazilian Journal of Chemical Engineering**, v. 25, n. 1, p. 143–151, 2008.
- GUGUSHE, A. S. et al. Adsorptive removal of cd, cu, ni and mn from environmental samples using fe₃o₄-zro₂@aps nanocomposite: Kinetic and equilibrium isotherm studies. **Molecules**, v. 26, n. 11, 2021.
- HACKBARTH, F. V. **REMOÇÃO DE METAIS DE EFLUENTES PETROQUÍMICOS UTILIZANDO BIOMASSA DE MACROALGA MARINHA PELVETIA CANALICULATA COMO ADSORVENTE**. Florianópolis: UFSC, 2014.
- HIKMAT, N. A.; QASSIM, B. B.; KHETHI, M. T. Thermodynamic and Kinetic Studies of Lead Adsorption from Aqueous Solution onto Petiole and Fiber of Palm Tree. **American Journal of Chemistry**, v. 4, n. 4, p. 116–124, 2014.
- HO, Y. S.; MCKAY, G. Pseudo-second order model for sorption processes. **Process Biochemistry**, v. 34, n. 5, p. 451–465, 1999.
-

- HOSSAIN, A. et al. Biosorption of Cu(II) From Water by Banana Peel Based Biosorbent: Experiments and Models of Adsorption and Desorption. n. January 2012, 2012.
- HUSSAIN, A. et al. Synthesis and Application of Modified Orchard Waste Biochar for Efficient Scavenging of Copper from Aqueous Solutions. **Arabian Journal for Science and Engineering**, n. 0123456789, 2021.
- IBGE. **Pesquisa nacional de saneamento básico 2017: abastecimento de água e esgotamento sanitário**. [s.l.: s.n.].
- IGHALO, J. O. et al. Mitigation of clofibric acid pollution by adsorption: A review of recent developments. **Journal of Environmental Chemical Engineering**, v. 8, n. 5, 2020a.
- IGHALO, J. O. et al. Competitive adsorption of Pb(II), Cu(II), Fe(II) and Zn(II) from aqueous media using biochar from oil palm (*Elaeis guineensis*) fibers: a kinetic and equilibrium study. **Indian Chemical Engineer**, v. 0, n. 0, p. 1–11, 30 jun. 2020b.
- IRAVANI MOHAMMADABADI, S.; JAVANBAKHT, V. Fabrication of dual cross-linked spherical treated waste biomass/alginate adsorbent and its potential for efficient removal of lead ions from aqueous solutions. **Industrial Crops and Products**, v. 168, n. April, p. 113575, 2021.
- JUMINA et al. Synthesis of C-4-hydroxy-3-methoxyphenylcalix[4]resorcinarene and its application as adsorbent for lead(II), copper(II) and chromium(III). **Bulletin of the Chemical Society of Japan**, v. 92, n. 4, p. 825–831, 2019.
- JUMINA et al. Simultaneous removal of lead(II), chromium(III), and copper(II) heavy metal ions through an adsorption process using C-phenylcalix[4]pyrogallolarene material. **Journal of Environmental Chemical Engineering**, v. 8, n. 4, p. 103971, 2020.
- KADIRI, L. et al. Mathematical modeling and thermodynamic study of copper (II) removal from aqueous solution by *Coriandrum Sativum* seeds. **Mediterranean Journal of Chemistry**, v. 7, n. 6, p. 478–490, 2019.
- KAMARI, A. et al. Biosorptive removal of Cu(II), Ni(II) and Pb(II) ions from aqueous solutions using coconut dregs residue: Adsorption and characterisation studies. **Journal of Environmental Chemical Engineering**, v. 2, n. 4, p. 1912–1919, 2014.
- KHEDDO, A. et al. Adsorption of synthetic dyed wastewater using activated carbon from rice husk. **SN Applied Sciences**, v. 2, n. 12, p. 1–14, 2020.
- KOVÁCS, E. et al. Investigation into the mechanism of stimulation by low-concentration stressors in barley seedlings. **Journal of Plant Physiology**, v. 166, n. 1, p. 72–79, 2009.
- LAGERGREN, S. Zur Theorie der Sogenannten Adsorption Gelöster Stoffe, Kungliga Svenska Vetenskapsakademiens. **Handlingar**, v. 24, n. 4, p. 1–39, 1898.
- LI, C. et al. Facile synthesis of low-cost magnetic biosorbent from peach gum polysaccharide
-

- for selective and efficient removal of cationic dyes. **International Journal of Biological Macromolecules**, v. 107, p. 1871–1878, 2018.
- LI, H. et al. Modified carbon spheres as universal materials for adsorption of cationic harmful substances (paraquat and dyes) in water. **Microporous and Mesoporous Materials**, v. 297, n. June 2019, p. 110040, 2020.
- LI, W. C.; LAW, F. Y.; CHAN, Y. H. M. Biosorption studies on copper (II) and cadmium (II) using pretreated rice straw and rice husk. **Environmental Science and Pollution Research**, v. 24, n. 10, p. 8903–8915, 2017.
- LIMA, V. F.; MERÇON, F. Metais Pesados no Ensino de Química. **Química Nova Na Escola**, v. 33, n. 4, p. 199–205, 2011.
- LIU, R.; LIAN, B. Non-competitive and competitive adsorption of Cd²⁺, Ni²⁺, and Cu²⁺ by biogenic vaterite. **Science of the Total Environment**, v. 659, n. 1, p. 122–130, 2019.
- LIU, X. et al. Competitive adsorption of heavy metal ions from aqueous solutions onto activated carbon and agricultural waste materials. **Polish Journal of Environmental Studies**, v. 29, n. 1, p. 749–761, 2020.
- LONG, Y. et al. Packed bed column studies on lead(II) removal from industrial wastewater by modified *Agaricus bisporus*. **Bioresource Technology**, v. 152, p. 457–463, 2014.
- LOPES, P. S. N. et al. **Frutas Nativas da Região Centro-Oeste do Brasil**. 1^a edição ed. Planaltina - DF: [s.n.].
- LOULIDI, I. et al. Adsorption of Crystal Violet onto an Agricultural Waste Residue: Kinetics, Isotherm, Thermodynamics, and Mechanism of Adsorption. **Scientific World Journal**, v. 2020, 2020.
- LOW, M. J. D. Kinetics of chemisorption of gases on solids. **Chemical Reviews**, v. 60, n. 3, p. 267–312, 1960.
- MAALOUL, N. et al. Synthesis and characterization of eco-friendly cellulose beads for copper (II) removal from aqueous solutions. **Environmental Science and Pollution Research**, v. 27, n. 19, p. 23447–23463, 2020.
- MACIEL, T. C. M. et al. SUBSTRATO À BASE DE PEQUI (*Caryocar coriaceum*) NA PRODUÇÃO DE MUDAS DE TOMATE E PIMENTÃO. **Revista De Agricultura Neotropical**, v. 4, n. 2, p. 9–16, 2017.
- MADALA, S. et al. Equilibrium, kinetics and thermodynamics of Cadmium (II) biosorption on to composite chitosan biosorbent. **Arabian Journal of Chemistry**, v. 10, p. S1883–S1893, 2017.
- MAHDI, Z.; YU, Q. J.; EL HANANDEH, A. Competitive adsorption of heavy metal ions (Pb²⁺, Cu²⁺, and Ni²⁺) onto date seed biochar: batch and fixed bed experiments. **Separation**
-

- Science and Technology (Philadelphia)**, v. 54, n. 6, p. 888–901, 2019.
- MALIK, D. S.; JAIN, C. K.; YADAV, A. K. Heavy Metal Removal by Fixed-Bed Column – A Review. **ChemBioEng Rev**, v. 5, n. 3, p. 173–179, 2018.
- MENEZES, J. M. C. et al. Equilibrium, kinetics and thermodynamics of lead (II) adsorption in bioadsorbent composed by Caryocar coriaceum Wittm barks. **Chemosphere**, v. 261, 2020.
- MINISTÉRIO DA SAÚDE. Portaria MS N°2914/2011. **Dou 14/12/2011**, 2011.
- MOHAMMAD, S. G.; AHMED, S. M.; EL-SAYED, M. M. H. Removal of copper (II) ions by eco-friendly raw eggshells and nano-sized eggshells: a comparative study. **Chemical Engineering Communications**, v. 0, n. 0, p. 1–13, 2020.
- MONDAL, S.; MAJUMDER, S. K. **Honeycomb-like porous activated carbon for efficient copper (II) adsorption synthesized from natural source: Kinetic study and equilibrium isotherm analysis**. [s.l.] Elsevier Ltd, 2019. v. 7
- MORAIS, M. J. DE et al. CARACTERIZAÇÃO DA CASCA DE PEQUI (Caryocar Brasiliense Camb.) PARA SUA UTILIZAÇÃO COMO BIOMASSA. **III Congresso de Ensino, Pesquisa e Extensão da UEG**, v. 2, n. 1c, p. 17, 2016.
- MOREIRA, A. DA S. **BIOSSORÇÃO UTILIZANDO ALGA MARINHA (SARGASSUMsp.) APLICADA EM MEIO ORGÂNICO**. [s.l.] UFRN, 2007.
- MOREIRA, S. D. A. **ADSORÇÃO DE ÍONS METÁLICOS DE EFLUENTE AQUOSO USANDO BAGAÇO DO PEDÚNCULO DE CAJU: ESTUDO DE BATELADA E COLUNA DE LEITO FIXO**. [s.l.] UFC, 2008.
- MORENO-BENAVIDES, J. A.; PEÑA-SALAMANCA, E. J.; BENÍTEZ-CAMPO, N. Reducing Cr 6+ in electroplating wastewater with Bacillus cereus strain B 1. **Universitas Scientiarum**, v. 24, n. 1, p. 73–89, 2019.
- MORIN-CRINI, N. et al. Hemp-based adsorbents for sequestration of metals: a review. **Environmental Chemistry Letters**, 2018.
- NASCIMENTO, R. F. DO et al. **ADSORÇÃO: Aspectos teóricos e aplicações ambientais**. 2ª ed. Fortaleza - Ce: Imprensa Universitária UFC, 2020.
- NERIS, J. B. et al. Evaluation of adsorption processes of metal ions in multi-element aqueous systems by lignocellulosic adsorbents applying different isotherms: A critical review. **Chemical Engineering Journal**, v. 357, n. April 2018, p. 404–420, 2019.
- OLIVEIRA, M. E. B. DE et al. Aspectos Agronômicos e de Qualidade do Pequi. **Embrapa**, v. 113, p. 33, 2008.
- OLIVEIRA, S. A. DE. **ESTUDO DE ADSORÇÃO DE METAIS PESADOS EM ZEÓLITAS PARA FINS DE USO EM BARREIRA REATIVA**. [s.l.] UFRJ, 2011.
- OLIVEIRA, W. L. DE. **Boas Práticas de Manejo para p Extrativismo Sustentável do**
-

Pequi. Brasília: [s.n.].

PEREIRA, F. D. A. et al. ANÁLISE DA ATIVIDADE EXTRATIVISTA DO PEQUI (*Caryocar coriaceum* Wittm) EM COMUNIDADES DA CHAPADA DO ARARIPE NA REGIÃO DO CARIRI CEARENSE. **Conexões Ciência e Tecnologia**, v. 8, p. 59–66, 2014.

PEREIRA, J. E. S. **Biossorção de cobre em solução aquosa utilizando os pós das folhas do cajueiro (*Anacardium occidentale* L.) e da carnaúba (*Copernicia prunifera*).** [s.l.] UFRN, 2017.

PEREZ, I. C.; CORRÊA, R. G.; PIRES, J. L. *Gestão Ambiental - Galvanoplastia, orientações para o controle ambiental.* p. 48, 2014.

PINO, G. A. H. **Biossorção de Metais Pesados Utilizando Pó da Casca de Coco Verde (*Cocos nucifera*).** [s.l.] PUC - Rio de Janeiro, 2005.

PINO, G. H.; TOREM, M. L. ASPECTOS FUNDAMENTAIS DA BISSORÇÃO DE METAIS NÃO FERROSOS ESTUDO DE CASO. **Tecnologia em Metalurgia e Materiais**, 2011.

POLICARPO, L. M. **ESTUDO DE EQUILÍBRIO E CINÉTICA DA BISSORÇÃO DE COBRE (II) POR RHIZOPUS MICROSPORUS.** São Paulo - SP: USP, 2015.

RAGAVENDRAN, P. et al. FUNCTIONAL GROUP ANALYSIS OF VARIOUS EXTRACTS OF *Aerva lanata* (L.,) BY FTIR SPECTRUM. **Pharmacologyonline**, v. 364, p. 358–364, 2011.

RAMOS, K. M. C.; SOUZA, V. A. B. DE. Características físicas e químico-nutricionais de frutos de pequi (*Caryocar coriaceum* Wittm.) em populações naturais da região meio-norte do Brasil. **Revista Brasileira de Fruticultura**, v. 33, n. 2, p. 500–508, 2011.

RAMOS, R. et al. Produção de adsorventes a base de borra de café industrializado e folhas de *Corymbia citriodora* (eucalipto limão). **Dissertar Produção**, v. 1, n. 28–29, p. 17–22, 2017.

RASOULPOOR, K.; POURSATTAR MARJANI, A.; NOZAD, E. Competitive chemisorption and physisorption processes of a walnut shell based semi-IPN bio-composite adsorbent for lead ion removal from water: Equilibrium, Kinetic and Thermodynamic studies. **Environmental Technology and Innovation**, v. 20, p. 101133, 2020.

RAY, S.; MISHRA, A. K.; KALAMDHAD, A. S. Adsorption and Hydraulic Conductivity Studies on Bentonite in Presence of Copper Solution. **Journal of Hazardous, Toxic, and Radioactive Waste**, v. 25, n. 2, p. 06020007, 2021.

REGALBUTO, J. R.; ROBLES, JAIME O. **The Engineering of Pt / Carbon Catalyst Preparation For application on Proton Exchange Fuel Cell Membrane (PEFCM).** Chicago: [s.n.].

REICHENBERG, D. Properties of Ion-Exchange Resins in Relation to their Structure. III.

- Kinetics of Exchange. **Journal of the American Chemical Society**, v. 75, n. 3, p. 589–597, 1953.
- RENGEL, Z. Aluminium cycling in the soil-plant-animal-human continuum. **BioMetals**, v. 17, n. 6, p. 669–689, 2004.
- RODRIGUES, R. F. et al. HEAVY METALS SORPTION ON TREATED WOOD SAWDUST (In Portuguese). **Quimica Nova**, 2007.
- RUTHVEN, D. M. **Principles of adsorption and adsorption processes**. New York: John Wiley&Sons, 1984. v. 4
- ŠABANOVI, E. et al. Simultaneous adsorption of heavy metals from water by novel lemon-peel based biomaterial. **Polish Journal of Chemical Technology**, v. 22, n. 1, p. 46–53, 2020.
- ŠABANOVIĆ, E. et al. Pulverized Banana Peel as an Economical Sorbent for the Preconcentration of Metals. **Analytical Letters**, v. 48, n. 3, p. 442–452, 2015.
- SABELA, M. I. et al. Removal of copper (II) from wastewater using green vegetable waste derived activated carbon: An approach to equilibrium and kinetic study. **Arabian Journal of Chemistry**, v. 12, n. 8, p. 4331–4339, 2019.
- SAHA, U. K.; TANIGUCHI, S.; SAKURAI, K. Simultaneous Adsorption of Cadmium, Zinc, and Lead on Hydroxyaluminum- and Hydroxyaluminosilicate-Montmorillonite Complexes. **Soil Science Society of America Journal**, v. 66, n. 1, p. 117–128, 2002.
- SAHMOUNE, M. N. Evaluation of thermodynamic parameters for adsorption of heavy metals by green adsorbents. **Environmental Chemistry Letters**, v. 17, n. 2, p. 697–704, 2019.
- SALAME, I. I.; BANDOSZ, T. J. Surface chemistry of activated carbons: Combining the results of temperature-programmed desorption, Boehm, and potentiometric titrations. **Journal of Colloid and Interface Science**, v. 240, n. 1, p. 252–258, 2001.
- SALIHI, I. U. et al. Adsorption of copper using modified and unmodified sugarcane bagasse. **International Journal of Applied Engineering Research**, v. 10, n. 19, p. 40434–40438, 2015.
- SANTANA, A. H. **REMOÇÃO DE ÍONS COBRE E CHUMBO DE ÁGUAS RESIDUAIS UTILIZANDO VAGENS DE *Dimorphandra gardneriana* Tulasne (FAVA D'ANTA)**. [s.l.] URCA, 2018.
- SANTANA, A. H. et al. Copper and lead ion removal from wastewater using fava d'anta fodder (*Dimorphandra gardneriana* Tulasne). **Environmental Geochemistry and Health**, v. 0123456789, 2020.
- SANTHOSH, A.; DAWN, S. S. Synthesis of zinc chloride activated eco-friendly nano-adsorbent (activated carbon) from food waste for removal of pollutant from biodiesel wash
-

- water. **Water Science and Technology**, v. 00, n. 0, p. 1–12, 2021.
- SCHNEIDER, I. A. H. **Biossorção de Metais Pesados com a Biomassa de Macrófitos Aquáticos**. [s.l.] UFRGS, 1955.
- SCHNEIDER, R. M. et al. **BIOMASSAS PARA A ADSORÇÃO DO METAL CROMO III DE EFLUENTE**. Gramado - RS: [s.n.].
- ŠĆIBAN, M.; KLAŠNJA, M.; ŠKRBIĆ, B. Modified softwood sawdust as adsorbent of heavy metal ions from water. **Journal of Hazardous Materials**, v. 136, n. 2, p. 266–271, 2006.
- ŠĆIBAN, M.; KLAŠNJA, M.; ŠKRBIĆ, B. Adsorption of copper ions from water by modified agricultural by-products. **Desalination**, v. 229, n. 1–3, p. 170–180, 2008.
- SEBRAE. Lapidando a imagem da jóia brasileira. 2007.
- SEBRAE. Industria da Moda: Gemas e Joias. **Estudo de Mercado**, 2017.
- SEMACE. Resolução COEMA nº02, de 02 de fevereiro de 2017. p. 56–61, 2017.
- ŞENEL, G. U. Adsorption of Copper (II) from Aqueous Solution by Using Carbonized Peanut Hull: Determination of the Equilibrium, Kinetic and Thermodynamic Parameters. **Journal of Anatolian Environmental and Animal Sciences**, v. 90, n. 533, 2020.
- SENTHIL KUMAR, P. et al. Adsorption of metal ions onto the chemically modified agricultural waste. **Clean - Soil, Air, Water**, v. 40, n. 2, p. 188–197, 2012.
- SHAHAT, A. et al. Novel hierarchical composite adsorbent for selective lead(II) ions capturing from wastewater samples. **Chemical Engineering Journal**, v. 332, n. September 2017, p. 377–386, 2018.
- SHAMIM, S. Biosorption of Heavy Metals. **Biosorption**, 2018.
- SIQUEIRA, B. DOS S. et al. PECTINA EXTRAÍDA DE CASCA DE PEQUI E APLICAÇÃO EM GELEIA LIGHT DE MANGA. **revista brasileira fruticultura**, v. 34, n. 2, p. 560–567, 2012.
- SOETAREDJO, F. E. et al. Incorporation of selectivity factor in modeling binary component adsorption isotherms for heavy metals-biomass system. **Chemical Engineering Journal**, v. 219, p. 137–148, 2013.
- SOUSA NETO, V. O. et al. Use of coconut bagasse as alternative adsorbent for separation of copper (II) ions from aqueous solutions: Isotherms, kinetics, and thermodynamic studies. **BioResources**, v. 6, n. 3, p. 3376–3395, 2011.
- SOUZA, J. P. DE et al. PEQUI (*Caryocar coriaceum* Wittm) PRODUCT STABILITY UNDER FREEZING IN DIFFERENT TYPES OF PACKAGING (In Portuguese). **Revista Brasileira de Fruticultura**, v. 35, n. 4, p. 971–976, 2013.
- TANG, X. et al. Extremely efficient and rapidly adsorb methylene blue using porous
-

- adsorbent prepared from waste paper: Kinetics and equilibrium studies. **Journal of Hazardous Materials**, v. 402, n. July 2020, p. 123579, 2021.
- TARIBA LOVAKOVIĆ, B. Cadmium, arsenic, and lead: elements affecting male reproductive health. **Current Opinion in Toxicology**, v. 19, n. Figure 1, p. 7–14, 2020.
- TARLEY, C. R. T.; ARRUDA, M. A. Z. Biosorption of heavy metals using rice milling by-products. Characterisation and application for removal of metals from aqueous effluents. **Chemosphere**, v. 54, n. 7, p. 987–995, 2004.
- TAŞAR, Ş.; ÖZER, A. A thermodynamic and kinetic evaluation of the adsorption of pb(Ii) ions using peanut (arachis hypogaea) shell-based biochar from aqueous media. **Polish Journal of Environmental Studies**, v. 29, n. 1, p. 293–305, 2020.
- TAVANA, M.; PAHLAVANZADEH, H.; ZAREI, M. J. The novel usage of dead biomass of green algae of *Schizomeris leibleinii* for biosorption of copper(II) from aqueous solutions: Equilibrium, kinetics and thermodynamics. **Journal of Environmental Chemical Engineering**, v. 8, n. 5, p. 104272, 2020.
- TEIXEIRA, R. N. P. **REMOÇÃO DE Cu(II), Ni(II), Cd(II) E Pb(II) DE EFLUENTES DE INDÚSTRIAS DE GALVANOPLASTIA USANDO O SISTEMA HÍBRIDO ADSORÇÃO- ELETRO-FLOTAÇÃO-COAGULAÇÃO**. [s.l.] UFC, 2015.
- TOUIHRI, M. et al. Single and simultaneous adsorption of Cr(VI) and Cu (II) on a novel Fe₃O₄/pine cones gel beads nanocomposite: Experiments, characterization and isotherms modeling. **Chemical Engineering Journal**, v. 416, n. February, 2021.
- USLU, G.; TANYOL, M. Equilibrium and thermodynamic parameters of single and binary mixture biosorption of lead (II) and copper (II) ions onto *Pseudomonas putida*: Effect of temperature. **Journal of Hazardous Materials**, v. 135, n. 1–3, p. 87–93, 2006.
- VERÍSSIMO, L. S.; CAVALCANTE, I. N. AS ÁGUAS SUBTERRÂNEAS DO CRAJUBAR, REGIÃO DO CARIRI - ESTADO DO CEARÁ - BRASIL. **1st Joint World Congress on GroundWaterr**, n. 85, p. 1–17, 2000.
- WANG, J.; GUO, X. Adsorption kinetic models: Physical meanings, applications, and solving methods. **Journal of Hazardous Materials**, v. 390, n. November 2019, p. 122156, 2020.
- WEBER, W. J.; MORRIS, J. C. Kinetics of adsorption on carbon from solution. **Journal of the Sanitary Engineering Division**, v. 89, p. 31–60, 1963.
- WONG, K. K. et al. Removal of Cu and Pb from electroplating wastewater using tartaric acid modified rice husk. **Process Biochemistry**, v. 39, n. 4, p. 437–445, 2003.
- YADAV, V.; BHAGAT, M. Isotherm , kinetics and thermodynamic parameters study of arsenic (III) and copper (II) adsorption onto *Limonia acidissima* shell carbon. **Desalination and Water Treatment**, v. 184, n. April, p. 214–224, 2020.
-

YADAV, V.; TIWARI, D. P.; BHAGAT, M. Isotherm, kinetic and thermodynamic parameters study of arsenic (III) and copper (II) adsorption onto *Limonia acidissima* shell carbon. **Desalination and Water Treatment**, v. 184, n. April, p. 214–224, 2020.

ZHU, Y.; HU, J.; WANG, J. Competitive adsorption of Pb(II), Cu(II) and Zn(II) onto xanthate-modified magnetic chitosan. **Journal of Hazardous Materials**, v. 221–222, p. 155–161, 2012.

ZOU, W.; BAI, H.; GAO, S. Competitive adsorption of neutral red and Cu²⁺ onto pyrolytic char: Isotherm and kinetic study. **Journal of Chemical and Engineering Data**, v. 57, n. 10, p. 2792–2801, 2012.

**CAPÍTULO III: TERCEIRO ARTIGO TÉCNICO SUBMETIDO EM PERIÓDICO
CIENTÍFICO**

**COMPETITIVE BIOADSORPTION OF Pb^{+2} AND Cu^{+2} IONS BY *CARYOCAR
CORIACEUM* WITTM BARKS**

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ABSTRACT

The deterioration of the environment and damage to the health of living beings are characteristics of the inadequate disposal of waste containing toxic metals such as copper and lead ions. Among several techniques, bioadsorption stands out for being a cheap and easy-to-operate technique for removing contaminants, such as toxic metals, in aqueous environments. The adsorption of chemical species in multielement systems is characterized by its competition for active sites present on the bioadsorbent surface. This work aimed to evaluate the use of discarded *Caryocar Coriaceum* WITTM bark residues as a possible bioadsorbent for the removal of Pb^{+2} and Cu^{+2} ions in mono and multielement systems, presented in aqueous solutions. Characterization techniques like SEM-EDS, XRD, FTIR and pH_{PZC} were used to study the bioadsorbent. The results showed that all the systems follow the pseudo second order model, the diffusing process was chemisorption associated with ions change. Langmuir model presented a better fit than Freundlich model. The maximum adsorptive capacity ($mg.g^{-1}$) obtained was 47.6 for Pb^{+2} and 20.4 for Cu^{+2} . It was found that there was an inhibitory effect between Cu^{+2} and Pb^{+2} , which resulted in a reduction of q_{max} values by approximately 37%, for Cu^{+2} , and 55%, for Pb^{+2} . As a conclusion, it was found that the bark of *Caryocar Coriaceum* Wittm could be used as a bioadsorbent for solutions containing dissolved Pb^{+2} and Cu^{+2} , for both mono and multielemental systems.

Keywords: Competitive Bioadsorption; Toxic Metals; Wastewater treatment; Agricultural Waste Reuse.

HIGHLIGHTS:

- *Caryocar Coriaceum* WITTM bark was studied as an adsorbent for Cu^{+2} and Pb^{+2} metals ions in aqueous solutions, in mono and multielement adsorption systems.
 - *Caryocar Coriaceum* WITTM bark was characterized before and after being used as an adsorbent.
 - *Caryocar Coriaceum* WITTM bark could be used as an adsorbent to remove Cu^{+2} and Pb^{+2} metals ions in aqueous solutions, enabling the noble use of these wastes before being discarded.
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1 - INTRODUCTION

Toxic metals have great potential for impacting the environment due to their toxicity and non-biodegradability. When introduced into aquatic environments, toxic metals can still be bioaccumulated in the chain of living beings, becoming a global environmental problem (DENG et al., 2017; SAHMOUNE, 2019).

Some metallic ions, in trace amounts, such as Copper (Cu^{+2}) and Nickel are essential nutrients for the human body, but in high concentrations they can cause various health problems such as kidney and liver failure and gastrointestinal disorders. The Lead (Pb^{+2}), in turn, it has no essential function for human beings, in addition to having several undesirable effects, such as damage to the kidneys and disturbance of the nervous system, in plants, it can damage the lipid membrane and chlorophyll, influencing the photosynthetic process (FUTALAN et al., 2011; JUMINA et al., 2019).

For the treatment of water contaminated with toxic metals, techniques such as precipitation, flocculation, membrane separation, adsorption, or even biological methods can be applied (LIU et al., 2020), however, disadvantages such as: inefficiency, high costs, not being easily operated or not being selective, are characteristics of these processes (ESCUADERO-OÑATE; VILLAESCUSA, 2018)

Among the processes mentioned, adsorption, more specifically as biosorption, stands out for the removal of toxic metals from liquid effluents, since it uses natural and biological materials, with characteristics favorable to the sequestration of contaminants present in solutions and available in abundance in the environment (AL-QODAH; YAHYA; AL-SHANNAG, 2017), besides consisting of a simple, easy to operate and profitable process (BURAKOV et al., 2018).

Several types of lignocellulosic bioadsorbers have been tested for the removal of toxic metals, biochar from oil palm (*Elaeis guineensis*) fibers (IGHALO et al., 2020b), coconut shell (SOUSA NETO et al., 2011), sugar beet shreds (BLAGOJEV et al., 2019), banana peel

(HOSSAIN et al., 2012), chitosan-pyromellitic dianhydride modified biochar (DENG et al., 2017), sugarcane bagasse (GIRALDO; MORENO-PIRAJÁN, 2008), Sesame Husk (EL-ARABY et al., 2017), waste paper (TANG et al., 2021), among others.

Popularly known as pequi, the *Caryocar Coriaceum* Wittm is a fruit found in the Brazilian cerrado biome, with large production in the Chapada do Araripe region, between the states of Ceará, Pernambuco and Piauí, and playing an important socioeconomic role for this region, being easily found for sale in markets and small roadside stalls. Of the fruit, often only the seed is used, which corresponds to approximately 6% of its weight, while the skin corresponds to 84% (MORAIS et al., 2016). As bark is no longer useful for sale, it is easily found discarded in markets, generating large volumes of waste to be disposed in dumps or landfills.

Therefore, this work aimed to study the feasibility of applying *Caryocar Coriaceum* Wittm bark (CCB) residues, as a possible bioadsorbent in a mono and multielemental adsorption systems, containing Cu^{+2} and Pb^{+2} ions, presenting a characterization study using techniques like SEM - EDS, FTIR, XRD and pH_{pzc} , and detailed Kinect, diffusion and equilibrium studies.

2 - MATERIALS AND METHODS

2.1 - Absorbent Collection and Preparation



Figure 1: CCB adsorbent preparation steps. (a) Collection and washing of CCB waste. (b) Peeling. (c) Natural drying. (d) Crushing. (e) Granulometric adjustment (32mesh). (f) Washing the crushed material. (g) Oven drying and stock for use in analysis.

CCB residues were collected in the public market in the city of Crato, in the state of Ceará, located in the northeast of Brazil. The preparation of the CCB adsorbent was carried out on the premises of the Analytical Center of the Federal University of Cariri - UFCA, according to the methodology described by (MENEZES et al., 2020), which included steps of peeling, to obtain the fraction of the exocarp of the residues, a first washing step, followed by solar drying (8h for 3 days, totaling 24h), crushing and granulometric adjustment (32mesh), finally, a second stage of washing and drying in an oven. Figure 1 presents the steps of preparation of the CCB adsorbent.

2.2 - Material characterization

The morphological characteristics of the adsorbent was observed from the analysis of the micrographs, obtained using a scanning electron microscope (SEM), (Quanta 450 FEG – Fei) at the dependences of the Analytical Center at the Federal University of Ceará (UFC). The chemical compositions of adsorbents, before and after the adsorption tests, was determined

using an Energy-dispersive X-ray spectroscopy (EDS) detector equipped at the SEM equipment.

An XPert Pro MPD - Panalytical diffractometer was used to obtain the X-Ray Diffraction (XRD) patterns, using cobalt $K\alpha$ radiation, 40 kV voltage and 40 mA electrical current, initial and final angles of 5° e 70° (2θ). The diffractometer is located on the premises of the x-ray laboratory at the Federal University of Ceará (UFC).

A spectrum two model spectrophotometer from the brand PerkinElmer, was used to investigate the functional groups present on the surface of the adsorbents, before and after the adsorptive process. To obtain the FT-IR spectra, the spectrophotometer was used in the transmittance mode and KBr pellets containing the samples were prepared and 48 scans were performed with a resolution of 4cm^{-1} , recorded in the spectral range of 4000 to 450 cm^{-1} . The spectrophotometer is located on the premises of the materials characterization laboratory at the UFCA

To determine the pH at Zero Charge Point (pH_{PZC}), the methodology described by Regalbuto and Robles (2004) was used, and consist to plot a graph between the pH value before and after the adsorbent is subjected to contact for 2h with solutions with an initial pH between 1 and 11. The mean of the initial pH that presented a strong buffering effect on the final pH value was attributed as the pH_{PZC} .

2.3 - Batch Adsorption Experiments

The adsorption tests were carried out at the central analytical laboratory of UFCA, Juazeiro do Norte, Ceará, Brazil. For this, three stock solutions were prepared, Copper (Cu^{+2}), Lead (Pb^{+2}) and one containing a mixture of the two metals (Cu^{+2} and Pb^{+2}). Stock solutions were prepared using salts of Copper Nitrate ($\text{Cu}(\text{NO}_3)_2$) and Lead Nitrate ($\text{Pb}(\text{NO}_3)_2$) from the Dynamic brand.

For the kinetic tests, the aforementioned solutions were used, which had initial metal concentrations of approximately 100 mg/L, and were submitted to 12 different contact times, within a time interval of 1 minute to 6 hours. The experiment was carried out at room temperature (22°C) and in duplicate. Approximately 50 mg of the CCB adsorbent material was weighed in a 150 mL Erlenmeyer flask, for each contact time, and subsequently, 10 mL of the desired metallic solution was added, buffered at pH 5.5 (acetate buffer). The adsorbents with the Cu^{+2} and Pb^{+2} metallic ion solutions were stirred, for the desired times, with a rotation of 150 RPM, on a Nova 109 Ethics shaking table, model 109, and after that, the samples were filtered and analyzed by flame atomic absorption spectroscopy (FAAS), using a Varian spectrometer, model SpectrAA 50B, at the Analytical Center laboratory at UFCA.

The isotherm tests were performed in a similar way to the kinetics, but the initial concentrations of the metallic solutions were varied (20 - 500 mg/L) and the contact time was fixed at 120 minutes.

All the results of adsorption of the metals in this study were analyzed in terms of adsorptive capacity (q_e), determined through the equation 1.

$$q_e = \frac{(C_i - C_e) \times V}{m_{ads}} \quad (1)$$

Where C_i e C_e correspond to initial and equilibrium concentration of metal ions (mg.L^{-1}), respectively, V represents the volume of the solution (L), and m_{ads} refers to the mass of the adsorbent in grams (g).

The experimental results were applied in well-established and widespread adsorption kinetics, diffusions and isotherms models. The models used in this study are shown in table 1.

Table 3: Adsorption models used in this Study

	Models	Linearized form of equations	Parameters
Kinetics	Pseudo – First Order	$\ln(q_e - q_t) = \ln(q_e) - K_1 t$	q_e e q_t : adsorbed amounts per gram of adsorbent at equilibrium and at t time, respectively (mg.g ⁻¹);
	Pseudo – Second Order	$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t$	T: Time (min);
	Elovich	$q = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t)$	q_{max} : Maximum adsorption capacity of the adsorbent (mg.g ⁻¹);
Diffusion	Weber - Moris	$q_t = K_d * t^{0.5} + C$	α : initial adsorption rate (mg.g ⁻¹ .min ⁻¹);
	Boyd	$F = \frac{q_t}{q_e}$	β : desorption constant (mg.g ⁻¹);
		$F > 0.85: Bt = -0.4977 - \ln(1 - F)$	K_d : Intraparticle diffusion coefficient (mg.g ⁻¹ .min ^{-0.5});
		$F < 0.85: Bt = \left(\sqrt{\pi} - \sqrt{\left(\pi - \left(\frac{\pi^2 * F}{3} \right) \right)} \right)^2$	C: Constant related to diffusion resistance (mg.g ⁻¹);
Isotherms	Langmuir Isotherm	$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{q_{max} * K_L}$	K_L : Equilibrium constant (L.g ⁻¹);
	Freundlich Isotherm	$\ln(q_e) = \ln(K_F) + \frac{1}{n} \ln(C_e)$	k_1 : Pseudo-first order reaction rate constant (min ⁻¹);
			k_2 : Pseudo-second order reaction rate constant (g.mg ⁻¹ .min ⁻¹);
			K_F : Adsorption capacity constant ((mg.g ⁻¹)(L.mg ⁻¹) ^{1/n});
			B: Boyd Constant
			$1/n$: Adsorption Intensity Constant.

Source: (GUGUSHE et al., 2021; IRAVANI MOHAMMADABADI; JAVANBAKHT, 2021; LIU; LIAN, 2019; TAŞAR; ÖZER, 2020)

Finally, CCB samples before and after the adsorption experiments were collected, to be analyzed by FTIR and SEM - EDS, in order to investigate changes in the morphology and composition of the surface of the CCB adsorbent.

3 - RESULTS AND DISCUSSION

3.1 - Material Characterization:

The morphological analysis of the adsorbent material (Figure 2), performed through the SEM-EDS technique, indicated that the material may have great potential for the technique of

adsorption of toxic metals, since it presents an amorphous and heterogeneous structure, with rough textured characteristics, many cavities or pores on its surface, which according to Touihri et al. (2021), it is important because surface roughness plays a fundamental role in the binding of metal ions, since it increases the contact area of the adsorbent with the adsorbate, facilitating metal sorption.

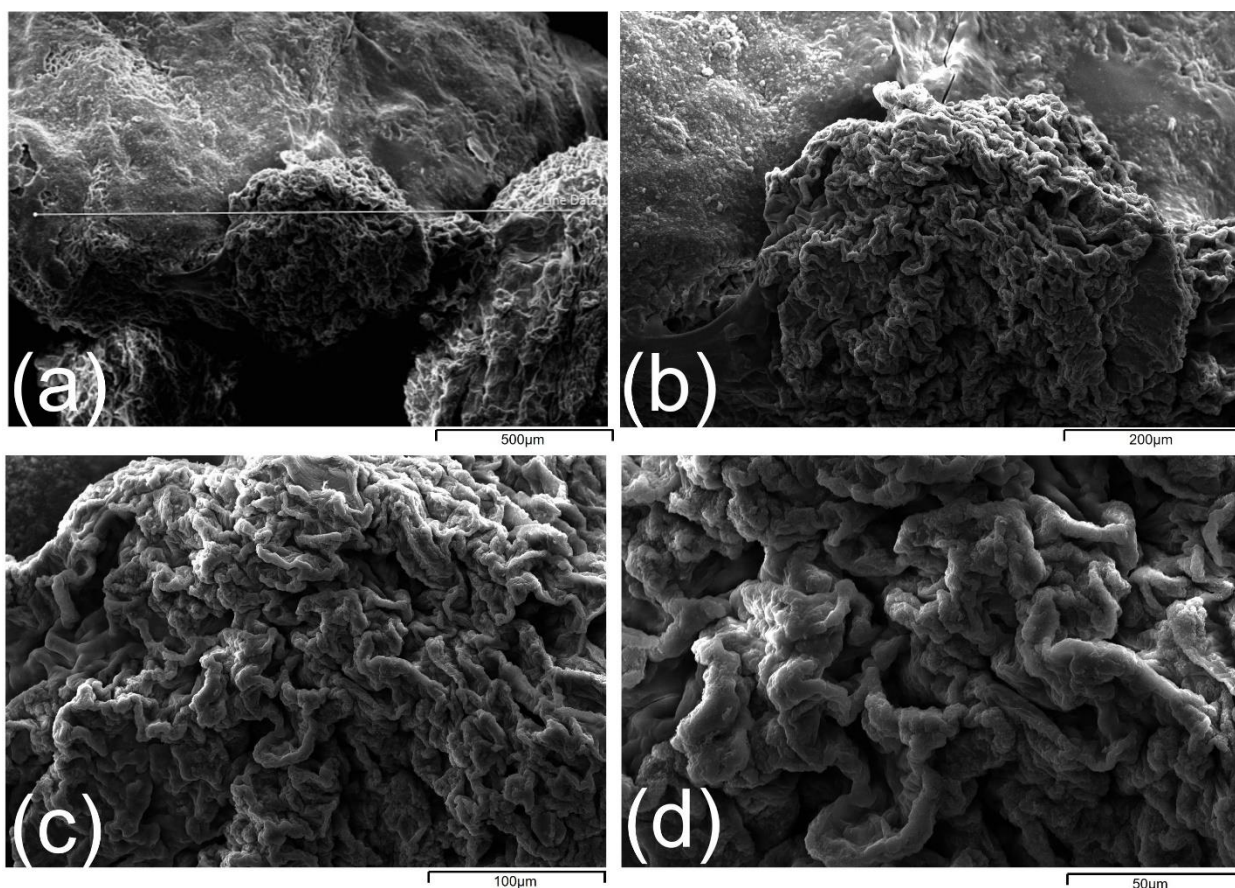


Figure 2: SEM images of CCB before adsorption of metal ions at (a) 160x magnification (b) 600x magnification (c) 1200x magnification (d) 2500x magnification.

The XRD results (figure 3a) showed a high intensity peak with increased broadening without any secondary peaks, obtained between 20° - 30° , which corresponds to the (002) plane and indicates the existence of highly distorted carbon atoms, characterizing an amorphous phase (FALAKI; BASHIRI, 2021; SANTHOSH; DAWN, 2021).

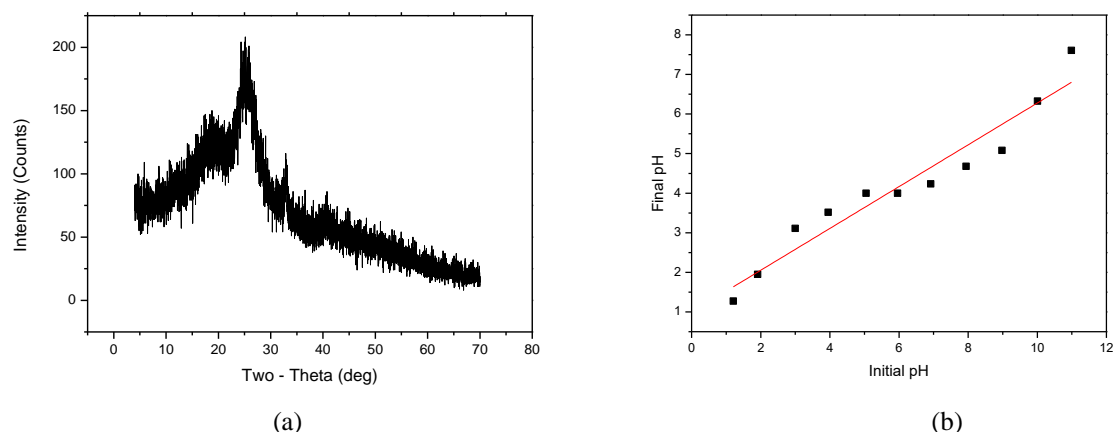


Figure 3: Characterization of CCB adsorbent before bioadsorption tests. (a) XRD pattern. (b) pH_{PZC} curve.

According to Azoulay et al. (2020) the pH value for which the net surface charge is null corresponds to the pH of the zero charge point. Thus, for solutions with pH values below the pH_{pzc} value, the adsorbent will present a positive overall surface charge, favoring the adsorption of species with negative charge, while for pH values higher than pH_{pzc} , species with positive charge will be favored.

Through the pH_{PZC} curve (Figure 3b), it was observed that the pH_{pzc} value for the CCB adsorbent was 4.1, which corresponded to the average value of the pH range where there was a strong buffering effect. Thus, in order to favor the adsorption process of positively charged species, such as toxic metals, the pH value of 5.5 was adopted for the tests in this study, which corresponds to a value higher than the pH_{pzc} .

3.2 - Post adsorption results:

3.2.1 - Energy-dispersive X-ray spectroscopy (EDS)

With the results of the characterization of the adsorbent CCB by the SEM-EDS technique (Figure 4a), it could be seen that the adsorbent material before the adsorptive process had mainly in its composition the elements C and O (indicated by the two largest peaks in the graph). After the adsorptive experiments, it was found that there was a considerable increase in

the concentration of Cu^{+2} and Pb^{+2} elements for the mono and multielemental systems, confirming the occurrence of adsorption of toxic metals on the surface of the adsorbent, even after being washed.

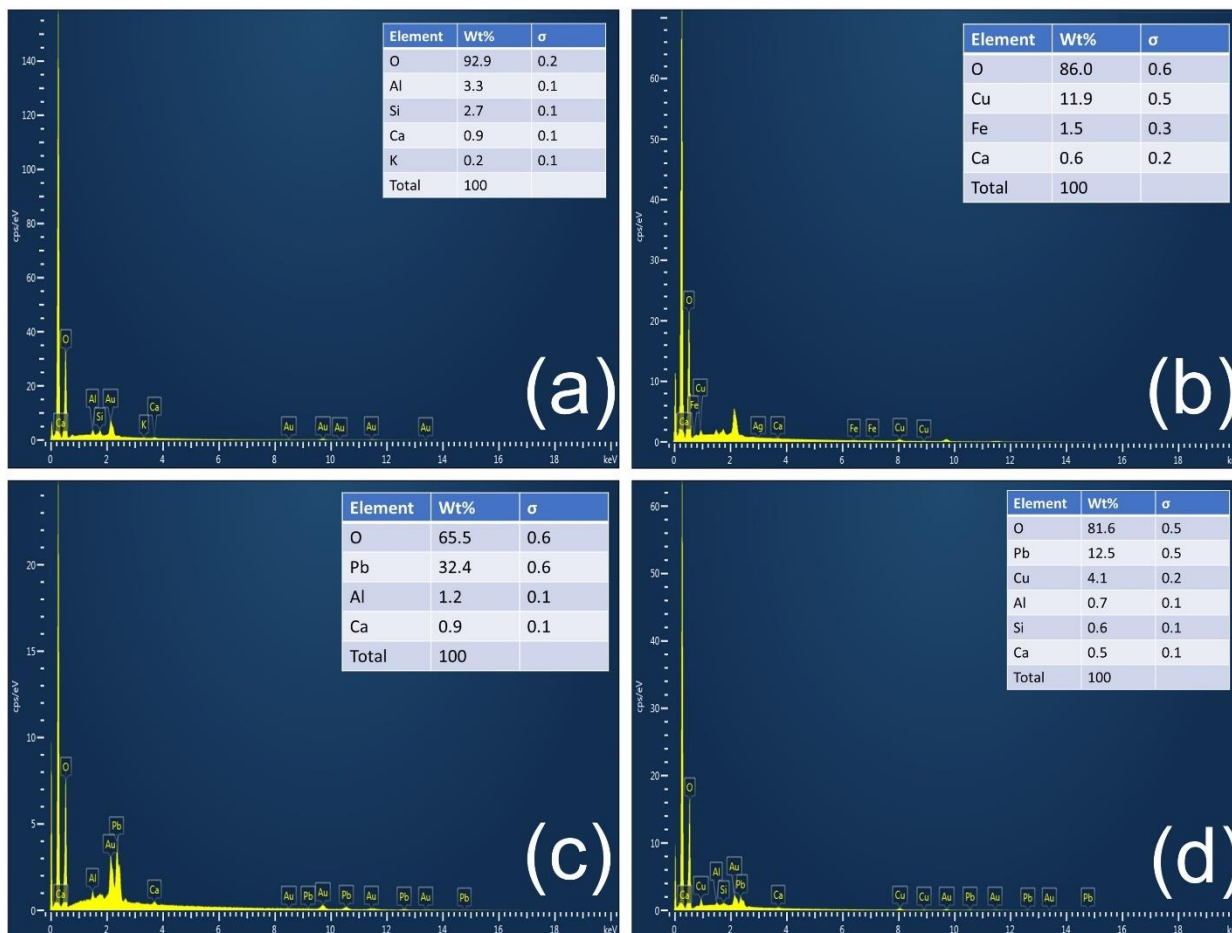


Figure 4: EDS characterization of CCB (a) before adsorption; (b) after Cu^{+2} nonelement adsorption; (c) after Pb^{+2} monoelement Adsorption; (d) after Cu^{+2} and Pb^{+2} multielement adsorption.

Concentration values of 11.9% of Cu^{+2} (figure 4b) and 32.4% of Pb^{+2} (figure 4c) were reached in the composition of CCB for the monoelemental systems and 4.1% of Cu and 12.5% of Pb, for the multielemental systems, configuring a percentage reduction of 65.5% for Cu^{+2} and 61.4% for Pb^{+2} comparing the mono and multielemental systems. Thus, it could be observed that when the adsorption of toxic metals occurs simultaneously, the percentages present in the composition of the adsorbent are smaller, it can be justified due to the competition between those metal ions for the active sites available on the surface of the adsorbent.

It was also found that there was greater adsorption affinity between CCB and Pb^{+2} , than the CCB and Cu^{+2} , for both mono and multielemental systems. This may occur because Pb^{+2} has characteristics such as heavy metal ionic size, weight, and charge more favorable than Cu^{+2} , according to Liu et al. (2020).

3.2.2 - Infrared Spectroscopy Analysis

Through the infrared spectrum (Figure 5), it can be seen that the CCB adsorbent in its raw form, presents the functional groups commonly found in lignocellulosic materials, such as absorption bands between $3600 - 3000$, $1750 - 1500$, and $1125 - 900 \text{ cm}^{-1}$, indicative of stretching of O-H, N-H and C=O (carboxylic acids, esters or carboxylate ions) and C-O stretching (esters, ether or alcohols) (NERIS et al., 2019). It was also possible to verify the presence of an angular deformation of CH_2 of groups CH_3 (1337 cm^{-1}) and a peak at 757 cm^{-1} , indicative of polysaccharides (AMORIM et al., 2016; BREDA et al., 2017; RAGAVENDRAN et al., 2011).

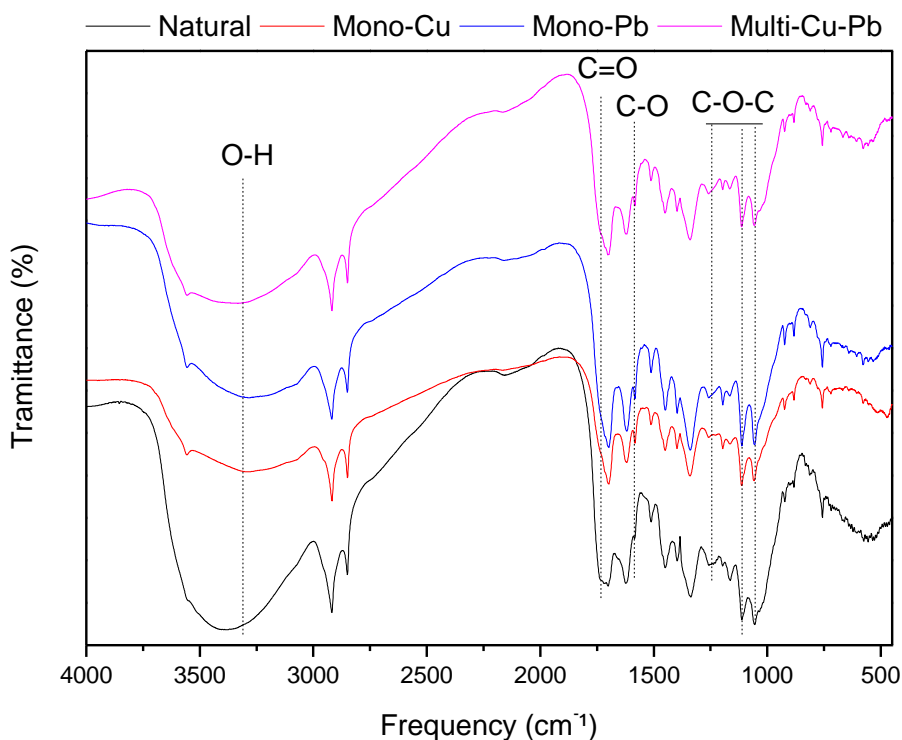


Figure 5: Comparison between the IR spectra of the adsorbent before and after adsorption.

When comparing the infrared spectra before and after the adsorptive process, it is noticed the occurrence of minimization of the intensity of the broadband (OH stretching vibration) with a frequency between $3500 - 3000 \text{ cm}^{-1}$, both in the mono and multielemental process, as well as its displacement from 3390 cm^{-1} to 3284 cm^{-1} (Cu^{+2} monoelemental), 3277 cm^{-1} (Pb^{+2} monoelemental) and 3366 cm^{-1} (Cu^{+2} and Pb^{+2} multielemental). There was also a minimization of peak intensity related to the carbonyl group and glycoside grouping, centered at 1700 and 1164 cm^{-1} , respectively, after adsorption of metallic ions for both mono and multielemental systems.

A peak intensification, in 1580 cm^{-1} , was observed after the interaction of metallic ions with the CCB adsorbent, such intensification can be attributed to the interaction of metal ions with other functional groups, facilitating the bending vibration of amine group (KAMARI et al., 2014).

Such changes in FTIR spectra can be justified by the coordination of metal ions to the surface functional groups of the CCB adsorbent, minimizing (inactivating clusters), displacing peaks (hindering molecular vibrations), or even intensifying signals, by facilitating the vibration of links of some functional groups.

3.2.3 - Adsorption Kinetics

As can be seen in figures 6 (a - c), it was found that the adsorption capacity (q_e) presents a fast initial growth behavior, starting to reduce its speed until reaching adsorption equilibrium in approximately 120 minutes, for the mono elemental ($q_{e\text{Cu}}$: 16.4 mg/g ; $q_{e\text{Pb}}$: 31.3 mg/g) and multielemental ($q_{e\text{Cu}}$: 12.9 mg/g ; $q_{e\text{Pb}}$: 10.4 mg/g) systems, with 100 mg/L of initial concentration. After 30 minutes, metal ion removal efficiency was higher than 70% in mono

and multi-elementary systems, presenting at equilibrium a removal of approximately 85% (Cu^{+2}) and 90% (Pb^{+2}) for both mono and multielemental systems.

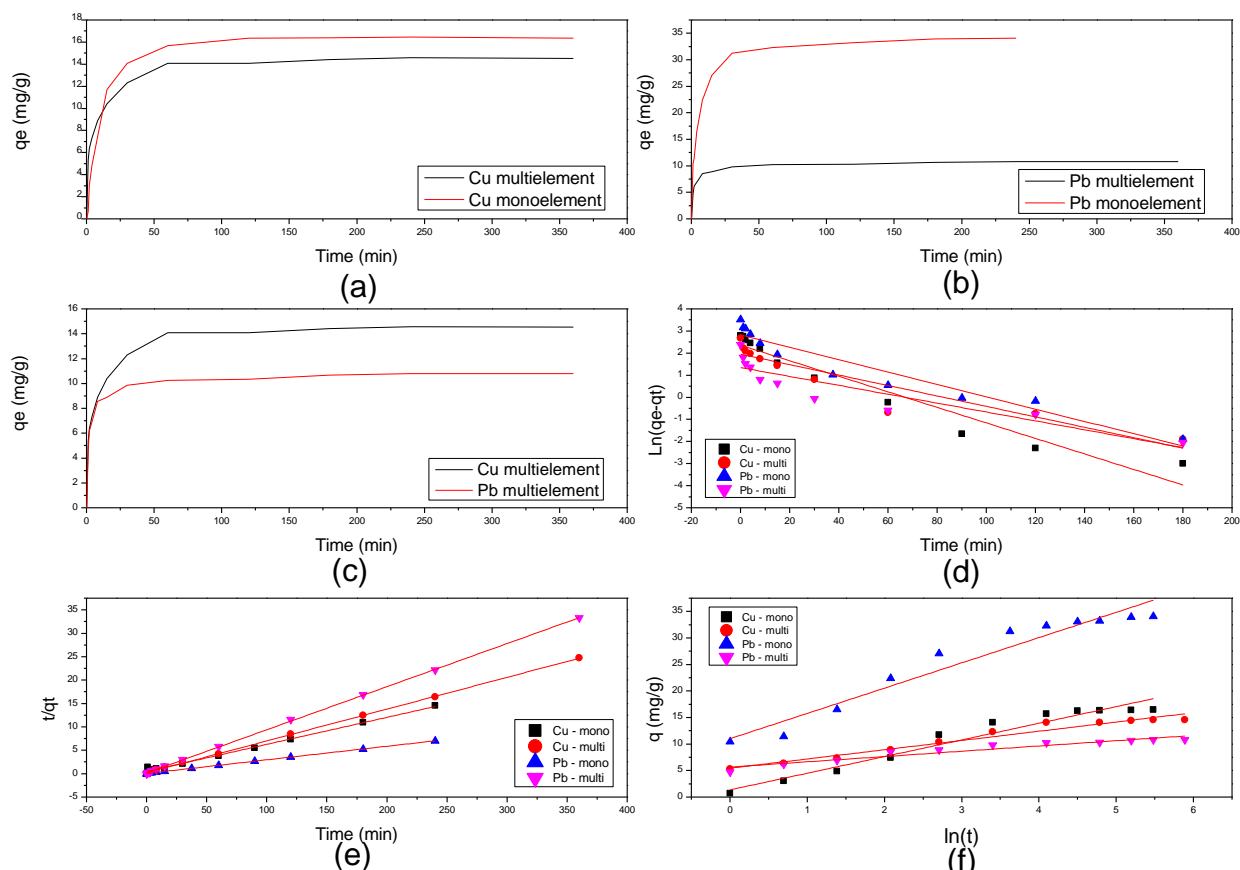


Figure 6: Adsorptions Kinetics (a) Cu^{+2} mono and multielements. (b) Pb^{+2} mono and multielements (c) Cu^{+2} and Pb^{+2} multielements. (d) Experimental data applied to the pseudo-first order model. (e) Experimental data applied to the pseudo-second order model. (f) Experimental data applied to the Elovich model.

Such behavior can be attributed to the abundant availability of active sites in the first stage of the adsorptive process, being later limited in the final stage of the experiment (LI et al., 2018).

In general, it was observed that there was a reduction in the adsorptive capacity for the two metal ions, when the experiment was carried out in a multielement system, this occurs due to competition between them for the active sites available on the surface of the adsorbent, obtaining percentages of reduction of q_e of approximately 14% and 69% for Cu^{+2} and Pb^{+2} ions, respectively.

The high reduction in the adsorptive capacity for Pb^{+2} ions, compared to Cu^{+2} ions, can be attributed to the fast adsorption kinetics presented by the Cu^{+2} ions, which has a smaller atomic radius (Cu - 0.73 Å; Pb - 1.19 Å), providing high hydration capacity and mobility in the adsorbent (JUMINA et al., 2019; NERIS et al., 2019).

Figures 6 (d-e) presents the experimental data applied to the pseudo first and second order linear models, while the kinetic parameters obtained by these models are shown in table 2.

Table 2: Kinetics parameters obtained from the pseudo-first and second models

Metal	system	q _e exp	Pseudo-first Order			Pseudo-second Order			Elovich		
			K ₁	q _e	R ²	K ₂	q _e	R ²	α	β	R ²
Cu^{+2}	Mono	16.4	-3.51×10^{-2}	10.6	0.9383	3.29×10^{-4}	17.3	0.9950	4.9	0.32	0.9509
	Multi	12.9	-2.36×10^{-2}	7.1	0.8802	4.56×10^{-4}	14.7	0.9998	40.41	0.57	0.9596
Pb^{+2}	Mono	31.3	-2.79×10^{-2}	16.8	0.9257	8.29×10^{-5}	34.5	0.9997	48.47	0.21	0.9509
	Multi	10.4	-2.01×10^{-2}	3.9	0.8235	8.36×10^{-4}	10.9	0.9998	303.56	1.00	0.9217

Units: q_e (mg/g); K₁(min⁻¹); K₂ (g/mg.min); α (mg/g.min); β (g/mg).

The experimental data fitted better in the pseudo second order model (R² greater than 0.9990), compared to the pseudo first order (R² between 0.82 and 0.93), which resulted in experimental values of q_e close to the theoretical (table 2) for the pseudo second order, for both mono and multielemental systems. It is also highlighted that there was a reduction in the value of the adsorption constant K₂, from monoelemental to multielemental systems, indicating that there was a disadvantage in the adsorption rate for the ions metallic, making the process slower.

It is also verified that the experimental data, for the mono and multielemental systems, presented a good fit to the Elovich model, presenting R² varying between 0.92 and 0.96.

Thus, it is verified that the adsorptive process follows a pseudo second order kinetic model and because it presents a good fit to the Elovich model, it is indicated that there is a multilayer adsorption, with a complex rate-controlling mechanism, involving ion exchange systems and chemisorption (IGHALO et al., 2020b; MADALA et al., 2017; ZOU; BAI; GAO, 2012).

3.2.4 - Diffusion models:

The Weber Morris model was used in order to understand the influence of resistance to mass transfer between the adsorbates and the adsorbent. Three steps were observed from figure 7 (a-b), noting that more than one adsorptive process occurs in the experiment. In the first step, the external surface of the adsorbents is the target for the adsorption of the ions, while in the second step, the adsorbate adsorption starts in the adsorbent pores, finally, in the third step, the end of the adsorptive process is characterized., where there is equilibrium (MAALLOUL et al., 2020).

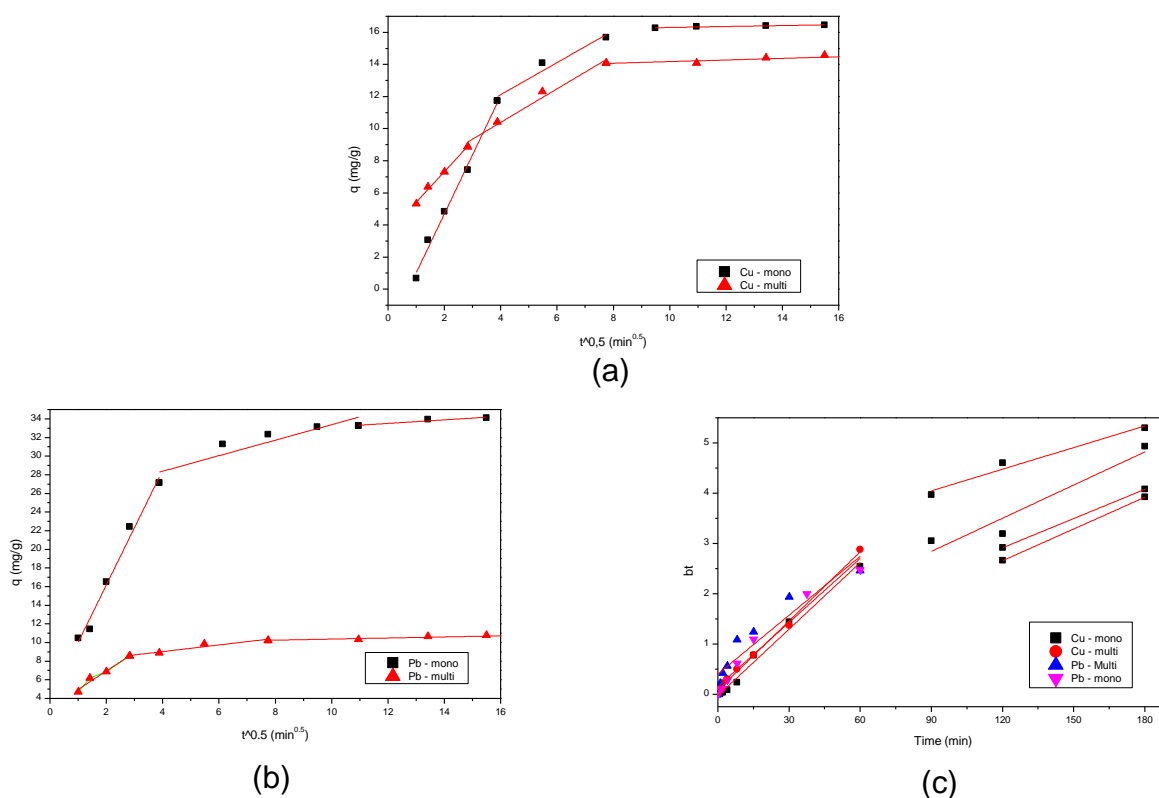


Figure 7: (a) Cu^{+2} mono and multielement applied to the Weber-Morris diffusion Model. (b) Pb^{+2} mono and multielement applied to the Weber-Morris diffusion Model. (c) Cu^{+2} and Pb^{+2} mono and multielement applied to the Boyd diffusion Model.

The intraparticle rate constant k and intercept (C), for each step of the process are tabulated in Table 3. As can be seen, the values of C , for the mono and multielemental systems,

did not correspond to zero, therefore, the linear regression does not cross the origin (0.0), indicating that intraparticle diffusion is not the only limiting step of the process (GUGUSHE et al., 2021). There is still an increase in C values during the steps for all systems, such behavior is attributed to the increase in film thickness on the adsorbent.

The constant K presents high values during the first step of the adsorptive process, starting to gradually reduce until the final step, which indicates that there is a strong adsorptive effect, and its efficiency is reduced during the steps. From the competitive point of view between Cu^{+2} and Pb^{+2} ions, it was found that the values of K were higher for Cu^{+2} ions in the first two steps of the process, evidencing an ease of diffusion of this species against Pb^{+2} ions, only in the last stage, there was an equalization of rates.

Figure 7(c) shows the application of experimental data to Boyd's model, where a multilinearity behavior occurred. Therefore, it was necessary to use only the first step of the linear region (data up to 60 minutes) for the determination of model parameters. The data obtained with this analysis are presented in table 3.

Table 3: Parameters obtained by the Weber Morris and Boyd models.

Parameters		Cu^{+2}	Cu^{+2}	Pb^{+}	Pb^{+2}	
		monoelemental	multielemental	monoelemental	multielemental	
Weber Morris model	Step I	K	3.676	1.9066	6.1579	1.9767
		C	-2.6182	3.5329	3.9222	3.0233
		R ²	0.99	0.9948	0.9838	0.9709
	Step II	K	0.9987	1.0446	0.8323	0.3569
		C	8.1419	6.2315	25.078	7.6198
		R ²	0.9562	0.9805	0.8355	0.9402
	Step III	K	0.0296	0.0501	0.1903	0.0572
		C	16.02	13.688	31.248	9.8188
		R ²	0.9402	0.7992	0.9079	0.8634
Boyd Model	B (slope)	0.0441	0.0459	0.0536	0.0601	
	Intercept	-0.0234	0.0844	0.0831	0.2665	
	D	0.0099	0.0103	0.0121	0.0135	
	R ²	0.9901	0.9964	0.9754	0.9181	

Units: K ($\text{mg/g}\cdot\text{min}^{1/2}$); D (cm^2/min).

As can be seen, with the linear regression analysis, intercept values different from zero were obtained, thus not passing through the origin of the graph (0.0). Such behavior indicates that the diffusion of the film or a combination with other adsorptive mechanisms control the adsorptive process (GUGUSHE et al., 2021; WANG; GUO, 2020), reinforcing the data presented by the Weber Morris model.

3.2.5 - Adsorption isotherms:

The adsorptions of Pb^{2+} and Cu^{2+} in aqueous solutions for mono and multi-element systems were investigated. The adsorption isotherms of Pb^{2+} and Cu^{2+} in CCB in mono and multielemental systems and the application of experimental data in the Langmuir and Freundlich models are presented in Figure 8 (a-e), the isothermal parameters obtained by applying the data in the aforementioned models, are shown in table 4.

It is possible to observe that, in general, the values of q_e increase with the increase of C_e , until reaching a constant behavior at equilibrium. When comparing the values of q_e between the mono and multielemental systems, there is a reduction from 32.4 to 20.4 mg.g^{-1} (corresponding to 37%) for Cu^{+2} , and from 106.4 to 47.6 mg.g^{-1} (corresponding to 55%) for Pb^{+2} .

Similar behavior of reduction of q_e are found in the literature, for example, (DENG et al., 2017) obtained a q_{max} reduction of 55% for Cu^{+2} and 48.2% for Pb^{+2} , comparing the adsorption, in mono and multielemental systems, on chitosan - pyromellitic dianhydride

modified biochar. Mahdi et al (2019) found a reduction of 36.5% Cu^{+2} and 63% for Pb^{+2} , in date seed biochar.

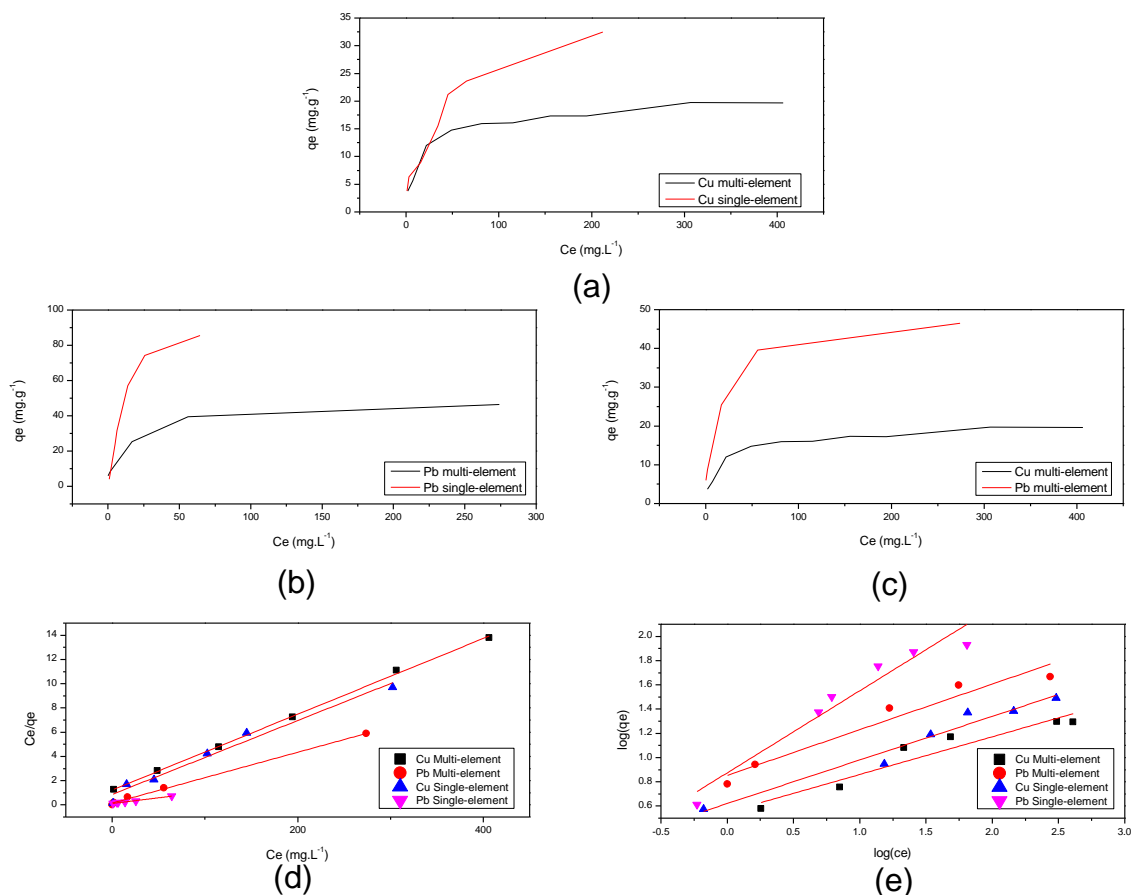


Figure 8: Isotherms adsorptions (a) Cu^{+2} mono and multielemental isotherms. (b) Pb^{+2} mono and multielemental isotherms. (c) multielemental. (d) Langmuir for Cu^{+2} and Pb^{+2} mono and multielemental isotherms. (e) Freundlich for Cu^{+2} and Pb^{+2} mono and multielemental isotherms.

Table 4: Isothermal parameters obtained with the Langmuir and Freundlich models.

Metal	Adsorption systems	Langmuir			Freundlich		
		K_L	q_{\max}	R^2	K_F	n	R^2
Cu^{+2}	Mono-element	0.0251	32.4	0.9770	4.3092	2.7465	0.9609
	Multi-element	0.0477	20.4	0.9958	3.5942	3.2062	0.9285
Pb^{+2}	Mono-element	0.0012	106.4	0.9910	7.5197	1.4760	0.9470
	Multi-element	0.0035	47.62	0.9978	7.1713	2.6560	0.9492

The greater reduction observed for the values of q_e for the Pb^{+2} ions, compared to the Cu^{+2} ions, can be explained by the greater hydration capacity and mobility for the adsorbent by elements with smaller cationic radius, such as the case of Cu^{+2} ion (62 pm) compared to Pb^{+2}

ion (119 pm), which in a competitive system, may have favored the adsorption speed for Cu^{+2} ions (JUMINA et al., 2020).

Even with a greater reduction in q_e values, comparing the adsorption of metallic ions between the mono and multielemental systems, the Pb^{+2} ion still showed greater adsorption capacity, in the multielemental system, in relation to the Cu^{+2} ion (Figure 8c), with q_{max} values of 47.6 mg.g^{-1} (ion Pb^{+2}) and 20.4 mg.g^{-1} (ion Cu^{+2}) (Table 4).

Zhu et al. (2012), using xanthate-modified magnetic chitosan as adsorbent, obtained similar behavior to this study, by finding greater adsorption capacity for Pb^{+2} compared to Cu^{+2} , in a Ternary system composed by Pb^{+2} , Cu^{+2} e Zn^{+2} . In the same way, Fei and Bei (2007) studied the adsorption of metals in multielemental systems with peat and also found greater adsorption capacity for Pb^{+2} compared to Cu^{+2} .

According to Saha et al.(2002), this behavior may be associated with different properties of these metallic ions, such as metal hydrolysis, electronegativity and softness. For Mahdi et al. (2019) such behavior is associated with the difference in their covalent binding indexes, where metals presenting a higher covalent index have greater chelating affinity with ligands in relation to ionic interactions and since the covalent index for Pb^{+2} is 11.1, it will present a greater tendency than the Cu^{2+} ion (with a covalent index of 5.7), to form covalent bonds with the adsorbent ligands.

Regarding the isothermal models, the data showed better fit for the Langmuir model (R^2 between 0.977 and 0.998) compared to the Freundlich model (R^2 between 0.928 and 0.961), but even with lower R^2 values, the Freundlich model also obtained good fitting. This result indicates that the system has a predominant monolayer adsorption behavior on the surface of the

adsorbent, however, through capillary action on the mesopores of the bioadsorbent, there is the possibility of adsorption in multilayers (MOHAMMAD; AHMED; EL-SAYED, 2020).

Even with q_{\max} reductions presented, the CCB adsorbent still has a high adsorptive capacity. Table 5 presents q_{\max} values obtained in other studies for adsorbents submitted to a multielemental adsorptive processes of Cu^{+2} and Pb^{+2} ions.

Table 5: Comparison of q_{\max} for Cu^{+2} and Pb^{+2} in multi-element systems, in different adsorbents.

Adsorbente	q_{\max} (mg.g ⁻¹)		Reference
	Cu^{+2}	Pb^{+2}	
Chitosan immobilized on bentonite	18.08	17.09	(FUTALAN et al., 2011)
Rice straw	5.66	23.35	(SOETAREDJO et al., 2013)
Date Seed Biochar	12.3	54.3	(MAHDI; YU; EL HANANDEH, 2019)
Peat	18.3	88.1	(FEI; BEI, 2007)
CCB	20.4	47.6	This study

4 - CONCLUSIONS

The adsorption of Cu^{+2} and Pb^{+2} ions in mono and multielemental systems was studied using the CCB adsorbent. The q_{\max} values obtained were higher for the Pb^{+2} ion compared to the Cu^{+2} ion for both mono and multielemental systems.

The experimental data of adsorption of Cu^{+2} and Pb^{+2} ions, for the mono and multielemental systems, fit better to the Langmuir model, but they also present good R^2 values for the Freundlich model, indicating that there is predominantly monolayer adsorption on the surface of the adsorbent, but there may be cases of multilayer adsorption.

There was a reduction in the isotherm constants for the multielemental systems, indicating the existence of competition between the Cu^{+2} and Pb^{+2} ions for the active sites present on the surface of the CCB adsorbent.

The two adsorbates studied fitted the pseudo second order and Elovich kinetic models for the mono and multielemental systems, indicating a chemisorption and ion exchange as rate-limiting steps.

Thus, the results presented in this study demonstrate that the bark of *Caryocar Coriaceum* Wittm can be used as an adsorbent material for the removal of Cu^{+2} and Pb^{+2} , both in monoelemental and multielemental systems. It is also noteworthy that the bark of *Caryocar Coriaceum* Wittm consisted of a residue of a food collected in a public market and that it can have a new function before being discarded. Another highlighted point is that the CCB Adsorbent did not presented any chemical modifications, reducing the generation of waste and costs for its preparation.

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REFERENCES

- ABDI, O.; KAZEMI, M. A review study of biosorption of heavy metals and comparison between different biosorbents. **Journal of Materials and Environmental Science**, v. 6, n. 5, p. 1386–1399, 2015.
- ABDIĆ et al. Adsorptive removal of eight heavy metals from aqueous solution by unmodified and modified agricultural waste: tangerine peel. **International Journal of Environmental Science and Technology**, v. 15, n. 12, p. 2511–2518, 2018.
- ACHARYA, J.; KUMAR, U.; RAFI, P. M. Removal of Heavy Metal Ions from Wastewater by Chemically Modified Agricultural Waste Material as Potential Adsorbent-A Review. **International Journal of Current Engineering and Technology**, v. 8, n. 3, p. 526–530, 2018.
- AHAYLA, N.; RAMACHANDRA, T. V. Biosorption of heavy metals. **Biotechnology progress**, v. 11, n. 3, p. 235–50, 1995.
- AL-QODAH, Z.; YAHYA, M. A.; AL-SHANNAG, M. On the performance of bioadsorption processes for heavy metal ions removal by low-cost agricultural and natural by-products bioadsorbent: a review. **Desalination and Water Treatment**, v. 85, n. August, p. 339–357, 2017.
- ALMEIDA, A. Avaliação ecológica do extrativismo do pequi (*Caryocar coriaceum* Wittm.) na Floresta Nacional do Araripe, Ceará: informações para um plano de uso sustentável. **Tese de Doutorado**, p. 164, 2014.
- AMIN, M. T.; ALAZBA, A. A.; AMIN, M. N. Absorption behaviours of copper, lead, and arsenic in aqueous solution using date palm fibres and orange peel: Kinetics and thermodynamics. **Polish Journal of Environmental Studies**, v. 26, n. 2, p. 543–557, 2017.
- AMORIM, D. J. et al. Characterization of Pequi (*Caryocar brasiliense*) Shells and Evaluation of Their Potential for the Adsorption of PbII Ions in Aqueous Systems. **Journal of the Brazilian Chemical Society**, v. 27, n. 3, p. 616–623, 2016.
-

ARAÚJO, R. R. D. L. **MODELAGEM DO PROCESSO DE BIODSORÇÃO DE CHUMBO UTILIZANDO A MACRÓFITA AQUÁTICA *Eichhornia crassipes***. Curitiba - PR: UFPR, 2011.

ARSLANOĞLU, E. et al. Fabrication, characterization, and adsorption applications of low-cost hybrid activated carbons from peanut shell-vinasse mixtures by one-step pyrolysis. **Biomass Conversion and Biorefinery**, 2021.

ATKINS, P.; JONES, L.; LAVERMAN, L. **Princípios de Química, questionando a vida moderna e o meio ambiente**. 7^a ed. Porto Alegre: [s.n.].

AVDEEV, Y. G.; LUCHKIN, A. Y.; KUZNETSOV, Y. I. Adsorption of IFKhAN-92 Inhibitor on Low Carbon Steel from Sulfuric Acid Solution. **Protection of Metals and Physical Chemistry of Surfaces**, v. 56, n. 7, p. 1244–1248, 2020.

AWUAL, M. R. Mesoporous composite material for efficient lead(II) detection and removal from aqueous media. **Journal of Environmental Chemical Engineering**, v. 7, n. 3, p. 103124, 2019a.

AWUAL, M. R. et al. Introducing an alternate conjugated material for enhanced lead(II) capturing from wastewater. **Journal of Cleaner Production**, v. 224, p. 920–929, 2019.

AWUAL, M. R. Innovative composite material for efficient and highly selective Pb(II) ion capturing from wastewater. **Journal of Molecular Liquids**, v. 284, p. 502–510, 2019b.

AWUAL, M. R. et al. Naked-eye lead(II) capturing from contaminated water using innovative large-pore facial composite materials. **Microchemical Journal**, v. 154, n. November 2019, p. 104585, 2020.

AWUAL, M. R.; HASAN, M. M. Novel conjugate adsorbent for visual detection and removal of toxic lead(II) ions from water. **Microporous and Mesoporous Materials**, v. 196, p. 261–269, 2014.

AWUAL, M. R.; HASAN, M. M. A ligand based innovative composite material for selective lead(II) capturing from wastewater. **Journal of Molecular Liquids**, v. 294, p. 111679, 2019.

AZARI, A. et al. Comprehensive systematic review and meta-analysis of dyes adsorption by carbon-based adsorbent materials: Classification and analysis of last decade studies.

Chemosphere, v. 250, n. 5, p. 126238, 2020.

AZOULAY, K. et al. Comparative study between static and dynamic adsorption efficiency of dyes by the mixture of palm waste using the central composite design. **Chemical Data**

Collections, v. 27, 2020.

BANERJEE, M. et al. Removal of Cr(VI) from Its Aqueous Solution Using Green Adsorbent Pistachio Shell: a Fixed Bed Column Study and GA-ANN Modeling. **Water Conservation**

Science and Engineering, v. 3, n. 1, p. 19–31, 2018.

BARROS, A. J. M. et al. ESTUDO TERMOGRAVIMÉTRICO DO PROCESSO DE SORÇÃO DE METAIS PESADOS POR RESÍDUOS SÓLIDOS ORGÂNICOS. **Engenharia**

Sanitaria e Ambiental, v. 11, p. 184–190, 2006.

BARROS, A. J. M. **Estudo da Formação de Complexos Pelo Processo de Biossorção**. Joao Pessoa: UFPB, 2006.

BISWAS, K.; SAHA, S. K.; GHOSH, U. C. Adsorption of fluoride from aqueous solution by a synthetic iron(III)-aluminum(III) mixed oxide. **Industrial and Engineering Chemistry**

Research, v. 46, n. 16, p. 5346–5356, 2007.

BLAGOJEV, N. et al. A new approach for modelling and optimization of Cu(II) biosorption from aqueous solutions using sugar beet shreds in a fixed-bed column. **Journal of Hazardous**

Materials, v. 363, n. June 2018, p. 366–375, 2019.

BOEHM, H. P. Surface oxides on carbon and their analysis: A critical assessment. **Carbon**, v. 40, n. 2, p. 145–149, 2002.

BOPARAI, H. K.; JOSEPH, M.; O’CARROLL, D. M. Kinetics and thermodynamics of cadmium ion removal by adsorption onto nano zerovalent iron particles. **Journal of**

Hazardous Materials, v. 186, n. 1, p. 458–465, 2011.

BOYD, G. E.; SCHUBERT, J.; ADAMSON, A. W. The Exchange Adsorption of Ions from

- Aqueous Solutions by Organic Zeolites. Ion-exchange Equilibria. **Journal of the American Chemical Society**, v. 69, n. 11, p. 2818–2829, 1947.
- BREDA, C. A. et al. Processing and Characterization of Chitosan Films with Incorporation of Ethanolic Extract from “Pequi” Peels. **Macromolecular Research**, 2017.
- BURAKOV, A. E. et al. Adsorption of heavy metals on conventional and nanostructured materials for wastewater treatment purposes: A review. **Ecotoxicology and Environmental Safety**, v. 148, n. August 2017, p. 702–712, 2018.
- CAO, M. LI et al. Functionalized graphene nanosheets as absorbent for copper (II) removal from water. **Ecotoxicology and Environmental Safety**, v. 173, n. September 2018, p. 28–36, 2019.
- CONAMA. Resolução CONAMA 430/2011. **Diário Oficial da União**, p. 9, 2011.
- CONICELLI, B. P. **BIOSSORÇÃO DE CHUMBO E MERCÚRIO PELAS LINHAGENS SELVAGEM E RECOMBINANTE DE C. metallidurans EM MEIO AQUOSO**. [s.l.] USP, 2018.
- CORDEIRO, M. W. S. et al. PHYSICAL CHARACTERISTICS, CHEMICAL-NUTRITIONAL COMPOSITION AND ESSENTIAL OILS OF *Caryocar brasiliense* NATIVE FROM THE STATE OF MATO GROSSO (In Portuguese). **Revista Brasileira de Fruticultura**, v. 35, n. 4, p. 1127–1139, 2013.
- CORDEIRO, R. D. M. **AS AGLOMERAÇÕES PRODUTIVAS DE CALÇADOS, FOLHEADOS E DE JOIAS DO CRAJUBAR (CE): FORMAÇÃO, PRODUÇÃO, TRABALHO, IMPLICAÇÕES SOCIOESPACIAIS**. [s.l.] Unesp, 2015.
- COSTA, D. A.; MENDONÇA, R. H.; WYSARD JUNIOR, M. M. Evaluation of removal of chromium (III) by composite porous adsorbents materials of PE-g-MA, coconut fiber and chitosan using experimental design (In Portuguese). **Engenharia Sanitaria e Ambiental**, v. 22, n. 6, p. 1203–1213, 2017.
- COSTA, A. P. F. DA; PINTO, E. G.; SOARES, D. S. B. Obtenção de farinha do mesocarpo
-

de pequi. **Revista Agrarian**, p. 113–119, 2017.

COSTA, T. B. DA; SILVA, M. G. C. DA; VIEIRA, M. G. A. Recovery of rare-earth metals from aqueous solutions by bio/adsorption using non-conventional materials: a review with recent studies and promising approaches in column applications. **Journal of Rare Earths**, v. 38, n. 4, p. 339–355, 2020.

COSTA, W. D. et al. Removal of copper(II) ions and lead(II) from aqueous solutions using seeds of *Azadirachta indica* A. Juss as bioadsorbent. **Environmental Research**, v. 183, n. June 2019, p. 109213, 2020.

CRINI, G. et al. Conventional and non-conventional adsorbents for wastewater treatment. **Environmental Chemistry Letters**, n. 0123456789, 2018.

CUI, H. et al. Dry-wet and freeze-thaw aging activate endogenous copper and cadmium in biochar. **Journal of Cleaner Production**, v. 288, p. 125605, 2021.

DADA, A. O.; ADEKOLA, F. A.; ODEBUNMI, E. O. A novel zerovalent manganese for removal of copper ions : synthesis , characterization and adsorption studies. **Applied Water Science**, 2015.

DE AQUINO SARAIVA, R. et al. *Caryocar coriaceum* Wittm. **Medicinal and Aromatic Plants of South America**, v. 5, p. 153–162, 2018.

DE MAGALHÃES, V. H. P.; NEVES, M. A. F. E S. UTILIZAÇÃO DO PERICARPO DE COCO VERDE (*Cocos nucifera* L . - ARECACEAE) PARA A REMOÇÃO DE RESÍDUOS DE ÍONS CROMO (VI) EM SOLUÇÕES AQUOSAS. **Perspectivas da Ciência e Tecnologia**, v. 3, p. 10–16, 2011.

DE OLIVEIRA, M. N. S. et al. Estádio de maturação dos frutos e fatores relacionados aos aspectos nutritivos e de textura da polpa de pequi (*Caryocar brasiliense* Camb.). **Revista Brasileira de Fruticultura**, v. 28, n. 3, p. 380–386, 2006.

DELBIANCO, G. A. B. **Estudo de Rejeitos de Galvanoplastia e a sua Aplicação na Fabricação de Peças Cerâmicas Rústicas para Fins Decorativos**. [s.l.] UNESP, 2008.

- DENG, J. et al. Competitive adsorption of Pb(II), Cd(II) and Cu(II) onto chitosan-pyromellitic dianhydride modified biochar. **Journal of Colloid and Interface Science**, v. 506, p. 355–364, 2017.
- DUARTE- NETO, J. F. et al. Processos de adsorção de corantes em argilas esmectíticas: uma revisão. **Revista Eletrônica de Materiais e Processos**, v. 9, p. 51–59, 2014.
- EL-ARABY, H. A. et al. Sesame Husk as Adsorbent for Copper(II) Ions Removal from Aqueous Solution. **Journal of Geoscience and Environment Protection**, v. 05, n. 07, p. 109–152, 2017.
- ELOVICH, S. Y.; LARINOV, O. G. Theory of adsorption from solutions of non electrolytes on solid (I) equation adsorption from solutions and the analysis of its simplest form,(II) verification of the equation of adsorption isotherm from solutions. **Izvestiya Akademii Nauk**, v. 2, n. 2, p. 209–216, 1962.
- ESCUADERO-OÑATE, C.; VILLAESCUSA, I. The Thermodynamics of Heavy Metal Sorption onto Lignocellulosic Biomass. **Heavy Metals**, 2018.
- FALAKI, Z.; BASHIRI, H. Preparing an adsorbent from the unused solid waste of Rosewater extraction for high efficient removal of Crystal Violet. **Journal of the Iranian Chemical Society**, v. 18, n. 10, p. 2689–2702, 2021.
- FEI, Q.; BEI, W. Single- and multi-component adsorption of Pb, Cu, and Cd on peat. **Bulletin of Environmental Contamination and Toxicology**, v. 78, n. 3–4, p. 265–269, 2007.
- FENG, N. et al. Biosorption of heavy metals from aqueous solutions by chemically modified orange peel. **Journal of Hazardous Materials**, v. 185, n. 1, p. 49–54, 2011.
- FUTALAN, C. M. et al. Comparative and competitive adsorption of copper, lead, and nickel using chitosan immobilized on bentonite. **Carbohydrate Polymers**, v. 83, n. 2, p. 528–536, 2011.
- GEÓCZE, K. C. **Exploratory analysis of carotenoids, essential oils and triacylglycerides of pequi (Caryocar brasiliense Camb.) from brazilian districts located in the cerrado**
-

biome (In Portugues). [s.l.] Universidade Federal de Viçosa, 2011.

GHOLAMIYAN, S.; HAMZEHLOO, M.; FARROKHANIA, A. RSM optimized adsorptive removal of erythromycin using magnetic activated carbon: Adsorption isotherm, kinetic modeling and thermodynamic studies. **Sustainable Chemistry and Pharmacy**, v. 17, n. May, p. 100309, 2020.

GIRALDO, L.; MORENO-PIRAJÁN, J. C. Pb²⁺ adsorption from aqueous solutions on activated carbons obtained from lignocellulosic residues. **Brazilian Journal of Chemical Engineering**, v. 25, n. 1, p. 143–151, 2008.

GUGUSHE, A. S. et al. Adsorptive removal of cd, cu, ni and mn from environmental samples using fe₃o₄-zro₂@aps nanocomposite: Kinetic and equilibrium isotherm studies. **Molecules**, v. 26, n. 11, 2021.

HACKBARTH, F. V. **REMOÇÃO DE METAIS DE EFLUENTES PETROQUÍMICOS UTILIZANDO BIOMASSA DE MACROALGA MARINHA PELVETIA CANALICULATA COMO ADSORVENTE**. Florianópolis: UFSC, 2014.

HIKMAT, N. A.; QASSIM, B. B.; KHETHI, M. T. Thermodynamic and Kinetic Studies of Lead Adsorption from Aqueous Solution onto Petiole and Fiber of Palm Tree. **American Journal of Chemistry**, v. 4, n. 4, p. 116–124, 2014.

HO, Y. S.; MCKAY, G. Pseudo-second order model for sorption processes. **Process Biochemistry**, v. 34, n. 5, p. 451–465, 1999.

HOSSAIN, A. et al. Biosorption of Cu(II) From Water by Banana Peel Based Biosorbent: Experiments and Models of Adsorption and Desorption. n. January 2012, 2012.

HUSSAIN, A. et al. Synthesis and Application of Modified Orchard Waste Biochar for Efficient Scavenging of Copper from Aqueous Solutions. **Arabian Journal for Science and Engineering**, n. 0123456789, 2021.

IBGE. **Pesquisa nacional de saneamento básico 2017: abastecimento de água e esgotamento sanitário**. [s.l: s.n.].

- IGHALO, J. O. et al. Mitigation of clofibric acid pollution by adsorption: A review of recent developments. **Journal of Environmental Chemical Engineering**, v. 8, n. 5, 2020a.
- IGHALO, J. O. et al. Competitive adsorption of Pb(II), Cu(II), Fe(II) and Zn(II) from aqueous media using biochar from oil palm (*Elaeis guineensis*) fibers: a kinetic and equilibrium study. **Indian Chemical Engineer**, v. 0, n. 0, p. 1–11, 30 jun. 2020b.
- IRAVANI MOHAMMADABADI, S.; JAVANBAKHT, V. Fabrication of dual cross-linked spherical treated waste biomass/alginate adsorbent and its potential for efficient removal of lead ions from aqueous solutions. **Industrial Crops and Products**, v. 168, n. April, p. 113575, 2021.
- JUMINA et al. Synthesis of C-4-hydroxy-3-methoxyphenylcalix[4]resorcinarene and its application as adsorbent for lead(II), copper(II) and chromium(III). **Bulletin of the Chemical Society of Japan**, v. 92, n. 4, p. 825–831, 2019.
- JUMINA et al. Simultaneous removal of lead(II), chromium(III), and copper(II) heavy metal ions through an adsorption process using C-phenylcalix[4]pyrogallolarene material. **Journal of Environmental Chemical Engineering**, v. 8, n. 4, p. 103971, 2020.
- KADIRI, L. et al. Mathematical modeling and thermodynamic study of copper (II) removal from aqueous solution by *Coriandrum Sativum* seeds. **Mediterranean Journal of Chemistry**, v. 7, n. 6, p. 478–490, 2019.
- KAMARI, A. et al. Biosorptive removal of Cu(II), Ni(II) and Pb(II) ions from aqueous solutions using coconut dregs residue: Adsorption and characterisation studies. **Journal of Environmental Chemical Engineering**, v. 2, n. 4, p. 1912–1919, 2014.
- KHEDDO, A. et al. Adsorption of synthetic dyed wastewater using activated carbon from rice husk. **SN Applied Sciences**, v. 2, n. 12, p. 1–14, 2020.
- KOVÁCS, E. et al. Investigation into the mechanism of stimulation by low-concentration stressors in barley seedlings. **Journal of Plant Physiology**, v. 166, n. 1, p. 72–79, 2009.
- LAGERGREN, S. Zur Theorie der Sogenannten Adsorption Gelöster Stoffe, *Kunliga*
-

Svenska Vetenskapsakademiens. **Handlingar**, v. 24, n. 4, p. 1–39, 1898.

LI, C. et al. Facile synthesis of low-cost magnetic biosorbent from peach gum polysaccharide for selective and efficient removal of cationic dyes. **International Journal of Biological Macromolecules**, v. 107, p. 1871–1878, 2018.

LI, H. et al. Modified carbon spheres as universal materials for adsorption of cationic harmful substances (paraquat and dyes) in water. **Microporous and Mesoporous Materials**, v. 297, n. June 2019, p. 110040, 2020.

LI, W. C.; LAW, F. Y.; CHAN, Y. H. M. Biosorption studies on copper (II) and cadmium (II) using pretreated rice straw and rice husk. **Environmental Science and Pollution Research**, v. 24, n. 10, p. 8903–8915, 2017.

LIMA, V. F.; MERÇON, F. Metais Pesados no Ensino de Química. **Química Nova Na Escola**, v. 33, n. 4, p. 199–205, 2011.

LIU, R.; LIAN, B. Non-competitive and competitive adsorption of Cd²⁺, Ni²⁺, and Cu²⁺ by biogenic vaterite. **Science of the Total Environment**, v. 659, n. 1, p. 122–130, 2019.

LIU, X. et al. Competitive adsorption of heavy metal ions from aqueous solutions onto activated carbon and agricultural waste materials. **Polish Journal of Environmental Studies**, v. 29, n. 1, p. 749–761, 2020.

LONG, Y. et al. Packed bed column studies on lead(II) removal from industrial wastewater by modified *Agaricus bisporus*. **Bioresource Technology**, v. 152, p. 457–463, 2014.

LOPES, P. S. N. et al. **Frutas Nativas da Região Centro-Oeste do Brasil**. 1^a edição ed. Planaltina - DF: [s.n.].

LOULIDI, I. et al. Adsorption of Crystal Violet onto an Agricultural Waste Residue: Kinetics, Isotherm, Thermodynamics, and Mechanism of Adsorption. **Scientific World Journal**, v. 2020, 2020.

LOW, M. J. D. Kinetics of chemisorption of gases on solids. **Chemical Reviews**, v. 60, n. 3, p. 267–312, 1960.

- MAALOUL, N. et al. Synthesis and characterization of eco-friendly cellulose beads for copper (II) removal from aqueous solutions. **Environmental Science and Pollution Research**, v. 27, n. 19, p. 23447–23463, 2020.
- MACIEL, T. C. M. et al. SUBSTRATO À BASE DE PEQUI (*Caryocar coriaceum*) NA PRODUÇÃO DE MUDAS DE TOMATE E PIMENTÃO. **Revista De Agricultura Neotropical**, v. 4, n. 2, p. 9–16, 2017.
- MADALA, S. et al. Equilibrium, kinetics and thermodynamics of Cadmium (II) biosorption on to composite chitosan biosorbent. **Arabian Journal of Chemistry**, v. 10, p. S1883–S1893, 2017.
- MAHDI, Z.; YU, Q. J.; EL HANANDEH, A. Competitive adsorption of heavy metal ions (Pb^{2+} , Cu^{2+} , and Ni^{2+}) onto date seed biochar: batch and fixed bed experiments. **Separation Science and Technology (Philadelphia)**, v. 54, n. 6, p. 888–901, 2019.
- MALIK, D. S.; JAIN, C. K.; YADAV, A. K. Heavy Metal Removal by Fixed-Bed Column – A Review. **ChemBioEng Rev**, v. 5, n. 3, p. 173–179, 2018.
- MENEZES, J. M. C. et al. Equilibrium, kinetics and thermodynamics of lead (II) adsorption in bioadsorbent composed by *Caryocar coriaceum* Wittm barks. **Chemosphere**, v. 261, 2020.
- MINISTÉRIO DA SAÚDE. Portaria MS N°2914/2011. **Dou 14/12/2011**, 2011.
- MOHAMMAD, S. G.; AHMED, S. M.; EL-SAYED, M. M. H. Removal of copper (II) ions by eco-friendly raw eggshells and nano-sized eggshells: a comparative study. **Chemical Engineering Communications**, v. 0, n. 0, p. 1–13, 2020.
- MONDAL, S.; MAJUMDER, S. K. **Honeycomb-like porous activated carbon for efficient copper (II) adsorption synthesized from natural source: Kinetic study and equilibrium isotherm analysis**. [s.l.] Elsevier Ltd, 2019. v. 7
- MORAIS, M. J. DE et al. CARACTERIZAÇÃO DA CASCA DE PEQUI (*Caryocar Brasiliense* Camb.) PARA SUA UTILIZAÇÃO COMO BIOMASSA. **III Congresso de Ensino, Pesquisa e Extensão da UEG**, v. 2, n. 1c, p. 17, 2016.
-

- MOREIRA, A. DA S. **BIOSSORÇÃO UTILIZANDO ALGA MARINHA (SARGASSUMsp.) APLICADA EM MEIO ORGÂNICO.** [s.l.] UFRN, 2007.
- MOREIRA, S. D. A. **ADSORÇÃO DE ÍONS METÁLICOS DE EFLUENTE AQUOSO USANDO BAGAÇO DO PEDÚNCULO DE CAJU: ESTUDO DE BATELADA E COLUNA DE LEITO FIXO.** [s.l.] UFC, 2008.
- MORENO-BENAVIDES, J. A.; PEÑA-SALAMANCA, E. J.; BENÍTEZ-CAMPO, N. Reducing Cr 6+ in electroplating wastewater with *Bacillus cereus* strain B 1. **Universitas Scientiarum**, v. 24, n. 1, p. 73–89, 2019.
- MORIN-CRINI, N. et al. Hemp-based adsorbents for sequestration of metals: a review. **Environmental Chemistry Letters**, 2018.
- NASCIMENTO, R. F. DO et al. **ADSORÇÃO: Aspectos teóricos e aplicações ambientais.** 2ª ed. Fortaleza - Ce: Imprensa Universitária UFC, 2020.
- NERIS, J. B. et al. Evaluation of adsorption processes of metal ions in multi-element aqueous systems by lignocellulosic adsorbents applying different isotherms: A critical review. **Chemical Engineering Journal**, v. 357, n. April 2018, p. 404–420, 2019.
- OLIVEIRA, M. E. B. DE et al. Aspectos Agronômicos e de Qualidade do Pequi. **Embrapa**, v. 113, p. 33, 2008.
- OLIVEIRA, S. A. DE. **ESTUDO DE ADSORÇÃO DE METAIS PESADOS EM ZEÓLITAS PARA FINS DE USO EM BARREIRA REATIVA.** [s.l.] UFRJ, 2011.
- OLIVEIRA, W. L. DE. **Boas Práticas de Manejo para p Extrativismo Sustentável do Pequi.** Brasília: [s.n.].
- PEREIRA, F. D. A. et al. ANÁLISE DA ATIVIDADE EXTRATIVISTA DO PEQUI (*Caryocar coriaceum* Wittm) EM COMUNIDADES DA CHAPADA DO ARARIPE NA REGIÃO DO CARIRI CEARENSE. **Conexões Ciência e Tecnologia**, v. 8, p. 59–66, 2014.
- PEREIRA, J. E. S. **Biossorção de cobre em solução aquosa utilizando os pós das folhas do cajueiro (*Anacardium occidentale* L.) e da carnaúba (*Copernicia prunifera*).** [s.l.]
-

UFRN, 2017.

PEREZ, I. C.; CORRÊA, R. G.; PIRES, J. L. Gestão Ambiental - Galvanoplastia, orientações para o controle ambiental. p. 48, 2014.

PINO, G. A. H. **Biossorção de Metais Pesados Utilizando Pó da Casca de Coco Verde (Cocos nucifera)**. [s.l.] PUC - Rio de Janeiro, 2005.

PINO, G. H.; TOREM, M. L. ASPECTOS FUNDAMENTAIS DA BISSORÇÃO DE METAIS NÃO FERROSOS ESTUDO DE CASO. **Tecnologia em Metalurgia e Materiais**, 2011.

POLICARPO, L. M. **ESTUDO DE EQUILÍBRIO E CINÉTICA DA BISSORÇÃO DE COBRE (II) POR RHIZOPUS MICROSPORUS**. São Paulo - SP: USP, 2015.

RAGAVENDRAN, P. et al. FUNCTIONAL GROUP ANALYSIS OF VARIOUS EXTRACTS OF *Aerva lanata* (L.) BY FTIR SPECTRUM. **Pharmacologyonline**, v. 364, p. 358–364, 2011.

RAMOS, K. M. C.; SOUZA, V. A. B. DE. Características físicas e químico-nutricionais de frutos de pequi (Caryocar coriaceum Wittm.) em populações naturais da região meio-norte do Brasil. **Revista Brasileira de Fruticultura**, v. 33, n. 2, p. 500–508, 2011.

RAMOS, R. et al. Produção de adsorventes a base de borra de café industrializado e folhas de *Corymbia citriodora* (eucalipto limão). **Dissertar Produção**, v. 1, n. 28–29, p. 17–22, 2017.

RASOULPOOR, K.; POURSATTAR MARJANI, A.; NOZAD, E. Competitive chemisorption and physisorption processes of a walnut shell based semi-IPN bio-composite adsorbent for lead ion removal from water: Equilibrium, Kinetic and Thermodynamic studies. **Environmental Technology and Innovation**, v. 20, p. 101133, 2020.

RAY, S.; MISHRA, A. K.; KALAMDHAD, A. S. Adsorption and Hydraulic Conductivity Studies on Bentonite in Presence of Copper Solution. **Journal of Hazardous, Toxic, and Radioactive Waste**, v. 25, n. 2, p. 06020007, 2021.

REGALBUTO, J. R.; ROBLES, JAIME O. **The Engineering of Pt / Carbon Catalyst**

Preparation For application on Proton Exchange Fuel Cell Membrane (PEFCM).

Chicago: [s.n.].

REICHENBERG, D. Properties of Ion-Exchange Resins in Relation to their Structure. III.

Kinetics of Exchange. **Journal of the American Chemical Society**, v. 75, n. 3, p. 589–597, 1953.

RENGEL, Z. Aluminium cycling in the soil-plant-animal-human continuum. **BioMetals**, v. 17, n. 6, p. 669–689, 2004.

RODRIGUES, R. F. et al. HEAVY METALS SORPTION ON TREATED WOOD SAWDUST (In Portuguese). **Quimica Nova**, 2007.

RUTHVEN, D. M. **Principles of adsorption and adsorption processes**. New York: John Wiley&Sons, 1984. v. 4

ŠABANOVI, E. et al. Simultaneous adsorption of heavy metals from water by novel lemon-peel based biomaterial. **Polish Journal of Chemical Technology**, v. 22, n. 1, p. 46–53, 2020.

ŠABANOVIĆ, E. et al. Pulverized Banana Peel as an Economical Sorbent for the Preconcentration of Metals. **Analytical Letters**, v. 48, n. 3, p. 442–452, 2015.

SABELA, M. I. et al. Removal of copper (II) from wastewater using green vegetable waste derived activated carbon: An approach to equilibrium and kinetic study. **Arabian Journal of Chemistry**, v. 12, n. 8, p. 4331–4339, 2019.

SAHA, U. K.; TANIGUCHI, S.; SAKURAI, K. Simultaneous Adsorption of Cadmium, Zinc, and Lead on Hydroxyaluminum- and Hydroxyaluminosilicate-Montmorillonite Complexes. **Soil Science Society of America Journal**, v. 66, n. 1, p. 117–128, 2002.

SAHMOUNE, M. N. Evaluation of thermodynamic parameters for adsorption of heavy metals by green adsorbents. **Environmental Chemistry Letters**, v. 17, n. 2, p. 697–704, 2019.

SALAME, I. I.; BANDOSZ, T. J. Surface chemistry of activated carbons: Combining the results of temperature-programmed desorption, Boehm, and potentiometric titrations. **Journal**

of **Colloid and Interface Science**, v. 240, n. 1, p. 252–258, 2001.

SALIHI, I. U. et al. Adsorption of copper using modified and unmodified sugarcane bagasse.

International Journal of Applied Engineering Research, v. 10, n. 19, p. 40434–40438, 2015.

SANTANA, A. H. **REMOÇÃO DE ÍONS COBRE E CHUMBO DE ÁGUAS RESIDUAIS UTILIZANDO VAGENS DE *Dimorphandra gardneriana* Tulasne (FAVA D'ANTA)**. [s.l.] URCA, 2018.

SANTANA, A. H. et al. Copper and lead ion removal from wastewater using fava d'anta fodder (*Dimorphandra gardneriana* Tulasne). **Environmental Geochemistry and Health**, v. 0123456789, 2020.

SANTHOSH, A.; DAWN, S. S. Synthesis of zinc chloride activated eco-friendly nano-adsorbent (activated carbon) from food waste for removal of pollutant from biodiesel wash water. **Water Science and Technology**, v. 00, n. 0, p. 1–12, 2021.

SCHNEIDER, I. A. H. **Biossorção de Metais Pesados com a Biomassa de Macrófitos Aquáticos**. [s.l.] UFRGS, 1955.

SCHNEIDER, R. M. et al. **BIOMASSAS PARA A ADSORÇÃO DO METAL CROMO III DE EFLUENTE**. Gramado - RS: [s.n.].

ŠĆIBAN, M.; KLAŠNJA, M.; ŠKRBIĆ, B. Modified softwood sawdust as adsorbent of heavy metal ions from water. **Journal of Hazardous Materials**, v. 136, n. 2, p. 266–271, 2006.

ŠĆIBAN, M.; KLAŠNJA, M.; ŠKRBIĆ, B. Adsorption of copper ions from water by modified agricultural by-products. **Desalination**, v. 229, n. 1–3, p. 170–180, 2008.

SEBRAE. Lapidando a imagem da jóia brasileira. 2007.

SEBRAE. Industria da Moda: Gemas e Joias. **Estudo de Mercado**, 2017.

SEMACE. Resolução COEMA nº02, de 02 de fevereiro de 2017. p. 56–61, 2017.

ŞENEL, G. U. Adsorption of Copper (II) from Aqueous Solution by Using Carbonized Peanut

Hull: Determination of the Equilibrium, Kinetic and Thermodynamic Parameters. **Journal of Anatolian Environmental and Animal Sciences**, v. 90, n. 533, 2020.

SENTHIL KUMAR, P. et al. Adsorption of metal ions onto the chemically modified agricultural waste. **Clean - Soil, Air, Water**, v. 40, n. 2, p. 188–197, 2012.

SHAHAT, A. et al. Novel hierarchical composite adsorbent for selective lead(II) ions capturing from wastewater samples. **Chemical Engineering Journal**, v. 332, n. September 2017, p. 377–386, 2018.

SHAMIM, S. Biosorption of Heavy Metals. **Biosorption**, 2018.

SIQUEIRA, B. DOS S. et al. PECTINA EXTRAÍDA DE CASCA DE PEQUI E APLICAÇÃO EM GELEIA LIGHT DE MANGA. **revista brasileira fruticultura**, v. 34, n. 2, p. 560–567, 2012.

SOETAREDJO, F. E. et al. Incorporation of selectivity factor in modeling binary component adsorption isotherms for heavy metals-biomass system. **Chemical Engineering Journal**, v. 219, p. 137–148, 2013.

SOUSA NETO, V. O. et al. Use of coconut bagasse as alternative adsorbent for separation of copper (II) ions from aqueous solutions: Isotherms, kinetics, and thermodynamic studies. **BioResources**, v. 6, n. 3, p. 3376–3395, 2011.

SOUZA, J. P. DE et al. PEQUI (*Caryocar coriaceum* Wittm) PRODUCT STABILITY UNDER FREEZING IN DIFFERENT TYPES OF PACKAGING (In Portuguese). **Revista Brasileira de Fruticultura**, v. 35, n. 4, p. 971–976, 2013.

TANG, X. et al. Extremely efficient and rapidly adsorb methylene blue using porous adsorbent prepared from waste paper: Kinetics and equilibrium studies. **Journal of Hazardous Materials**, v. 402, n. July 2020, p. 123579, 2021.

TARIBA LOVAKOVIĆ, B. Cadmium, arsenic, and lead: elements affecting male reproductive health. **Current Opinion in Toxicology**, v. 19, n. Figure 1, p. 7–14, 2020.

TARLEY, C. R. T.; ARRUDA, M. A. Z. Biosorption of heavy metals using rice milling by-

products. Characterisation and application for removal of metals from aqueous effluents.

Chemosphere, v. 54, n. 7, p. 987–995, 2004.

TAŞAR, Ş.; ÖZER, A. A thermodynamic and kinetic evaluation of the adsorption of pb(II) ions using peanut (*arachis hypogaea*) shell-based biochar from aqueous media. **Polish**

Journal of Environmental Studies, v. 29, n. 1, p. 293–305, 2020.

TAVANA, M.; PAHLAVANZADEH, H.; ZAREI, M. J. The novel usage of dead biomass of green algae of *Schizomeris leibleinii* for biosorption of copper(II) from aqueous solutions:

Equilibrium, kinetics and thermodynamics. **Journal of Environmental Chemical**

Engineering, v. 8, n. 5, p. 104272, 2020.

TEIXEIRA, R. N. P. **REMOÇÃO DE Cu(II), Ni(II), Cd(II) E Pb(II) DE EFLUENTES DE INDÚSTRIAS DE GALVANOPLASTIA USANDO O SISTEMA HÍBRIDO ADSORÇÃO- ELETRO-FLOTAÇÃO-COAGULAÇÃO**. [s.l.] UFC, 2015.

TOUIHRI, M. et al. Single and simultaneous adsorption of Cr(VI) and Cu (II) on a novel Fe₃O₄/pine cones gel beads nanocomposite: Experiments, characterization and isotherms modeling. **Chemical Engineering Journal**, v. 416, n. February, 2021.

USLU, G.; TANYOL, M. Equilibrium and thermodynamic parameters of single and binary mixture biosorption of lead (II) and copper (II) ions onto *Pseudomonas putida*: Effect of temperature. **Journal of Hazardous Materials**, v. 135, n. 1–3, p. 87–93, 2006.

VERÍSSIMO, L. S.; CAVALCANTE, I. N. AS ÁGUAS SUBTERRÂNEAS DO CRAJUBAR, REGIÃO DO CARIRI - ESTADO DO CEARÁ - BRASIL. **1st Joint World Congress on GroundWaterr**, n. 85, p. 1–17, 2000.

WANG, J.; GUO, X. Adsorption kinetic models: Physical meanings, applications, and solving methods. **Journal of Hazardous Materials**, v. 390, n. November 2019, p. 122156, 2020.

WEBER, W. J.; MORRIS, J. C. Kinetics of adsorption on carbon from solution. **Journal of the Sanitary Engineering Division**, v. 89, p. 31–60, 1963.

WONG, K. K. et al. Removal of Cu and Pb from electroplating wastewater using tartaric acid

modified rice husk. **Process Biochemistry**, v. 39, n. 4, p. 437–445, 2003.

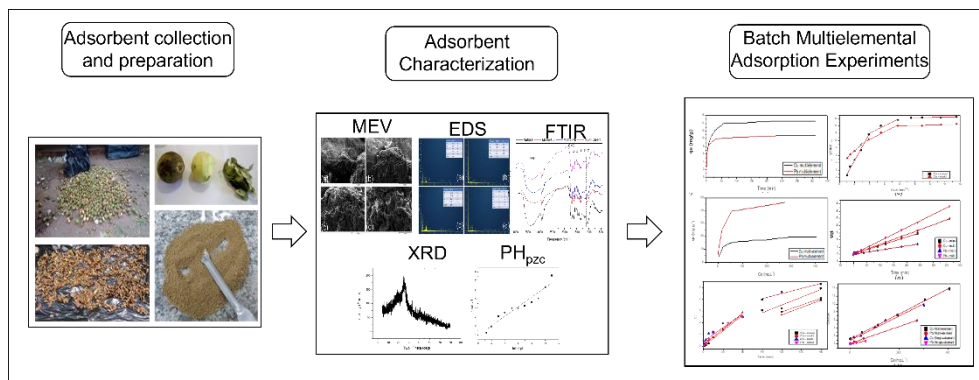
YADAV, V.; BHAGAT, M. Isotherm , kinetics and thermodynamic parameters study of arsenic (III) and copper (II) adsorption onto Limonia acidissima shell carbon. **Desalination and Water Treatment**, v. 184, n. April, p. 214–224, 2020.

YADAV, V.; TIWARI, D. P.; BHAGAT, M. Isotherm, kinetic and thermodynamic parameters study of arsenic (III) and copper (II) adsorption onto Limonia acidissima shell carbon. **Desalination and Water Treatment**, v. 184, n. April, p. 214–224, 2020.

ZHU, Y.; HU, J.; WANG, J. Competitive adsorption of Pb(II), Cu(II) and Zn(II) onto xanthate-modified magnetic chitosan. **Journal of Hazardous Materials**, v. 221–222, p. 155–161, 2012.

ZOU, W.; BAI, H.; GAO, S. Competitive adsorption of neutral red and Cu²⁺ onto pyrolytic char: Isotherm and kinetic study. **Journal of Chemical and Engineering Data**, v. 57, n. 10, p. 2792–2801, 2012.

GRAPHICAL ABSTRACT



Este estudo apresentou alguns dos possíveis impactos que podem ser causados ao meio ambiente e aos seres vivos, devido à presença em concentrações excessiva de metais tóxicos em corpos aquáticos.

Com o intuito de gerar novas alternativas para minimização de tais impactos, foram apresentados dados experimentais referentes à aplicação da técnica de adsorção para alguns metais tóxicos (Cu^{2+} e Pb^{2+}), presentes em soluções sintéticas, porém fez-se uso de um adsorvente de origem natural, composto do resíduo da casca do *Caryocar Coriaceum* Wittm, mais conhecido popularmente como Pequi.

Almejou-se utilizar tal material para preparação do adsorvente, pois o Pequi apresenta grande comercialização durante sua safra, e como geralmente é utilizado apenas seu caroço, facilmente encontram-se descartados nos mercados públicos, grandes quantidades de resíduos de suas cascas, que não apresentará mais utilidade alguma para o comerciante ou consumidor.

Assim, com a realização deste estudo, constatou-se que a casca do *Caryocar coriaceum* Wittm (CCB) pode ser utilizada como material adsorvente, com origem natural, barata e disponível em grande abundância no ambiente, para a aplicação da técnica de adsorção para a remoção dos íons metálicos Cu^{2+} e Pb^{2+} , presentes em soluções mono e multielementares, utilizando-se reatores em bateladas.

Por meio das técnicas de caracterizações de materiais estudadas, foi possível obter informações importantes do CCB preparado, bem como para a aplicação da técnica de adsorção dos metais tóxicos.

Com a técnica de FTIR, foi possível observar grande disponibilidade de bandas espectrais geradas pelos grupos funcionais presentes na superfície do CCB, indicativos de substâncias com potencial de adsorver os adsorbatos estudados, tais como aminoácidos, carboidratos e polissacarídeos (pectina, celulose, hemicelulose e lignina). Também se destacou a presença de alterações dessas bandas, seja por deslocamento ou minimização de intensidade de sinal (observadas principalmente na região entre 1600 e 1000 cm^{-1}) quando comparados os espectros de infravermelho do CCB antes e após a aplicação da técnica de adsorção, indicando assim que os metais tóxicos estudados possivelmente se coordenaram aos grupos funcionais presentes nas superfícies do CCB, necessitando de maiores energias para promover as vibrações moleculares.

Através da titulação de Boehm, foi possível reforçar alguns dados apresentados pela técnica de FTIR, pois essa indica a presença de grupos funcionais fenólicos, carboxílicos e lactônicos, presentes na superfície do CCB. Comparando-se os resultados obtidos antes e após o ensaio de adsorção de íons Cu^{+2} , verificou-se que houve uma redução na concentração de grupos carboxílicos e lactônicos, 60% e 14%, respectivamente, sugerindo um favorecimento da adsorção dos íons presentes na solução por tais grupamentos.

A caracterização morfológica do adsorvente CCB foi realizada utilizando-se as técnicas de DRX e MEV, onde através do difratograma obtido pela primeira técnica, verificou-se a presença de um único pico intenso entre $20^\circ - 30^\circ$, o que indicava a presença de átomos de carbono distorcidos e assim indicando que o adsorvente apresentava uma fase amorfa. Tal comportamento foi reforçado pela técnica da MEV, pode-se constatar que o CCB apresentava características favoráveis à adsorção, uma vez que tinha uma superfície amorfa e heterogênea, com cavidades e poros, que aumentavam a área de contato do adsorvente com o adsorvato, possivelmente facilitando a adsorção destes.

A faixa de pH favorável para a realização dos testes de adsorção foi obtido com a aplicação do teste pH de potencial de carga zero (pHpzc), que indicou que o pH em que o CCB apresenta carga zerada é de 4,1, com isso definiu-se o valor de pH para realização dos testes em 5,5, tendo em vista favorecer a adsorção de espécies de carga positiva (como é o caso dos metais tóxicos) sem que haja sua precipitação química.

Com a técnica de FRX, foi possível afirmar que houve adsorção de íons Cu^{+2} à superfície do CCB, no sistema monoelementar, uma vez que na caracterização deste material antes dos ensaios de adsorção, não se verificou presença de tais componentes, enquanto que para o material pós ensaio adsorvivo foi detectado concentração de aproximadamente 19%.

Para os sistemas multielementares, foi utilizada a técnica de MEV-EDS, onde constatou-se a efetividade da adsorção dos adsorvatos (Cu^{+2} e Pb^{+2}) na superfície do CCB, através da detecção destes elementos na composição do adsorvente após a realização dos ensaios adsorvivos, o que não foi verificado antes do estudo adsorvivo.

Com o ensaio cinético, constatou-se que, para o CCB, seriam necessárias duas horas de contato entre o adsorvente e a soluções sintéticas, mono e multielementares, para que fossem atingidos os equilíbrios de adsorção, com valores de q_e , para as soluções monoelementares, de 16 mg.g^{-1} para íons Cu^{2+} e 33 mg.g^{-1} para íons Pb^{2+} , para íons Cu^{2+} e Pb^{2+} , respectivamente, já para as soluções multielementares, foram obtidos valores de q_e de $12,9 \text{ mg.g}^{-1}$ para íons Cu^{2+} e $10,4 \text{ mg.g}^{-1}$ para íons Pb^{2+} , para íons Cu^{2+} e Pb^{2+} , respectivamente, sendo constatado uma redução nos valores de q_e para os dois adsorvatos, quando realizado o processo de forma multielementar, verificando a existência de uma competição entre estes pelos sítios ativos

presentes na superfície do adsorvente. Porém, mesmo com tal comportamento ainda foram verificados percentuais de remoções de íons metálicos presentes na solução superiores a 80% para íons Cu^{2+} e 90% para íons Pb^{2+} .

O modelo cinético de segunda ordem foi o que melhor se enquadrou aos dados experimentais, indicando que a taxa de adsorção é dependente da quantidade da espécie química adsorvida na superfície do adsorvente e a quantidade adsorvida no estado de equilíbrio.

Com o modelo de Weber-Morris, foi possível constatar a ocorrência de três estágios no processo adsorptivo, com difusão intrafilme controlando a adsorção, verificada pela ocorrência de coeficiente linear (C) diferente de zero no primeiro estágio. Também se observou que houve aumento deste valor no decorrer dos estágios, apontando para um aumento da espessura do filme e conseqüentemente reduzindo-se o coeficiente de difusão (K_d).

A respeito das isotermas de adsorção, os dados se enquadraram bem em todos os modelos aplicados para os dois metais tóxicos estudados, com exceção apenas do modelo D-R. Tal resultado possibilitou indicar a ocorrência predominante de adsorção em monocamada, com possibilidade de multicamadas por ação capilar nos mesoporos do adsorvente. Também foi possível indicar que a adsorção tratava-se de uma quimissorção, uma vez que se enquadrou bem ao modelo de Temkin e não ao de D-R. Por meio do Modelo de Langmuir foram determinados os valores de q_{max} , para os íons Cu^{2+} (26,9 mg.g^{-1}) e Pb^{2+} (106,4 mg.g^{-1}), nos sistemas monoelementares, e 20,4 mg.g^{-1} (Cu^{2+}) e 47,6 mg.g^{-1} (Pb^{2+}), nos multielementares, sendo considerado valores bem relevantes quando comparados a outros obtidos pela literatura, para adsorventes que não sofreram modificação química.

Por fim, realizou-se o estudo termodinâmico, em que possibilitou ver que a espontaneidade da adsorção dos íons Cu^{2+} era favorecida com o aumento da temperatura do sistema (processo endotérmico), obtendo-se um aumento do valor de q_e 16,8 mg.L^{-1} (5°C) para 20,4 mg.L^{-1} (35°C), enquanto que para os íons Pb^{2+} , era desfavorecida (processo exotérmico), apresentando redução do valor de q_e 15,6 mg.L^{-1} (5°C) para 13,5 mg.L^{-1} (35°C).

Os valores de ΔH° reforçaram os comportamentos endotérmicos ($\Delta H^\circ > 0$) e exotérmicos ($\Delta H^\circ < 0$) para as adsorções dos íons estudados, sendo 34,5 kJ.mol^{-1} para Cu^{2+} e -28,13 kJ.mol^{-1} para Pb^{2+} , bem como o processo trata-se também de uma quimissorção (valores de ΔH° entre 20 - 800 kJ.mol^{-1}).

5.1 PERSPECTIVAS DE INVESTIGAÇÕES FUTURAS

Devido a pandemia do COVID-19, muitas dificuldades de acesso aos laboratórios e realização de determinadas análises surgiram, durante o período de pesquisa deste doutorado,

com isso impossibilitando a realização de estudos mais aprofundados almejados por esta pesquisa.

Além dos resultados apresentados nos capítulos anteriores, alguns ensaios de adsorção dos íons Cu^{+2} e Pb^{+2} , em soluções monoelementares, utilizando colunas de leito fixo foram iniciados, porém ainda demandando a realização de novos testes para o possível fortalecimento dos argumentos observados pelos ensaios realizados, possibilitando assim a construção de novos artigos científicos.

ANEXO A - Primeira página do artigo publicado, referente ao capítulo I.

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Equilibrium, kinetics and thermodynamics of lead (II) adsorption in bioadsorbent composed by *Caryocar coriaceum* Wittm barks

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HIGHLIGHTS

- *Caryocar coriaceum* Wittm bark is a good bioadsorbent for solutions with Pb(II) ions.
- *Caryocar coriaceum* Wittm bark has high adsorptive capacity compared to other natural unmodified adsorbents.
- The use of *Caryocar coriaceum* Wittm bark tailings, as adsorbent, can minimize the amount of waste being sent to landfills.
- *Caryocar coriaceum* Wittm bark is an abundant and low-cost material to be used as a adsorbent.

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ABSTRACT

The improper disposal of waste containing toxic metals promotes serious environmental problems. Biosorption stands out as a powerful technique in removing toxic metals from aqueous solutions, making it an efficient and low-cost technique, since it makes use of abundant materials and of natural origins. This work aimed to study the application of the bark of *Caryocar coriaceum* Wittm, as a possible bio-adsorbent for the removal of Lead (II) present in aqueous solutions, for this, residues of this material were collected in a public market, where they were washed and dried, then crushed, sieved (32mesh) and washed again, to then be used in the kinetic, isotherm and thermodynamic tests of lead (II) ions adsorption. After the experiments, it was found that the increase of the temperature disfavored the rate of lead (II) adsorption, ranging from 15.6 to 13.5 mg.L⁻¹, for temperatures of 5 °C and 35 °C, respectively. The pseudo-second order kinetic model best characterizes the adsorption velocity obtaining a linear regression coefficient of 0.9997, while the pseudo-first order obtained a value of 0.7117. Adsorption occurred by chemisorption, with intra-film diffusion. The isothermal model that best represented the adsorption was Langmuir's (R² 0.99). It was concluded that the bark of *Caryocar coriaceum* Wittm is a good alternative to be used as a bioadsorbent for solutions containing dissolved lead (II).

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1. Introduction

Lead (Pb(II)) is associated with several human productive activities, due to its unique chemical and physical properties, considering high malleability, low melting point, ductility and corrosion resistance. Mining, galena, storage batteries, alloys, cable

sheaths, solder, industrial products for use in plastics, paints, automobiles, ceramics X-ray equipment and radiation shielding, are some of the applications of this metal (Awual et al., 2020; Shahat et al., 2018).

When incorrectly disposed or accumulated in groundwater and on the soil surface, as a waste of several industrial processes, the toxic metals, such as the Lead, tend to produce serious environmental problems, as they present difficult degradation, affect the self-cleaning processes of the environment and are still bio-accumulated in the chain of living beings, promoting toxicity to living organisms, damaging human brain, liver, kidneys and

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ANEXO B - Primeira página do artigo publicado, referente ao capítulo II.

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Kinetic and thermodynamic study of copper (II) IONS biosorption by *Caryocar Coriaceum* Wittm bark

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ABSTRACT

The improper disposal of waste containing toxic metals is a major environmental pollution problem. Among the different methodologies to deal with this problem, biosorption is considered one of the most efficient processes for the removal of toxic metals from aqueous solutions. The use of natural adsorbents, such as vegetable waste, in a process known as biosorption, stands out even more as it combines the remediation of polluted water with a reduction in the amount of solid waste. This work aimed to study the use of the bark of *Caryocar Coriaceum* Wittm, a fruit known as pequi, as a possible bioadsorbent for the removal of copper (II) from aqueous solutions. To this end, pequi bark was collected from a public city market, washed, dried up and crushed. The obtained material was then sieved and the 32-mesh fraction was collected, washed and dried again. The resulting material was then submitted to kinetic, isothermal and thermodynamic testing for copper (II) biosorption. We found that the copper (II) biosorption capacity is favored by increasing temperatures, ranging from 16.8 to 20.4 mg.L⁻¹ at 5 °C and 35 °C, respectively. The kinetic model that best fits de biosorption process was the pseudo-second order model, which produced a linear regression coefficient of 0.999, while the pseudo-first order model produced a value of 0.695. The bioadsorption process was characterized by chemisorption with intra-film diffusion. The isothermal model that best represented the biosorption was Langmuir's (R² = 0.99). In sight of the obtained results, we concluded that *Caryocar Coriaceum* Wittm bark is a good bioadsorbent alternative for solutions containing dissolved copper (II).

1. Introduction

The improper disposal of industrial and domestic waste may have a significant impact on the environment, as it carries several toxic components that, more often than not, are difficult to degrade, impairing the self-purifying processes of the environment and thus leading to adverse environmental effects.

Toxic metals outstand among the different toxic compounds found in these wastes because, besides not being chemically and/or biologically degraded, they also have certain characteristics in their electronic structures that make them highly reactive, tending to form complexes and, consequently, develop an intense biochemical and physiological activity, thus causing several environmental and health effects (Burakov et al., 2018).

Certain metals, such as copper (Cu), are essential in small quantities for plants and animals as they participate in biosynthetic and other essential processes involving nucleic acids and carbohydrates, bone and tissue improvement in the human body, as well as in maintaining the integrity of biological membranes (Rengel, 2004; Tavana et al., 2020). However, an excessive intake of Cu (II) ions may have toxic effects on living organisms and can have serious effects, such as gastric pain, nausea, vomiting, severe diarrhea, bleeding, cancer in the digestive tract and lungs, as well as Menkes', Parkinson's and Alzheimer's diseases (Acharya et al., 2018; Costa et al., 2017; Kovács et al., 2009; Maaloul et al., 2020; Rodrigues et al., 2007).

Techniques such as chemical precipitation, electrochemical treatment, oxide-reduction processes, ion exchange, reverse osmosis, and phytoremediation, among others, are commonly used in order to remove

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