

Removal of Cr(VI) ions from aqueous solution using orange peel residual biomass: thermodynamic and sorption–desorption study

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ABSTRACT

In the search for cost-effective materials able to remove heavy metals pollutants from aqueous solution, fruit peel emerges as an attractive source of biomass with remarkable adsorption properties. In this work, orange peel biomass was used to study the chromium uptake during sorption-desorption cycles. The cement-based immobilization technique was also applied for further biosorbent disposal. The biomass was characterized before and after adsorption via Fourier-transform infrared spectroscopy (FT-IR) analysis. The experiments were conducted in batch mode at fixed pH (2), contact time (5 h), and dosage (0.67 g). The operating temperature ranged from 306.9–349.4 K in order to assess the thermodynamics governing the adsorption process. For desorption cycles, two different agents were chosen (nitric acid and hydrochloric acid). The FT-IR spectrum showed peaks around 1,444; 1,650; and 3,300 cm^{-1} corresponding to the aliphatic, carbonyl, and hydroxyl functional groups. The standard Gibbs free energy ranged around 6.22–6.56 kJ mol^{-1} , while the standard enthalpy and entropy were calculated in 4.2 kJ mol^{-1} and $-0.0067 \text{ kJ mol}^{-1} \text{ K}^{-1}$, respectively. The adsorption capacity of orange peel biomass was reduced by 50% at the end of the third cycle. The highest mechanical resistance (34.07 kgf cm^{-2}) after biomass immobilization was reached for 5% biomass-blocks. For this block, the leaching tests reported the concentration of heavy metals in the leachate of 0.2134 ppm. These results confirmed the suitability of the stabilization/solidification technique to immobilize heavy metal ions for bricks with biomass composition of 5% and 7.5%.

Keywords: Adsorption; Desorption; Immobilization; Orange peel; Chromium

1. Introduction

The uncontrolled discharges of pollutants coming from industrial activities generate serious environmental issues affecting the biodiversity and human health worldwide, which motivates the search of suitable alternatives for wastewater treatment. Among the wide variety

of contaminants found in surface/subsurface water and landfill leachates, heavy metals are considered of major importance due to their extreme toxicity and bioaccumulation [1]. The presence of these toxic metals like nickel and zinc are commonly associated with brass manufacturing, mining processing, and batteries [2]. Based on the corollaries of heavy metals exposure, there is growing

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interest in enhancing the effectiveness (as well as reducing the cost) of alternatives implemented for heavy metals uptakes such as adsorption, ion exchange, flocculation, and chemical precipitation [3,4]. The adsorption technology has been addressed by several contributions owing to its advantages over other alternatives: (i) easy operation, (ii) high efficiency, (iii) cost-effectiveness, (iv) low generation of toxic sludge, (v) low energy requirements [5]. However, the efficiency of heavy metals adsorption is significantly affected by the type of material used as adsorbent as well as its physicochemical properties. For example, the functional groups in the adsorbent surface are responsible for the attachment and concentration of metal ions, which leads to high or low removal efficiency [6].

The use of agricultural biomasses for preparing cost-effective adsorbent has gained scientific attention because agricultural wastes like fruit peel, shells, and straw are low-cost, can be implemented under a simple approach, and have proved to adsorb efficiently heavy metal pollutants [7–9]. The juice industry generates a huge amount of valuable waste materials like orange peel, which exhibit excellent properties for pollutant uptake. Tejada-Tovar et al. [10] prepared a biosorbent from orange peel biomass for hexavalent chromium ions uptake and reported removal yield around 66.8%. Rane and Sapkal [11] also used orange peel powder to remove Cr(VI) ions from aqueous solution in batch adsorption experiments and obtained removal yields up to 98%. The main limitation of the adsorption process is the disposal of biosorbent after completing its useful life. Hence, alternatives for the encapsulation of heavy metals are being needed.

The aim of this work is to study sorption-desorption cycles of orange peel wastes used as biosorbent in the removal of hexavalent chromium ions. Besides, thermodynamics governing the adsorption process were analyzed by calculating standard entropies, enthalpies, and Gibbs free energy. The final disposition of polluted biomass was covered by the application of stabilization/cement-based solidification technique and evaluation of leaching and mechanical resistance of resulting blocks.

2. Methodology

2.1. Preparation of biomass

Orange peel biomass was provided by local markets in Cartagena de Indias (Colombia). This biomaterial was washed thoroughly with water in order to remove impurities that may hinder the adsorption process [10]. Then, moisture content was removed by drying biomass in an oven (Lauda Alpha, 97922 Lauda-Königshofen, Germany) at 60°C for 24 h. The dried biomass was grounded and sieve-meshed to a particle size of 1 mm according to the optimum conditions reported by authors in previous works [10,12]. Diversification of functional groups was tested by performing Fourier-transform infrared spectroscopy (FT-IR) before and after the adsorption process. This characterized was recorded in attenuated total reflectance mode over the range of 500–4,000 cm^{-1} using a Thermo Scientific Nicolet 6700 FT-IR spectrometer (168 3rd Ave, Waltham, MA 02451, United States of America).

2.2. Sorption-desorption cycles

The stock solution was prepared by dissolving $\text{K}_2\text{Cr}_2\text{O}_7$ (ACS reagent > 99%, Merck Millipore, 400 Summit Drive Burlington, Massachusetts, MA 01803, United States of America) into deionized water to obtain an initial concentration of 100 ppm. The initial solution pH was fixed at 2 by adding 1 M solution of HCl or NaOH. The values for other operating parameters as temperature, contact time, and biosorbent dosage were 25°C, 5 h, and 0.67 g, respectively. After completing the contact time, Cr(VI)-loaded biomass was subjected to desorption cycles with 100 mL of hydrochloric acid and nitric acid solutions as desorbing agents. For this purpose, stirring rate and desorption time were fixed in 150 rpm and 3 h, respectively. Also, three different concentrations (0.1, 0.5, and 1 M) were studied using the agent that reports the highest desorption yield. For regeneration, 20 mL of solution 1 M calcium chloride was kept in contact with the biomass previously filtered during 12 h at 4°C. Finally, the regenerated biomass is sent to an oven to reduce moisture content completing the requirements to start another cycle [13].

2.3. Thermodynamic study

The nature of chromium adsorption onto orange peel biomass was analyzed from a thermodynamic point of view by varying the temperature to 306.9, 328.2, and 349.4 K. The thermodynamic parameters such as Gibbs free energy, enthalpy and entropy provide relevant information related to the reversibility as well as endothermic or exothermic nature. The following equations were used to quantify the changes in these parameters based on the Van't Hoff's graphical method. In this method, ΔH° and ΔS° are determined from the slope and the y -axis intercept of $\ln K_c$ vs. T^{-1} .

$$K_c = \frac{(Q_T)}{C_T} \quad (1)$$

$$\ln K_c = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (2)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (3)$$

where ΔH° is the change in the enthalpy, ΔS° is the change in the entropy, ΔG° is the change in the standard Gibbs free energy, K_c is the equilibrium constant, Q_T is the adsorption capacity at equilibrium (mg g^{-1}), C_T is the equilibrium concentration (mg g^{-1}), R is the ideal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) and T is the absolute temperature (K).

2.4. Solidification/stabilization immobilization technique

An immobilization technique was applied in this work to avoid environmental issues concerning residual biosorbent disposal. After sorption-desorption cycles, polluted biomass was mixed with clay until achieving compositions of 5%, 7.5%, and 10% biomass. The resulting mixture was heated at 70°C before sending it to a muffle at 800°C, in which compact bricks are obtained [14]. The work performed by Ukwatta and Mohajerani [15] served as guidance

to perform mechanical compression resistance for determining the quality of the cement bricks. The presence of hexavalent chromium ions in the bricks may release leachates when contacting liquids; hence, the efficiency of the immobilization technique was evaluated via leaching tests. To this end, samples of bricks were mixed with 96.5 mL of water and acetic acid solution until pH = 4.93, the latter was chosen as extracting fluid based on the contributions available in the literature [15]. The experiments were carried out by adding 1 g of bricks into 20 mL of extracting fluid for 18 h. The final concentration of leachate was measured using UV-VIS spectroscopy and compared to environmental regulations.

3. Results and discussion

3.1. Biomass characterization

Fig. 1 shows the FT-IR spectrum for orange peel biomass before and after the adsorption process, which is used to analyze the presence of functional group vibrations. The peak around 1,444 cm^{-1} is assigned to aliphatic and aromatic groups. The stretching vibrations of C=C group were identified at 1,650 cm^{-1} frequently found in the lignin structure. The absorption bands at 3,300 and 3,400 cm^{-1} are attributed to stretching vibrations of hydroxyl groups [9,16]. It was also found a reduction in peaks intensity after adsorption for hydroxyl and carboxyl groups suggesting the interaction between heavy metal ions and biomass functional groups [17]. Similar results were reported by Garzón and González [18] using the orange peel for chromium biosorption. They found stretching of absorption bands corresponding to the carbonyl, carboxyl, and aliphatic groups.

3.2. Sorption–desorption study

3.2.1. Effect of desorbing agent type

In order to determine the type of desorbing agent that achieves the highest desorption yield, experiments were

performed using 1 M HNO_3 and HCl solutions. As is shown in Fig. 2, desorption yields were significantly low for both acid solutions suggesting that metallic ions are strongly fixed in biosorbent surface. These results were compared with those found in the literature. For example, Seco et al. [19] employed 0.01 M NaNO_3 solution for desorbing chromium ions from pine sawdust and oak ashes and reported desorption yields of 98% and 66%, respectively. Besides, Desance et al. [20] achieved desorption yields for *Lemna* biomass above 97% using 0.01 M ethylenediaminetetraacetic acid solution. The nitric acid solution was selected for performing sorption-desorption cycles because of its better results in comparison with hydrochloric acid.

After selecting the desorbing agent, different concentrations of nitric acid solution were tested in order to determine the most suitable value. As shown in Fig. 3, desorption yield increased with higher desorbing agent concentration, hence, 1 M solution was selected for carrying out further experiments. These results may be attributed to the changes in the point of zero charges of biomass leading to release heavy metal ions from the surface as pH becomes more acidic.

3.2.2. Sorption–desorption cycles

The sorption cycles were performed under operating conditions of temperature, pH, and biosorbent dosage of 25°C, 2, and 0.67 g, respectively. Desorption cycles were also carried out according to the results obtained for the type and concentration of desorbing agents. As depicted in Fig. 4, it was found that biomass reduced its adsorption capacity after several cycles because of the saturation of active sites. At the end of the third cycle, removal yield was reduced by 50%. Fig. 5 shows the effect of successive cycles on the desorption yields. Results reported yields around zero using nitric acid as a desorbing agent. Arroyave et al. [21] suggested that chromium adsorption is an irreversible process because of the insignificant value for the amount of desorbed heavy metal ions.

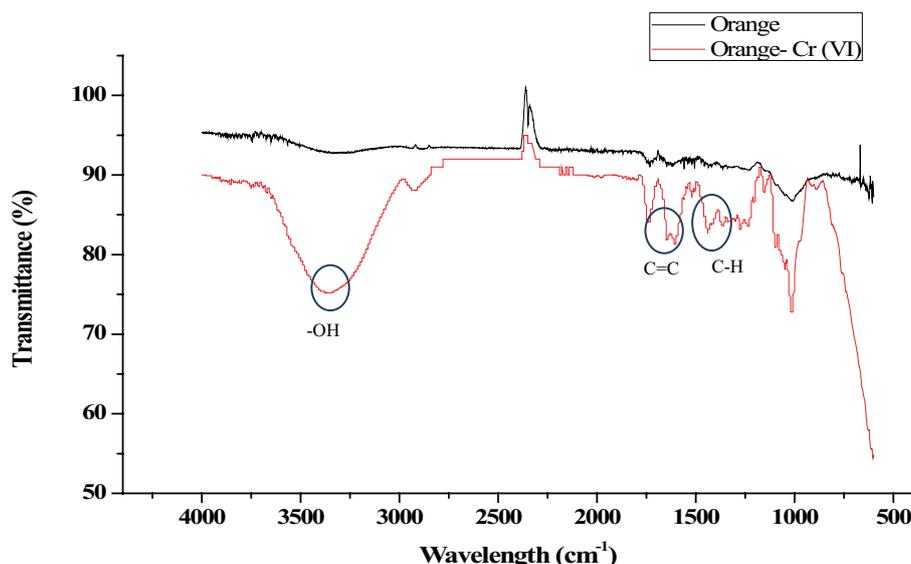


Fig. 1. FT-IR spectrum of orange peel biomass before and after Cr(VI) ions uptake.

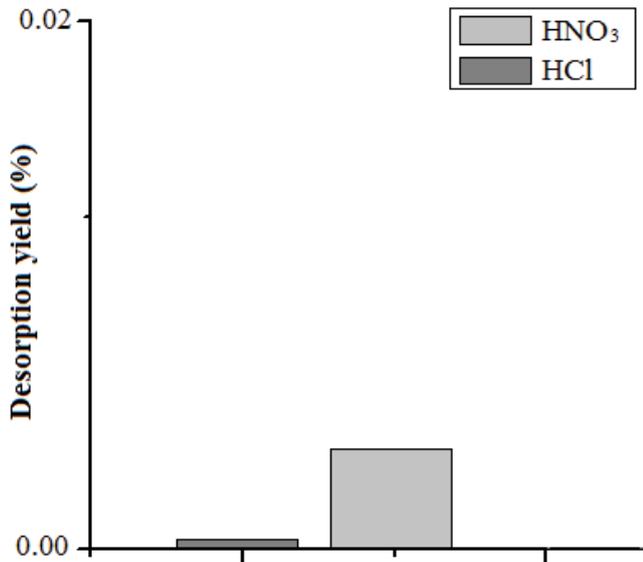


Fig. 2. Effect of desorbing agent type on desorption yields.

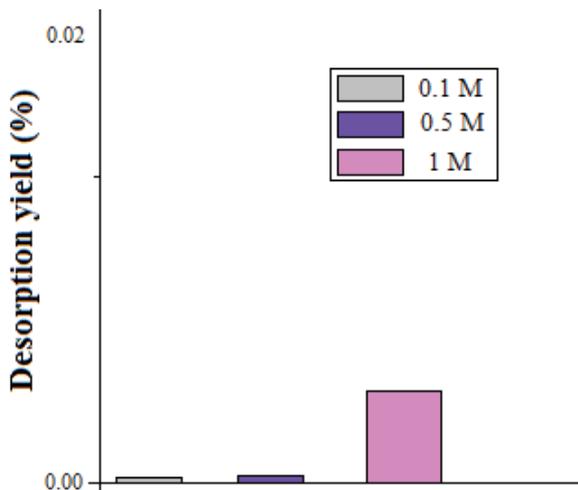


Fig. 3. Effect of desorbing agent concentration on desorption yields.

3.3. Thermodynamic study

Table 1 summarizes the values of thermodynamic parameters calculated for the three temperatures. The positive value of ΔH° suggested that the adsorption of chromium onto the biomass surface was endothermic and the energy required during removal must be externally supplied to

Table 1
Parameters results for different temperatures

Temperature (K)	ΔH° (kJ mol ⁻¹)	ΔS° (kJ mol ⁻¹ K ⁻¹)	ΔG° (kJ mol ⁻¹)
306.9	4.20	-0.0067	6.22
328.2	-	-	6.39
349.4	-	-	6.56

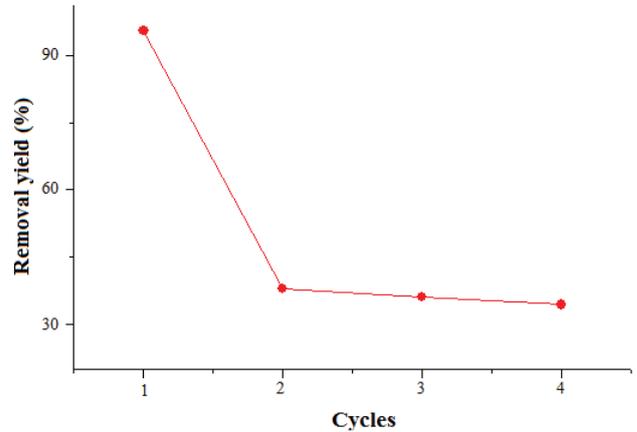


Fig. 4. Influence of cycles on removal yields.

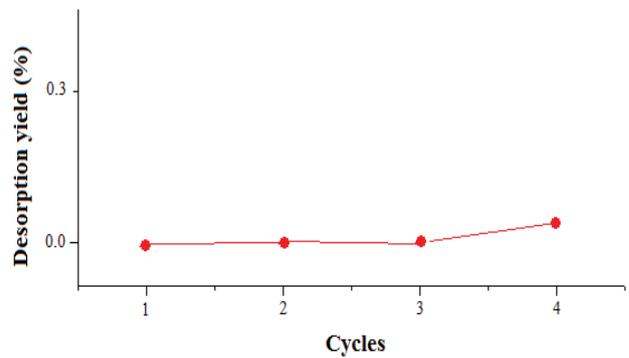


Fig. 5. Influence of cycles on desorption yields.

the system [22]. The negative value of ΔS° indicated that the links between ions and adsorbent surface obeyed the chemisorption process and the active sites of biomass have great affinity and selectivity to the heavy metal ions [23,24]. The positive values of ΔG° revealed that the process loses spontaneity and is not favorable; the increase in temperature of Gibbs free energy with temperature suggests that the process evolves on its own, naturally becoming favorable and spontaneous as temperature increases [25,26].

3.4. Mechanical resistance testing

The bricks prepared from clay and polluted biomass (5%, 7.5%, and 10% of biomass) were subjected to compression resistance testing. Table 2 summarizes the results obtained for the different compositions of bricks, which

Table 2
Mechanical resistance testing results

Biomass (%)	Area (cm ²)	Rupture force		Mechanical resistance	
		lb _f	kg _f	kgf cm ⁻²	Mpa
5	25	1,877.82	851.76	34.07	3.34
7.5	25	1,699.46	770.86	30.83	3.02
10	25	1,492.34	676.91	27.07	2.65

Table 3
Results for leaching tests

Biomass (%)	Leachate concentration (ppm)
5	0.2134
7.5	0.2574
10	0

were compared to the quality standard (3–14 MPa) [27]. It was found that compression resistance was reduced as increased the amount of polluted biomass, hence, bricks with 10% of biomass did not obey quality standards.

3.5. Leaching testing

A sample of bricks was mixed with the acetic acid solution under continuous stirring for 18 h and the leachate was characterized by UV-VIS spectrophotometry. As listed in Table 3, the leachate concentrations were within the limit stated by the environmental regulation (Decree 4741/2015) [28], suggesting the successful heavy metal ions encapsulation and applicability of these bricks without environmental impacts.

4. Conclusions

The behavior of orange peel biomass during Cr(VI) ions sorption-desorption cycles was analyzed in this work. The characterization of this biomaterial before and after adsorption suggested the interactions between functional groups on biomass surface and heavy metal ions. Despite the poor performance of both types of desorbing agents, it was selected the nitric acid solution at 1 M. The adsorption capacity of orange peel biomass decreased over the number of cycles exhibiting a reduction around 50% at the end of the third cycle. The thermodynamic parameters revealed that the adsorption process of chromium onto the biomass surface was endothermic and obeyed chemisorption. The application of the immobilization technique reported good results for both mechanical resistance and leachate concentration. The biomass concentration of 10% on bricks is not recommended for clay based-bricks preparation due to the low compression resistance below the quality standard.

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