

Efficiency of a Modified Rose-Stem-Based Bioadsorbent for the Removal of Cr (III) from Tannery Wastewater

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Abstract: The removal of Cr (III) from tannery effluents using rose stem waste as a bioadsorbent (BA) was investigated. First, sorption experiments were performed using virgin BA to verify its efficiency. Due to the BA's low retention capacity, it was chemically modified separately with H₂SO₄, NaOH, and Na₃C₆H₅O₇. The BA was characterized by means of a Fourier transform infrared (FT-IR) spectrometer, and subsequently, employed in sorption studies. Second, the effects of pH (2 - 6), adsorbent dose (33 - 300 g/L) and contact time (1 - 30 h) were examined through batch experiments. Synthetic solutions (250 ppm) prepared with Cr(OH)SO₄ were used to study these variables. Then, an actual tannery effluent was used to verify the ideal conditions selected for the synthetic solutions. An atomic absorption spectrophotometer was also utilized to determine the Cr (III) concentration. The results showed that the efficiency raised with increasing BA dose (200 g/L), contact time (20 h), and pH 6. The BA efficiency on Cr (III) removal of the tannery effluent (57 %) was lower than that of the synthetic samples (72 %). The pseudo-second-order kinetic model and equilibrium represented by the Sips isotherm, with a power of 5.1 mg Cr/g BA, best fit the experimental data.

Keywords: bioadsorbent, wastewater, rose-stem, chromium

Eficacia de un Bioadsorbente Modificado a Base de Tallo de Rosa para la Eliminación de Cr (III) de Aguas Residuales de Curtiembres

Resumen: Se investigó la eliminación de Cr (III) de efluentes de curtidurías utilizando residuos de tallo de rosa como bioadsorbente (BA). En primer lugar, se realizaron experimentos de sorción con BA virgen para verificar su eficacia. Debido a la baja capacidad de retención del BA, se le modificó químicamente con H₂SO₄, NaOH y Na₃C₆H₅O₇, por separado. El BA fue caracterizado mediante espectrometría infrarroja por transformada de Fourier (FT-IR), y a continuación, fue utilizado en los estudios de sorción. En segundo lugar, se investigaron los efectos del pH (2 - 6), la dosis de adsorbente (33 - 300 g/L) y el tiempo de contacto (1 - 30 h) mediante experimentos por lotes. Para estudiar las variables indicadas, se utilizaron soluciones sintéticas (250 ppm) preparadas con Cr(OH)SO₄. Posteriormente, se utilizó un efluente de curtiduría para aplicar las condiciones ideales seleccionadas para las soluciones sintéticas. Se empleó un espectrofotómetro de absorción atómica para determinar las concentraciones de Cr(III). Los resultados mostraron que la eficacia aumentaba con el incremento de la dosis de BA (200 g/L), el tiempo de contacto (20 h) y el pH 6. La eficacia del BA en la remoción del Cr(III) en el efluente real (57 %) fue inferior a la de las muestras sintéticas (72 %). El modelo cinético de pseudo-segundo orden y el equilibrio representado por la isoterma de Sips, con un rendimiento de 5,1 mg Cr/g BA, son los que mejor se ajustan a los datos experimentales.

Palabras clave: bioadsorbente, agua-residual, tallo-de-rosa, cromo

1. INTRODUCTION

The leather tanning industry has a significant economic impact worldwide; however, it has a negative impact on the environment, as chemical wastes generated during leather

processing are discharged into rivers and lakes, causing serious problems due to contaminated sediments. The tannery industry discharges a large quantity of wastewater without an adequate treatment, especially when the wastewater contains dissolved heavy metals. Effluents are often highly polluted with heavy metals, organic and inorganic substances (Chowdhury et al.,

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2015). Among these contaminants, Cr (III) dissolved in water poses a major health and environmental concern due to its high toxicity to various life forms (Prabhakaran et al., 2009). Generally, trivalent and hexavalent chromium are the two forms of Cr present in wastewater generated by these types of industries. Although both are hazardous, Cr (VI) is more dangerous since it is carcinogenic and mutagenic (AL-Othman et al., 2012).

The removal of chromium from aqueous solutions has been the subject of several high-tech methods, such as bipolar membrane electrodialysis (Wu et al., 2020), nanoadsorbents (Eyvazi et al., 2019), chemical coagulation and electrocoagulation processes (Martín-Domínguez et al., 2018), membrane processes (Noah et al., 2020), adsorption using nanomaterials, and activated carbon (Singh et al., 2018). Most of these methods have achieved a high degree of effectiveness, but they involve large production and operational costs, especially for adsorbents based on activated carbon. Disposal of residual metal sludge is another inconvenience. On the other hand, the adsorption technique using low-cost biosorbents is one of the methods currently preferred by researchers for the removal of heavy metals from aqueous solutions because it is an environmentally friendly technology (Simón et al., 2022).

Biosorption is a powerful technique in which biological materials have a high capacity to capture heavy metals from wastewater on their surface by metabolic or physicochemical means during the adsorption process (Abdulsalam, 2014a). Bioadsorbents are made from diverse biomasses, such as agro-by-products, including bagasse, sawdust, seeds, sugar industry waste, and sweet potato peel (Abiodun et al., 2023; Aguiar et al., 2022; Balintova & Estokova, 2024).

Rose farming represents an important economic activity worldwide; therefore, substantial amounts of waste are generated, which can be reused to synthesize these bioadsorbent materials. Rose stems are a compelling type of waste because they are a source of cellulose fibers (linear polymers). Their adsorption capacity has been little studied. Cellulose is a useful material for studying the adsorption of heavy metals and organic molecules owing to its mechanical strength, hydrogen-bonding capacity, high surface area, and crystallinity. However, although they lack functional groups that can bind metals, they can still form hydrogen bonds with different molecules (El Achaby et al., 2017; Ilyas et al., 2018; Moriana et al., 2016).

Nevertheless, biosorbents have low sorption capacities. The sorption performance of biosorbents depends on their surface properties and porosity. A cationic surfactant, hexadecyltrimethylammonium (HDTMA) bromide (Abiodun et al., 2023; Aguiar et al., 2022; Balintova & Estokova, 2024; Fertu et al., 2022; Namasivayam & Sureshkumar, 2008; Madeła & Skuza, 2021), strong acids, and bases can be used to modify surface properties to improve performance. Chemical treatment with a strong base solution (NaOH or KOH) has been used to solubilize and remove the hemicellulose fraction (Jiang and Hsieh, 2015). Nevertheless, most applied techniques involve hydrolysis with H_2SO_4 to obtain better properties such as small particle size,

crystallinity, and tensile strength (Kallel et al., 2016; Leite, et al., 2017). After modification, biomaterials exhibit high sorption capacities for both anionic and cationic substances. Since the regenerated bioadsorbent now contains functional groups (carboxyl, hydroxyl, sulfate, phosphate, and amino) they are capable of binding metal ions.

This study presents an important alternative that can take advantage of the large amount of biomaterials generated in rose farming. The use of these materials in the adsorptive method is a powerful way not only to remove toxic pollutants, such as chromium, from wastewater, but also to prevent them from accumulating in the environment. The present work focuses on the synthesis of an adsorbent based on rose stem by-products and its separate chemical modification with H_2SO_4 , NaOH, and $Na_3C_6H_5O_7$. Cr (III) removal from a synthetic aqueous solution was studied by varying pH, sorbent dosage, and contact time (Raji et al., 2023). Tannery wastewater was then treated under the selected conditions for the synthetic solutions. Langmuir-Freundlich isotherms were used for the analysis of the data, and the kinetics of the Cr (III) adsorption system were studied using pseudo-first- and second-order laws (Wiśniewska et al., 2022).

2. MATERIAL AND METHODS

2.1 Chemicals and instruments

All reagents used in this study were of analytical grade. Sulfuric acid (H_2SO_4), sodium hydroxide (NaOH), sodium citrate ($Na_3C_6H_5O_7$), and basic chromium sulfate [$Cr(OH)SO_4$]. Cr(III) analysis was performed using an Atomic Absorption spectrophotometer (Buck Scientific, Accusys 211) equipped with an acetylene flame and a hollow cathode lamp. The adsorbent was characterized through Fourier Transform Infrared (FTIR) spectroscopy using a JASCO FT/IR-100 spectrophotometer to determine the different functional groups found in the material.

2.2 Preparation of the biosorbent

Rose stem waste was obtained from a rose farm in Ecuador. The stems were chopped to a uniform size (1 inch), dried for five days in the sun, and then dried again in an oven (Memmert, UN30) for five hours at $105^\circ C$. The dried material was ground into a homogeneous powder and sieved to obtain the desired particle size fraction ($212 \mu m$). The sieved biomass was chemically modified using different compounds to obtain a higher adsorption capacity (Abdulsalam, 2014b; Namasivayam & Sureshkumar, 2008). Four grams of BA were placed in three beakers, and 20 mL of the modifier was added to each of them at the same concentration (0.5 mol/L). Sulfuric acid, sodium hydroxide, and sodium citrate were used as modifiers. The material was allowed to rest for 24 h, and then the BA was filtered under vacuum and dried at room temperature for 24 h. The dried materials used in the subsequent sorption studies are shown in Figure 1.

2.3 Tannery wastewater characterization

The physicochemical parameters determined in the tannery effluent include pH, temperature (Standard Methods 2550 B), conductivity (Standard Methods 2510), dissolved solids, suspended solids, and total solids (Standard Methods 2540 B). The concentration of chromium ions was determined using an Accusys 211 spectrophotometer (Standard Methods 3111 B direct air-acetylene flame method).



Figure 1. Chemically modified bioadsorbents

2.4 Biosorption experiments

Synthetic solutions containing 250 ppm of chromium were prepared with basic chromium sulfate to study the factors influencing the adsorption of this metal. The adsorbent dose was evaluated at concentrations of 33, 67, 100, 133, 167, 200, 233, 267, and 300 g/L. To study the influence of the pH on the adsorption process, variations of the pH (sodium hydroxide 6 mol/L) were carried out in five experimental units: 2, 3, 4, 5, and 6. The solutions were stirred for 30 h, and chromium was determined by taking samples at certain time intervals (1, 3, 5, 12, 18, 24, and 30 h). All tests were performed in triplicate. For the experiments with the tannery effluent, the ideal dosage and pH conditions selected for the synthetic solution were applied. The samples were characterized before the experiments to determine the initial values.

Cr (III) concentration was measured with an atomic absorption spectrophotometer (Buck Scientific, Accusys 211). To determine Cr (III), a hollow cathode lamp was set up in the spectrophotometer at 358 nm using an acetylene flame.

Equation (1) was used to calculate the amount of Cr (III) removed from the solution per mass unit of adsorbent (adsorption capacity):

$$q_e = \frac{(C_0 - C_f)}{m} V \quad (1)$$

Where q_e represents the Cr adsorption range (mg/L), C_0 represents the initial Cr concentration (mg/L), C_f represents the residual Cr concentration (mg/L), m represents the adsorbent dosage (g), and the sample volume is V (Bhattacharya and Sharma, 2005; Javed et al., 2007; Rafati et al., 2018). Subsequently, seven Cr concentrations ranging from 300 to 2,000 mg/L were prepared and analyzed in the experiments, which applied pseudo-first- and pseudo-second-order kinetics.

$$\log (q_e - q_t) = \log (q_e) - \frac{k_1}{2.303} t \quad (2)$$

Here in Equation (2), q_e and q_t represent the amounts of chromium adsorbed on the bioadsorbent at equilibrium (mg/L), t corresponds to the contact time (min), and k_1 (L/min) represents the adsorption rate constant of first-order kinetics.

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

Then, Equation (3) is the second-rate kinetic equation, where k_2 is the second-rate kinetic constant (g/mg.min), q_e is the amount of substance adsorbed at equilibrium in terms of the adsorption mass (mg/g), q_t is the amount of Cr adsorbed at equilibrium in terms of the adsorption mass at time t (mg/g), and t represents time (min) (Bhattacharya and Sharma, 2005).

$$q_e = \frac{q_{max} (K_s C_e)^{1/ns}}{1 + (K_s C_e)^{1/ns}} \quad (4)$$

In equation (4), the Langmuir-Freundlich adsorption model used to determine the adsorption isotherm, q_e corresponds to the adsorption capacity of the solid at equilibrium (mg/g); q_{max} represents the maximum adsorption capacity (mg/g); K_s corresponds to the Sips equilibrium constant or affinity constant, C_e is the equilibrium concentration of the metal in solution (mg/L), and $1/ns$ represents the heterogeneity factor of the system.

3. RESULTS AND DISCUSSION

3.1 Physicochemical Properties of Tannery effluent

The physicochemical parameters of the tannery effluent used in this study are listed in Table 1. The water required adequate treatment for human and environmental protection, as all the controlled parameters were beyond the established limit according to the World Health Organization standard. Chromium was the only heavy metal measured in this study since it is one of the most toxic for humans and the environment. It was found that the concentration of Cr in this effluent must be lowered before it is released into the environment.

Table 1. Tannery wastewater's physicochemical parameters

Parameter	Value	Potable water
Total chromium (mg/L)	1 540	-
pH	4.0	6 - 9
Temperature (°C)	21.0	< 40
Conductivity (µs/cm)	34.3	N/A
Total solids (mg/L)	983.0	1 600
Dissolved solids (mg/L)	343.0	-
Suspended solids (mg/L)	210.0	220

3.2 Preparation of the biosorbent

Chemically modified BA using sulfuric acid gave a better adsorption efficiency (71 %) in solutions with a relatively low concentration of the pollutant (250 ppm) compared to the concentration of the wastewater from the tannery industry (1,500 ppm). On the other hand, virgin BA adsorbed only 14 % of Cr (III). The low adsorptive rate of virgin BA justifies the chemical treatments carried out to modify it.

Table 2. Cr(III) adsorption capacity (%) of the modified bioadsorbents using 0.5 M of different solutions

Adsorbent	*[Cr] ₀ sample (ppm)	*[Cr] _f sample (ppm)	Adsorption (%)
Virgin	248.5	214.5	14
H ₂ SO ₄ modified BA	248.5	72.2	71

NaOH modified BA	248.5	79.1	68
Na ₂ C ₆ H ₅ O ₇ modified BA	248.5	77.9	69

*[Cr]₀ and *[Cr]_f are initial and final concentration of Cr (III) in the solutions, respectively

The spectra of rose stems are shown in Figure 2. The FT-IR analysis confirms that the modified bioadsorbents have more active sites for adsorption. The peak at 3,320.82 cm⁻¹

corresponds to the stretching vibration of the NH₂ groups (primary amines, aromatic amines, and amides) in Figure 2-a). An antisymmetric and symmetric stretching vibration band of aliphatic compounds of methyl and methylene groups (-CH₃ and -CH₂) is shown at 2,877.27 cm⁻¹.

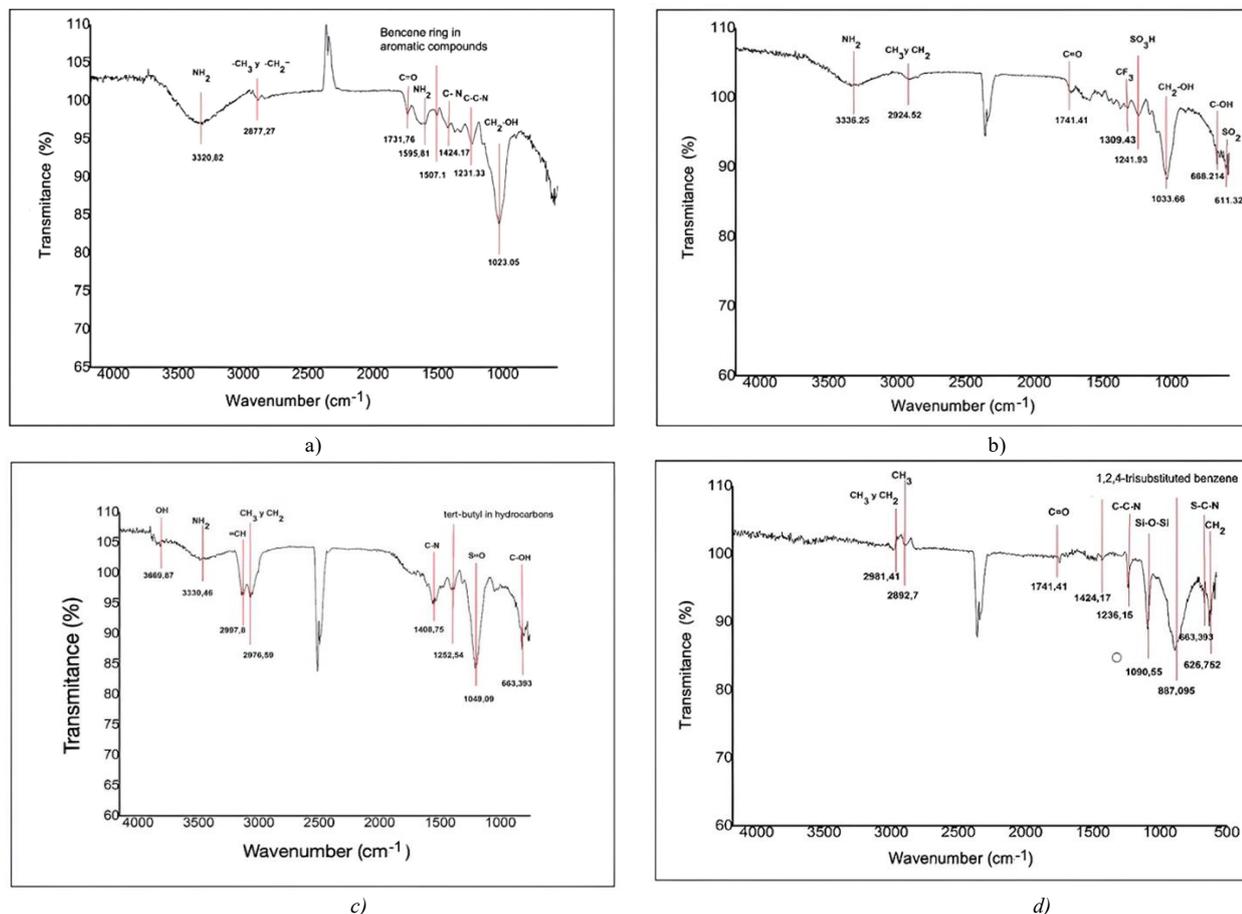


Figure 2. FT-IR spectra of a) virgin BA b) BA modified with H₂SO₄ c) BA modified with NaOH d) BA modified with Na₂C₆H₅O₇

The band at 1,731.76 cm⁻¹ corresponds to the stretching vibration of the C=O group of hemicellulose (Saurabh et al., 2016). The primary alkyl amide group (NH₂) belongs to the vibration at 1,595.81 cm⁻¹ (Zhang et al., 2018). The stretching vibration of a benzene ring in aromatic compounds is represented by a band at 1,507.1 cm⁻¹ (Ilyas et al., 2018). The C-N group of primary amides in proteins is represented by the stretching vibration at 1,424.17 cm⁻¹ (Jiang and Hsieh, 2015). The antisymmetric stretching vibration of the C-C-N groups in the amides is represented by a band at 1,231.33 cm⁻¹. The band at 1,023.35 cm⁻¹ corresponds to a cyclic carbon ring vibration (Zhang et al., 2018; Zhou et al., 2018).

Figure 2-b) shows a band at 1,309.43 cm⁻¹, which corresponds to the stretching of CF₃ attached to a benzene ring. The vibration of sulfonic acid (SO₃H) corresponds to the band at 1,241.93 cm⁻¹. The band at 1,033.66 cm⁻¹ corresponds to the vibration of primary alcohols (CH₂OH). The bending vibration of the CH-OH alcohol groups in cellulose was seen at 668.241 cm⁻¹. Finally, vibration of the sulfone group (SO₂) was observed at 611.324 cm⁻¹. The peak at 1,049.09 cm⁻¹ corresponds to the vibration of alkylsulfoxides (S=O), and the peak at 663.393 cm⁻¹ corresponds to the C-OH stretching

vibration in Figure 2 c) (Guerrero-Coronilla et al., 2014; Zhang et al., 2018).

Figure 2-d) shows two bands at 2,981.41 and 2,892.70 cm⁻¹. These bands represent the antisymmetric and symmetric stretching vibrations of aliphatic compounds (-CH₃ and -CH₂). The bending vibration of the siloxane groups causes a band at 1,236.15 cm⁻¹ (Si-O-Si). In addition, the band at 887.09 cm⁻¹ corresponds to the deformation vibration of 1,2,4-trisubstituted benzene. The stretching vibration of the thiocyanate group (S-C=N) is represented by the band at 663.39 cm⁻¹. Finally, the spectrum shows a band at 626.75 cm⁻¹ due to the curved vibration of the N-C=O groups in amides. In the FT-IR spectrum of H₂SO₄ modified BA, different functional groups such as alcohols, sulfonic groups, amides, and esters were observed. These groups favored the Cr (III) adsorption process. This is confirmed by the analysis presented in Table 2.

3.3 Adsorbent dose and pH effect

The effects of the BA's modifications and their dosages on Cr (III) uptake are shown in Figure 3. As the dosage of BA

increased, the percentage of uptake also increased as reported in another research (Abdulsalam, 2014b). The three modified BA maintained a similar behavior. Therefore, 200 g/L of BA modified with sulfuric acid and sodium hydroxide reached 72.68 % uptake of Cr (III) from the solution. In addition, 233 g/L of BA treated with sodium citrate achieved 69 %. Otherwise, the removal by virgin BA was only 14 %. The sulfuric acid-modified BA was the best, since it achieved 72 % of Cr(III) adsorption, with the same dose (200 g/L). However, as the dosage further increased, the efficiency of the removal process decreased; thus, equilibrium was reached at that dosage, and the desorption of the ions starts from there.

Figure 4 shows the effect of the pH on Cr (III) removal. The ideal dosage (200 g/L) was used in the experiment. As can be seen, increasing pH improved metal adsorption (up to 76 %); therefore, the maximum removal occurred at pH 6. If the pH increases further, the metal starts to precipitate as chromium hydroxide $\text{Cr}(\text{OH})_3$, and the adsorption process does not take

place properly (Abdulsalam, 2014b; Namasivayam and Sureshkumar, 2008).

3.4 Adsorption kinetics

Figure 5 shows that at the end of the first hour, the adsorption percentage is 24%. This value increases with contact time, reaching equilibrium at 72% adsorption after 20 hours, beyond which no significant variation is observed. A better description of Cr adsorption kinetics using the pseudo-second-order model is shown in Figure 6. Therefore, this model describes the experimental data in an acceptable manner, with $k_2 = 0.033$ and $q_e = 6.256$ mg/g, and a correlation coefficient R^2 of 0.919. Meanwhile, the pseudo-first-order model correlation coefficient was $R^2 = 0.889$. The pseudo-second-order model then describes the process as chemical adsorption or chemisorption, showing that Cr (III) adsorption occurs at two active sites in the BA (Salazar-Pinto et al., 2021).

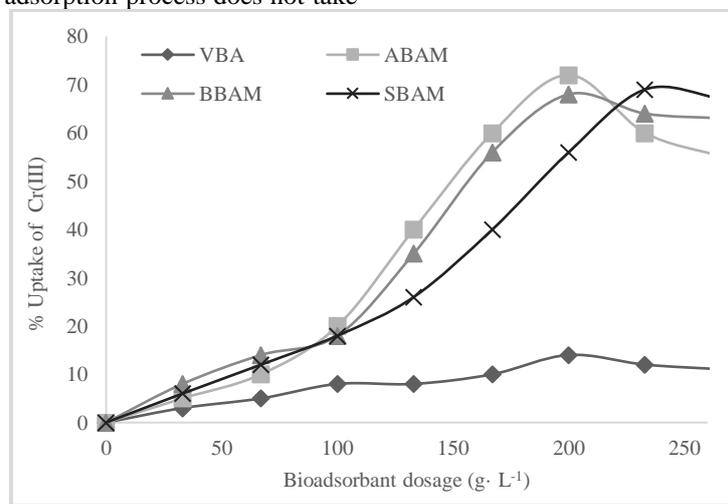


Figure 3. Effect of the biosorbent dosage on the uptake of Cr (III)

VBA: Virgin BA; ABAM: BA modified with sulfuric acid; BBAM: BA modified with sodium hydroxide; SBAM: BA modified with sodium citrate

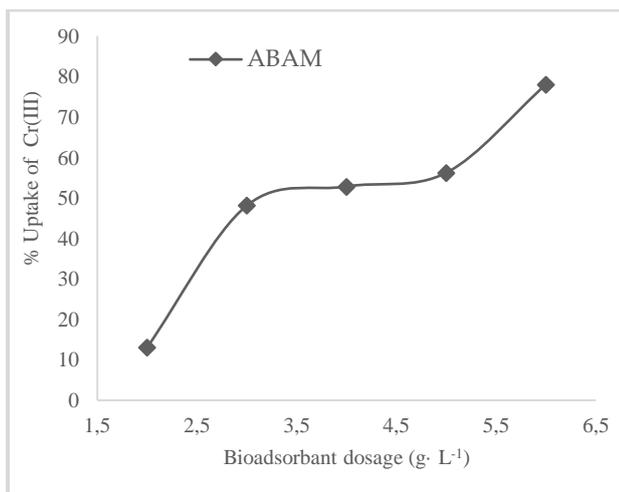


Figure 4. Effect of the pH value on the uptake of Cr(III)

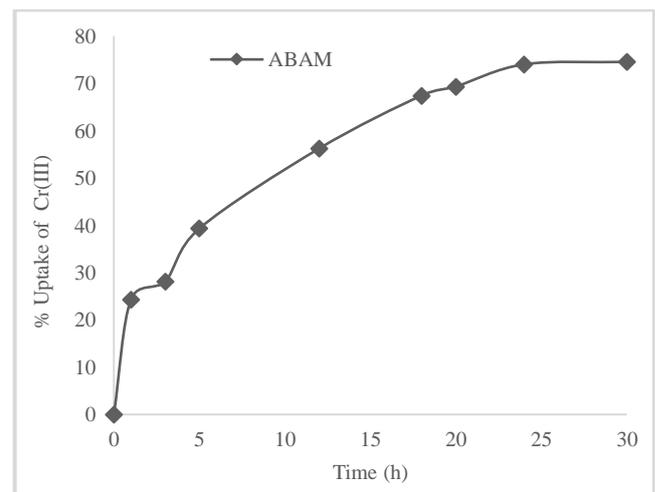


Figure 5. Adsorption kinetics of Cr(III) uptake from the solution

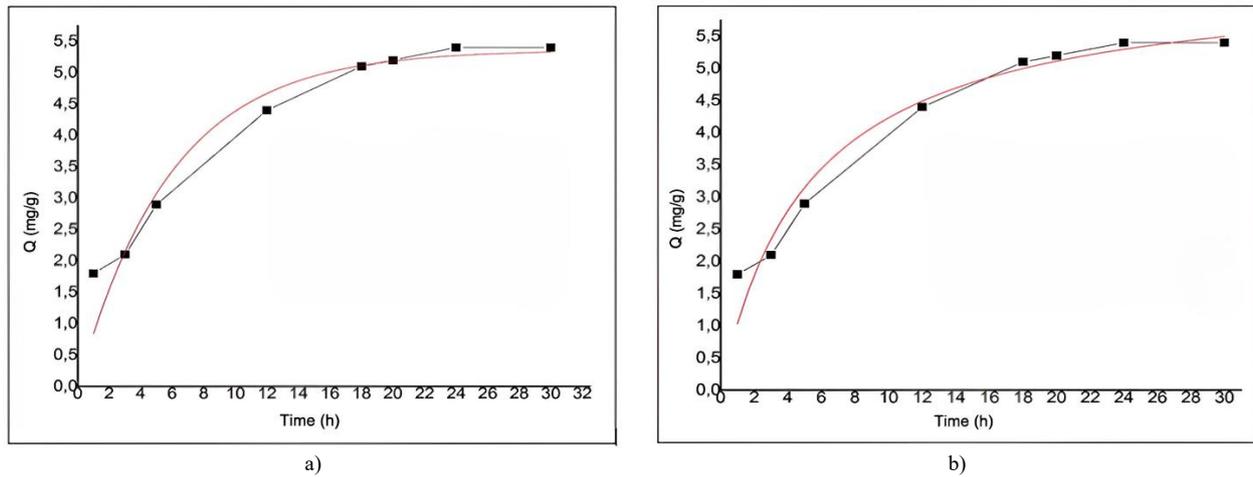


Figure 6. Pseudo-kinetics on the uptake of Cr (III) with two models: a) first order b) second order

In Figure 7, the Langmuir-Freundlich (Sips) model presents a correlation coefficient (R^2) of 0.986 and $n = 2.94$, indicating that the surface of the BA is heterogeneous (Pliego-Arreaga et al., 2013). The adsorption isotherm was S-shaped, meaning that the equilibrium concentration of Cr in solution (C_e) increases the adsorption capacity of the bioadsorbent (Q) until it reaches the saturation point of the active adsorption centers (Pliego-Arreaga et al., 2013). Furthermore, this isotherm occurs due to the low attractive intermolecular forces between the adsorbent and the adsorbate; at that point, the molecules of the solvent and other adsorbates compete with each other for the adsorption centers (Chi et al., 2020).

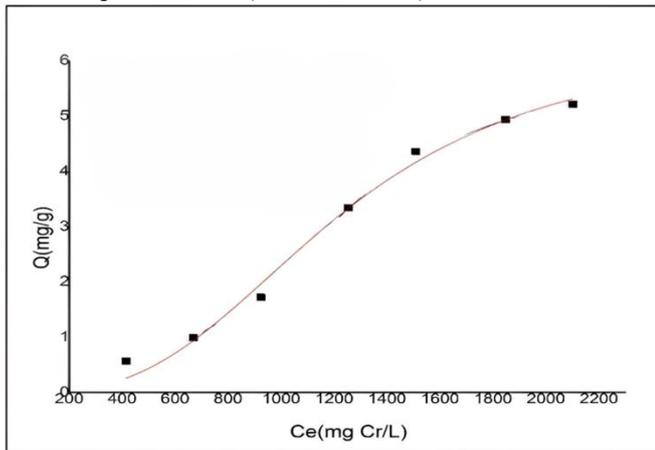


Figure 7. Langmuir-Freundlich adsorption isotherms and kinetic modeling of Cr

3.5 Adsorption study in a tannery wastewater under optimal conditions

The optimal conditions for the Cr adsorption from synthetic solutions, including adsorbent dosage (200 g/L), contact time (20 h), and pH (6), were used for the study, whose results are shown in Figure 8. The efficiency of the modified BA in removing Cr (III) from tannery effluent samples decreased from 1,500 (72 %) in the synthetic solutions to 645 ppm (57 %). The difference in adsorption might be due to the presence of other metallic cations and organic substances in the solution used in the tanning process (Chi et al., 2020). These substances in tannery wastewater compete with Cr (III) for active sites on

the material surface, thus reducing the adsorption capacity for Cr (Namasivayam and Sureshkumar, 2008). Therefore, we can affirm that rose stems have a high adsorption capacity for Cr (III) only when these ions are not competing with other cations. In this way, the stems of the roses could be used to absorb metals such as chromium that are present in the tannery water.

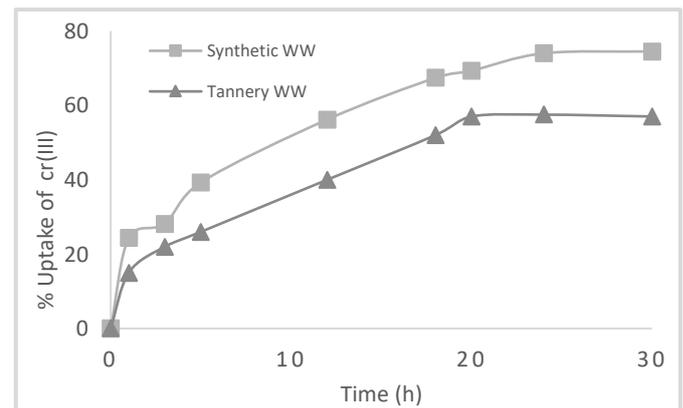


Figure 8. Adsorption kinetics of Cr(III) uptake from the solution using synthetic and tannery water.

4. CONCLUSIONS

The rose stem-based bioadsorbent was confirmed to be effective in removing Cr (III) ions from tannery effluents. The surface modification of BA by H_2SO_4 , ratified by the FT-IR analysis, significantly increased its chromium (III) adsorption efficiency compared to unmodified BA (14 %). Active adsorption sites were incorporated into the surface of the BA. A 72 % of Cr (III) was removed within 20 h from the synthetic solutions (250 ppm) at pH 6 and a BA dose of 200 g/L. However, 57 % of this heavy metal was removed by applying these conditions to wastewater from a tannery industry. This reduction can be explained by the presence of other metal cations and substances competing with Cr (III) for the active sites on the modified BA. The pseudo-second-order equation better represented the Cr removal kinetics since this model shows that Cr (III) adsorption occurs at two active sites and describes the process as chemisorption. Finally, the adsorption

isotherm was adjusted to the Langmuir-Freundlich model since this process occurs in multiple layers.

REFERENCES

- Abdulsalam, S. (2014a). Biosorption of Chromium (VI) Ion from Tannery Waste Water Using Two Novel Agricultural By-Products. *International Journal of Innovation, Management and Technology*, 5(2). <https://doi.org/10.7763/ijimt.2014.v5.490>
- Abdulsalam, S. (2014b). Biosorption of Chromium (VI) Ion from Tannery Waste Water Using Two Novel Agricultural By-Products. *International Journal of Innovation, Management and Technology*, 5(2), 78–82. <https://doi.org/10.7763/ijimt.2014.v5.490>
- Abiodun, O.-A. O., Oluwaseun, O., Oladayo, O. K., Abayomi, O., George, A. A., Opatola, E., Orah, R. F., Isukuru, E. J., Ede, I. C., Oluwayomi, O. T., Okolie, J. A., & Omotayo, I. A. (2023). Remediation of heavy metals using biomass-based adsorbents: Adsorption kinetics and isotherm models. *Clean Technologies*, 5(3), 934–960. <https://doi.org/10.3390/cleantechnol5030047>
- Aguiar, A. B., Costa, J. M., Santos, G. E., Sancinetti, G. P., & Rodriguez, R. P. (2022). Removal of metals by biomass derived adsorbent in its granular and powdered forms: Adsorption capacity and kinetics analysis. *Sustainable Chemistry*, 3(4), 535–550. <https://doi.org/10.3390/suschem3040033>
- AL-Othman, Z. A., Ali, R., & Naushad, M. (2012). Hexavalent chromium removal from aqueous medium by activated carbon prepared from peanut shell: Adsorption kinetics, equilibrium and thermodynamic studies. *Chemical Engineering Journal*, 184(March), 238–247. <https://doi.org/10.1016/j.cej.2012.01.048>
- Balintova, M., & Estokova, A. (2024). Materials for heavy metals removal from waters. *Materials*, 17(9), Article 1935. <https://doi.org/10.3390/ma17091935>
- Bhattacharya, K. G., & Sharma, A. (2005). Kinetics and thermodynamics of Methylene Blue adsorption on Neem (*Azadirachta indica*) leaf powder. *Dyes and Pigments*, 65(1), 51–59. <https://doi.org/10.1016/j.dyepig.2004.06.016>
- Chi, Y., Yang, P., Ren, S., & Yang, J. (2020). Sorption of heavy metals from aqueous solution by biochar derived from anaerobically digested sludge: Kinetics and mechanism. *Science of the Total Environment*, 715, 138954. <https://doi.org/10.1016/j.scitotenv.2020.138954>
- Chowdhury, M., Mostafa, M. G., Biswas, T. K., Mandal, A., & Saha, A. K. (2015). Characterization of the Effluents from Leather Processing Industries. *Environmental Processes*, 2(1), 173–187. <https://doi.org/10.1007/s40710-015-0065-7>
- El Achaby, M., El Miri, N., Aboukas, A., Zahouily, M., Bilal, E., Barakat, A., & Solhy, A. (2017). Processing and properties of eco-friendly bio-nanocomposite films filled with cellulose nanocrystals from sugarcane bagasse. *International Journal of Biological Macromolecules*, 96, 340–352. <https://doi.org/10.1016/j.ijbiomac.2016.12.040>
- Eyvazi, B., Jamshidi-Zanjani, A., & Khodadadi Darban, A. (2019). Synthesis of nano-magnetic MnFe₂O₄ to remove Cr(III) and Cr(VI) from aqueous solution: A comprehensive study. *Environmental Pollution*, (xxxx), 113685. <https://doi.org/10.1016/j.envpol.2019.113685>
- Fertu, D. I., Bulgariu, L., & Gavrilăscu, M. (2022). Modeling and optimization of heavy metals biosorption by low-cost sorbents using response surface methodology. *Processes*, 10(3), Article 523. <https://doi.org/10.3390/pr10030523>
- Guerrero-Coronilla, I., Morales-Barrera, L., Villegas-Garrido, T. L., & Cristiani-Urbina, E. (2014). Biosorption of amaranth dye from aqueous solution by roots, leaves, stems and the whole plant of *E. crassipes*. *Environmental Engineering and Management Journal*, 13(8), 1917–1926. <https://doi.org/10.30638/eemj.2014.212>
- Ilyas, R. A., Sapuan, S. M., & Ishak, M. R. (2018). Isolation and characterization of nanocrystalline cellulose from sugar palm fibres (*Arenga Pinnata*). *Carbohydrate Polymers*, 181, 1038–1051. <https://doi.org/10.1016/j.carbpol.2017.11.045>
- Javed, M. A., Bhatti, H. N., Hanif, M. A., & Nadeem, R. (2007). Kinetic and equilibrium modeling of Pb(II) and Co(II) sorption onto rose waste biomass. *Separation Science and Technology*, 42(16), 3641–3656. <https://doi.org/10.1080/01496390701710794>
- Jiang, F., & Hsieh, Y. Lo. (2015). Cellulose nanocrystal isolation from tomato peels and assembled nanofibers. *Carbohydrate Polymers*, 122, 60–68. <https://doi.org/10.1016/j.carbpol.2014.12.064>
- Kallel, F., Bettaieb, F., Khiari, R., García, A., Bras, J., & Chaabouni, S. E. (2016). Isolation and structural characterization of cellulose nanocrystals extracted from garlic straw residues. *Industrial Crops and Products*, 87, 287–296. <https://doi.org/10.1016/j.indcrop.2016.04.060>
- Leite, A. L. M. P., Zanon, C. D., & Menegalli, F. C. (2017). Isolation and characterization of cellulose nanofibers from cassava root bagasse and peelings. *Carbohydrate Polymers*, 157, 962–970. <https://doi.org/10.1016/j.carbpol.2016.10.048>
- Madela, M., & Skuza, M. (2021). Towards a circular economy: Analysis of the use of biowaste as biosorbent for the removal of heavy metals. *Energies*, 14(17), Article 5427. <https://doi.org/10.3390/en14175427>
- Martín-Domínguez, A., Rivera-Huerta, M. L., Pérez-Castrejón, S., Garrido-Hoyos, S. E., Villegas-Mendoza, I. E., Gelover-Santiago, S. L., ... Buelna, G. (2018). Chromium removal from drinking water by redox-assisted coagulation: Chemical versus electrocoagulation. *Separation and Purification Technology*, 200, 266–272. <https://doi.org/10.1016/j.seppur.2018.02.014>
- Moriana, R., Vilaplana, F., & Ek, M. (2016). Cellulose Nanocrystals from Forest Residues as Reinforcing Agents for Composites: A Study from Macro- to Nano-Dimensions. *Carbohydrate Polymers*, 139, 139–149. <https://doi.org/10.1016/j.carbpol.2015.12.020>
- Namasivayam, C., & Sureshkumar, M. V. (2008). Removal of chromium(VI) from water and wastewater using surfactant modified coconut coir pith as a biosorbent. *Bioresource Technology*, 99(7), 2218–2225.

- <https://doi.org/10.1016/j.biortech.2007.05.023>
 Noah, N. F. M., Sulaiman, R. N. R., Othman, N., Jusoh, N., & Rosly, M. B. (2020). Extractive continuous extractor for chromium recovery: Chromium (VI) reduction to chromium (III) in sustainable emulsion liquid membrane process. *Journal of Cleaner Production*, 247(Vi), 119167. <https://doi.org/10.1016/j.jclepro.2019.119167>
- Prabhakaran, S. K., Vijayaraghavan, K., & Balasubramanian, R. (2009). Removal of Cr(VI) ions by spent tea and coffee dusts: Reduction to Cr(III) and biosorption. *Industrial and Engineering Chemistry Research*, 48(4), 2113–2117. <https://doi.org/10.1021/ie801380h>
- Rafati, L., Ehrampoush, M. H., Rafati, A. A., Mokhtari, M., & Mahvi, A. H. (2018). Removal of ibuprofen from aqueous solution by functionalized strong nano-clay composite adsorbent: kinetic and equilibrium isotherm studies. *International Journal of Environmental Science and Technology*, 15(3), 513–524. <https://doi.org/10.1007/s13762-017-1393-0>
- Raji, Z., Karim, A., Karam, A., & Khalloufi, S. (2023). Adsorption of heavy metals: Mechanisms, kinetics, and applications of various adsorbents in wastewater remediation—A review. *Waste*, 1(3), 775–805. <https://doi.org/10.3390/waste1030046>
- Salazar-Pinto, B. M., Zea-Linares, V., Villanueva-Salas, J. A., & Gonzales-Condori, E. G. (2021). Cd (I) and pb (ii) biosorption in aqueous solutions using agricultural residues of phaseolus vulgaris l.: Optimization, kinetics, isotherms and desorption. *Revista Mexicana de Ingeniera Química*, 20(1), 305–322. <https://doi.org/10.24275/rmiq/IA1864>
- Saurabh, C. K., Mustapha, A., Masri, M. M., Owolabi, A. F., Syakir, M. I., Dungani, R., ... Abdul Khalil, H. P. S. (2016). Isolation and characterization of cellulose nanofibers from gigantochloa scortechinii as a reinforcement material. *Journal of Nanomaterials*, 2016. <https://doi.org/10.1155/2016/4024527>
- Simón, D., Palet, C., Costas, A., & Cristóbal, A. (2022). Agro-industrial waste as potential heavy metal adsorbents and subsequent safe disposal of spent adsorbents. *Water*, 14(20), Article 3298. <https://doi.org/10.3390/w14203298>
- Singh, N. B., Nagpal, G., Agrawal, S., & Rachna. (2018). Water purification by using Adsorbents: A Review. *Environmental Technology and Innovation*, 11, 187–240. <https://doi.org/10.1016/j.eti.2018.05.006>
- Wiśniewska, M., Marciniak, M., Gęca, M., Herda, K., Pietrzak, R., & Nowicki, P. (2022). Activated biocarbons obtained from plant biomass as adsorbents of heavy metal ions. *Materials*, 15(17), Article 5856. <https://doi.org/10.3390/ma15175856>
- Wu, X., Zhu, H., Liu, Y., Chen, R., Qian, Q., & Van der Bruggen, B. (2020). Cr(III) recovery in form of Na₂CrO₄ from aqueous solution using improved bipolar membrane electro dialysis. *Journal of Membrane Science*, 604(January), 118097. <https://doi.org/10.1016/j.memsci.2020.118097>
- Zhang, J. wei, Bi, F. zhi, Wang, Q. jia, Wang, W. lin, Liu, B., Lutts, S., ... Han, R. ming. (2018). Characteristics and influencing factors of cadmium biosorption by the stem powder of the invasive plant species Solidago canadensis. *Ecological Engineering*, 121(October), 12–18. <https://doi.org/10.1016/j.ecoleng.2017.10.001>
- Zhou, Z., Xu, Z., Feng, Q., Yao, D., Yu, J., Wang, D., ... Zhong, M. e. (2018). Effect of pyrolysis condition on the adsorption mechanism of lead, cadmium and copper on tobacco stem biochar. *Journal of Cleaner Production*, 187, 996–1005. <https://doi.org/10.1016/j.jclepro.2018.03.268>

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