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Production of biosorbent from peanut shell for hexavalent chromium removal from wastewater

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Abstract

The pyrolysis process was used for the production of biosorbent and carried out a study for removal of Cr (VI) in aqueous solutions. The material was classified as micro-mesoporous with surface area 326.5 $m^2.g^{-1}$, total pore volume 0.1849 $cm^3.g^{-1}$ and average pore size of 22.6 Å. The adsorption investigation showed that the contact time required between the biosorbent and the solution for Cr (VI) adsorption to occur is relatively high. In the equilibrium isotherms the best fitted was Langmuir model. The adjustment presented a coefficient of determination of 0.98 and an associated average error of 7.8%. From this adjustment, the maximum adsorption capacity of the adsorbent was determined to be approximately 33.79 mg of Cr (VI)/g of biosorbent. The results of this study show that this adsorbent material prepared by pyrolysis has a good response when applied to the removal of Cr (VI) in aqueous solutions when compared with other adsorbents.

Keywords: peanut shell; pyrolysis; hexavalent chromium; biochar; adsorption.

1. Introduction

Chromium, in metallic form or derivative products, such as salts, complexes, and alloys, has diverse applications across various industries, primarily in leather processing, the textile industry, the manufacture of metallic alloys, galvanization, and the production of electronic components [1, 2]. Chromium can be found in two forms in nature, Cr (VI) and Cr (III), with the hexavalent form being the most toxic [3]. Like other heavy metals, chromium is non-biodegradable and toxic to humans. Industrial effluents using Cr (VI) in production processes are major sources of water contamination with chromium [4]. Due to the toxicity of Cr (VI), it is crucial to control its concentrations in wastewater.

Removing toxic metal ions from contaminated wastewater is essential for environmental protection and water treatment. Various strategies, such as adsorption, extraction, and oxidation-reduction, have been adopted to eliminate radionuclides and heavy metal ions from water environments. Among these, adsorption is effective due to its simple design, wide adaptability, and easy operation [5]. The use of biosorbents as adsorbent materials has been studied in this context. Biosorbents are materials rich in carbon (65-90%) produced from the pyrolysis of biomass, containing oxygenated and aromatic functional groups and numerous pores [6].

This study aimed to analyze the performance of a biosorbent made from peanut shells in removing hexavalent chromium from simulated wastewater through adsorption. Peanut shells, representing 25-30% of the total weight of peanuts and often discarded [7], are abundant as industrial waste and are suitable for biosorbent production due to their high carbon content from cellulose and hemicellulose [8]. Batch adsorption tests were conducted to evaluate the biosorbent's potential for removing Cr (VI) from wastewater. The data were fitted to adsorption isotherms to determine the maximum removal capacity, which was then compared to other adsorbents for hexavalent chromium removal.

2. Methods

2.1 Biosorbent preparations and characterization

The biosorbent was prepared via pyrolysis process using a raw material peanut shell. The sample was pyrolyzed in a bench reactor. Then approximately 30 g peanut shell dried was used in a quartz tubular reactor and submitted at 800 ° C (5

°C.min^{-1}) for 30 min in inert atmosphere (N_2 at 0.15 L.min^{-1}). The resulting bio-oil and biosorbent were collected and weighed in order to determine the process yield, the gaseous fraction was quantified by difference. The samples (pean nutshell and biosorbent) were characterized using XRD, SEM, FTIR and N_2 adsorption/desorption isotherm techniques.

2.2 Adsorption assays

For the adsorption study, a stock solution of $K_2Cr_2O_7$ (500 ppm) was prepared. The assays were carried out in at 25ºC under vigorous stirred. For the equilibrium study, 0.2 g of biosorbent was added to 100 mL of solution at different initial concentration (15, 25, 45, 60 e 75 ppm) and the pH was adjusted at 2.5. Then, some aliquots were taken at different times during the experiment until the equilibrium. For the quantification of Cr (VI), the solid phase was separated by centrifugation and the concentration Cr (IV) in liquid phase was determined by spectrophotometry (λmax = 540 nm) using a spectrophotometer (BEL photonics, SP 1105). The samples were analyzed after complexation with 1,5-diphenylcarbazide.

For the adsorption study of Cr (VI) on the biosorbent, the expressions presented in Table 1 were used. To evaluate the adjustments of these equations, we used nonlinear regression analysis. The determination coefficient (R^2), adjusted determination coefficient (R^2 adj), and average relative error (ARE) were used to evaluate the fit quality.

Table 1. Equations used in adsorption study.

Parameter	Equation	Unit	Eq.	Ref.
Removal percentage and adsorption capacity				
removal percentage	$R = \frac{(C_0 - C_t)}{C_0} 100$	%	(1)	
qe equilibrium adsorption capacity	$q_e = \frac{V(C_0 - C_e)}{m}$	mg/g	(2)	
Equilibrium isotherms				
Freundlich	$q_e = k_F C_e^{\frac{1}{n}}$	mg/g	(3)	[9]
Langmuir	$q_e = \frac{q_m k_L C_e}{1 + k_L C_e}$	mg/g	(4)	[10]

3. Results and discussion

3.1 Biosorbent and characterization

Firstly, the yield for biosorbent was approximately 27.7 %, which confirms good performance of the pyrolysis process. The physical and chemical properties of peanut shell and its biochar are shown in Figure 1 and 2. The biosorbent presented a high BET surface area 326.5 m².g^{-1}, high total pore volume 0.1849 cm³.g^{-1} and average pore size of 22.6 Å. The N_2 adsorption/desorption isotherm (Fig 1 (a)) is a mixture of type I and II isotherms (a) with type H4 hysteresis loop [11], the pore structure of the biosorbent can be classified as micro-mesoporous. Figure 1 (b) shows the morphology of the char, examined by scanning electron microscope.

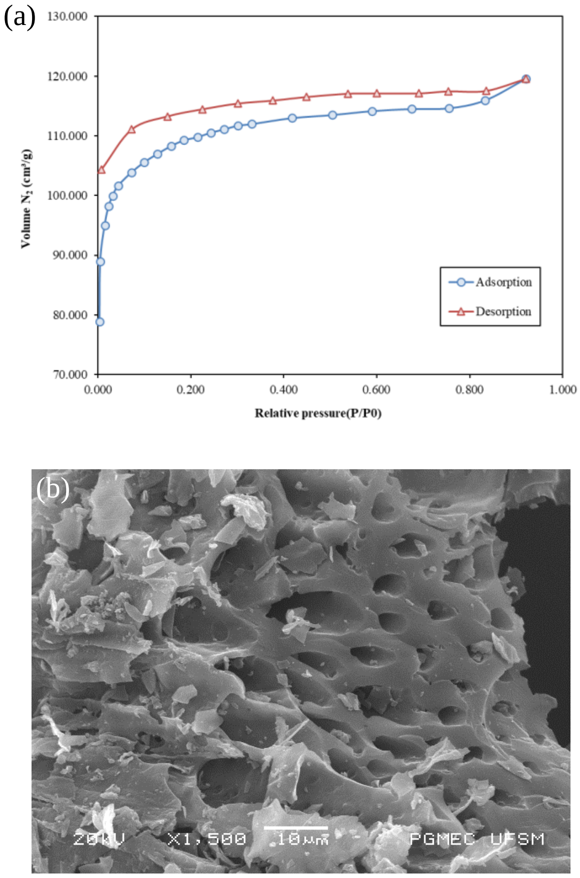

Figure 1. (a) Nitrogen adsorption–desorption isotherms and (b) SEM image of the biosorbent.

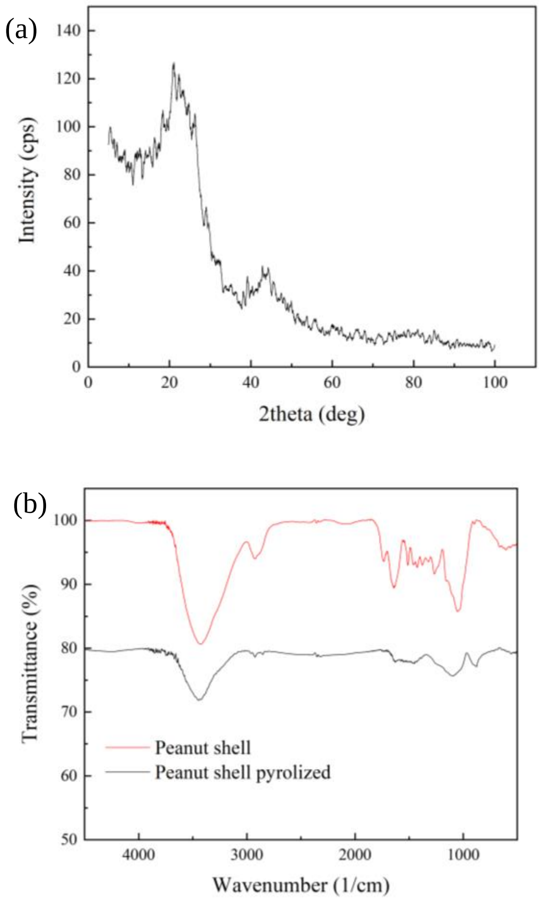

Figure 2. (a) XRD spectrum of the biosorbent (b) FTIR spectra of Peanut shell and biosorbent.

The X-ray diffraction patterns were measured to investigate the type of structure of this sample. The XRD diffraction patterns, shown in Fig. 2 (a), indicate that no crystalline phase was observed in this material. The sample exhibited an amorphous structure. Generally, an amorphous structure is suitable for dye adsorption purposes. An amorphous adsorbent has a more disorganized structure with more empty spaces, allowing the accommodation of large dye molecules on the adsorbent surface [12].

The FTIR vibrational spectra of peanut shell and pyrolyzed peanut shell are shown in Fig. 2(b). For the peanut shell, the main intense bands were observed at 3435 cm^{-1}, 2925 cm^{-1}, 1641 cm^{-1}, and 1052 cm^{-1}. The band at 3435 cm^{-1} is attributed to O-H stretching vibrations, the band at 2925 cm^{-1} to C-H, the band at 1641 cm^{-1} to C=C stretching of aromatic rings, and the band at 1052 cm^{-1} to C-O-C of an ether group. After pyrolysis, the volatile matter was removed, leaving only the 3435 and 1641 bands at lower intensity. This confirms the removal of volatile matter, likely increasing the material's surface area, as corroborated by SEM images, shown in Fig. 1(b), showing an irregular surface with pores formed from the peanut shell.

3.2 Adsorption study

Firstly, for lower initial concentrations of chromium (15 and 45 ppm) was observed that the equilibrium was reached close to 240 minutes. For higher concentrations (60 to 75 ppm) the equilibrium was observed after 24 hours. This means that the contact time required between the biosorbent and the solution for Cr (VI) adsorption to occur is relatively high. Regarding the removal capacity at equilibrium, qe, this was calculated after 24 hours, for each concentration and represented graphically in Figure 3. The simulation of equilibrium isotherms of Cr (VI) on the biosorbent at 298 K were in Figure 3 and the fitting results are presented in Table 2.

Both in the graph and in the table, the Langmuir model was the best fitted. The adjustment presented a coefficient of determination of 0.98 and an associated average error of 7.8%. The Freundlich model, was not a good representation of the data. This is reinforced by a low R^2 value (0.89) and high ARE value (17.3%). From this adjustment, the maximum adsorption capacity of the adsorbent (qm) was determined to be approximately 33.79 mg of Cr (VI)/g of biosorbent. Then, it was possible to compare the material studied here with other materials present in the literature, regarding the removal of hexavalent chromium. This comparison is represented in Table 3. As can be seen, the biosorbent from peanut shells has a high removal capacity, compared to other materials, in the adsorption of Cr (VI).

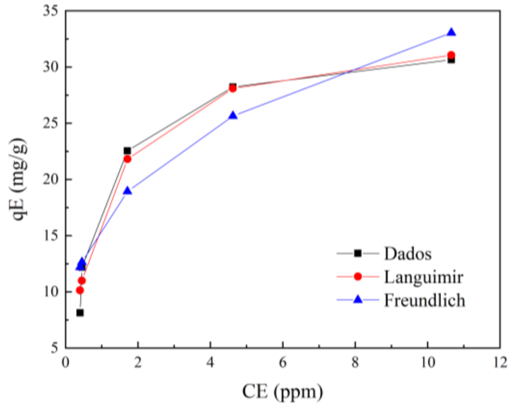

Figure 3. Comparison between experimental and Langmuir and Freundlich models.

Table 2. Isotherm parameters.

Model	Parameter	Value
Langmuir	q_m ($mg.g^{-1}$)	33.7921
	k_L ($L.mg^{-1}$)	1.0652
	R^2	0.9843
	ARE (%)	7.8599
Freundlich	k_F ($mg.g^{-1}$)($mg.L^{-1}$)$^{-1/n}$	16.0893
	1/n	0.3043
	R^2	0.8919
	ARE (%)	17.2858

Table 3. Comparison of the adsorption capacity of different biosorbents for the removal of Cr (VI).

Biosorbent	Adsorption capacity (mg/g)	Reference
Sisal fibers	0.39	[13]
Sugarcane bagasse	1.8	[14]
Potato starch modified	4.8 – 24.4	[15]
Potato peel	8.01	[16]
Rice husk	11.40	[17]
Coconut shell	18.70	[17]
Peanut shell	33.79	This study

4. Conclusion

In the present study, a biosorbent was produced and evaluated from peanut shells as an alternative adsorbent for the removal of hexavalent chromium from wastewater, with special interest in industrial effluents. The removal of Cr (VI) is necessary due to its toxicity and carcinogenic potential. The yield of the pyrolysis process was around 27.7% of biosorbent. The maximum adsorption capacity was around 34 $mg.g^{-1}$, indicating that the adsorption performance of the material prepared in this work was high when compared to other adsorbents reported in the literature. Findings suggest that pyrolysis has potential to create effective, adsorbents relevant to environmental ap plication. Finally, the results indicated that this biosorbent is an effective adsorbent for the removal of Cr (VI) ions from aqueous solutions, and it could be useful in treatment of Cr (VI) polluted wastewaters.

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