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Application of Adsorption and Immobilization Techniques to Reduce Hexavalent Chromium Pollution using Banana Peels Residual Biomass as Biosorbent

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Abstract

Background: Contamination with heavy metal ions has been recognized an important issue that require alternatives to be faced. Adsorption is considered a promising technique to remove these pollutants from aqueous solution. However, disposal problems of polluted biomass have limited its application. **Objective:** In this work, banana peels biomass is employed as biosorbent for hexavalent chromium uptake. **Methods/Statistical Analysis:** The effects of particle size, temperature and dosage were considered during adsorption batch experiments. Sorption-desorption cycles were performed in order to analyze the biosorbent useful life. To solve biomass disposal problems, solidification/stabilization immobilization technique was used for heavy metal ions encapsulation through bricks preparation. These bricks were subjected to mechanical resistance and leaching tests to identify if they obey quality and environmental standard. **Findings:** Results revealed that biosorbent dosage was the parameter that most contributed adsorption process. After sorption-desorption cycles, the biosorbent reduced its removal capacity by 30%. **Application/Improvements:** The mechanical resistance and leaching tests suggested the applicability of residual biosorbent for preparing bricks due to the low leachate concentration and high compression resistance.

Keywords: Adsorption, Biomass, Desorption, Heavy Metals, Immobilization

1. Introduction

Several heavy metals have been discharged into the environment by industrial activities worldwide. Hexavalent chromium is considered one of the most common pollutant because of its wide applicability[1]. This heavy metal is employed in many industries as electroplating, paints, pigments, textile dyeing and tanning[2]. Chromium represents a major health concern in marine ecosystems because it is non-biodegradable and highly toxic[3]. To face this environmental issue, researchers have focused their attention on the development of suitable removal methods including ion exchange, chemical precipitation and adsorption. The advantages

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that adsorption technique offers (efficiency, low cost and ease of operation) have allowed to identify this method as a promising solution for heavy metal pollution[4]. One of the main limitations for adsorption application is the disposal problem of adsorbent material after sorption-desorption cycles, hence, many works have proposed the use of heavy metal encapsulation technologies such as solidification/stabilization immobilization, which reduce the potential migration of these pollutants in the waste[5].

Biomass from agricultural wastes are widely employed for preparing adsorbents due to its effectiveness and availability[6]. In addition, disposal problems are reduced as well as the attraction of air or vector-borne diseases[7]. Biomaterials as almond hull, pecan shells, rice, lemon peels and cassava peels are tested in adsorption processes[8, 9]. Among these, banana peels are attractive source of biomass due to the huge amount wasted every year[10]. The peels represent about 35% of the whole fruit weight, hence, it is advantageous to add value to a waste while environmental problems are solved[11]. In this work, banana peels biomass was used to remove hexavalent chromium ions from aqueous solution. After sorption-desorption cycles, the residual biosorbent was subjected to solidification/stabilization technique to encapsulate the pollutants.

2. Materials and Methods

2.1 Biomass Preparation

In brief, the banana peels biomass was washed with distillate water in order to remove adhered particles that can affect adsorption process. The resulting material was dried for 24 h at 60°C for further particle size reduction procedure. It was selected different particle sizes (1, 0.5 and 0.355 mm) to evaluate the effect of this parameter on adsorption process, which were obtained by grounding and sieve-meshing[12]. The functional groups in biomass surface were identified by Fourier-Transform Infrared Spectroscopy (FT-IR) before and after hexavalent chromium uptake.

2.2 Adsorption Batch Experiments

The adsorption experiments were carried out by mixing $K_2Cr_2O_7$ into deionized water to achieve a 100 ppm solution. The solution pH was adjusted using HCl and NaOH solutions as reported by[13]. The effect of temperature, particle size and biosorbent dosage was assessed with the aim of identifying suitable conditions for performing adsorption process. The temperature was varied in 40, 55 and 70°C. The values for biosorbent dosage were 0.15, 0.325 and 0.5 g. The contact time as well as stirring was fixed in 5 h and 200 rpm, respectively. Adsorption kinetics was studied under two different conditions for particle size (0.355 and 0.5 mm), biosorbent dosage (0.5 and 0.67 g) and temperature (25 and 40°C).

2.3 Sorption-Desorption Cycles

After adsorption batch experiments, biomass was filtered and mixed with 1 M nitric acid that was selected as desorbing agent. Desorption cycles were performed in a stirring plate under room temperature during 3 h[14]. The resulting biomass was filtered and washed before regeneration process using calcium chloride at 4°C for 12 h. The regenerated biosorbent was filtered and dried to start the following sorption-desorption cycle[15].

2.4 Solidification/Stabilization Immobilization Technique

The dried residual biomass after several sorption-desorption cycles was used to prepare bricks using clay. The composition of biomass in bricks was varied in 5, 7.5 and 10% to study the influence of polluted biosorbent on achieving quality and environmental standards. The mixture of clay and biomass was heated at 70°C for 24 h. Then, it was sent to a muffle at 800°C for 3 h in order to obtain compact bricks[16]. The mechanical resistance of these bricks was determined according to the methodology proposed by Ukwatta and Mohajerani[17]. Leaching tests were also performed to determine the applicability of this technique obeying environmental regulation. A bricks sample was collected and added to 96.5 mL of distillate water. Then, pH was measured and adjusted below 5 using HCl solution in order to identify the extraction fluid used in these tests[17]. To prepare the extraction fluid, 5.7 mL of acetic acid was added in 1000 mL of water. The leaching experiments were performed by mixing 1 g of bricks with 20 mL of extraction fluid under continuous stirring (30 rpm) for 18 h, followed by filtration.

3. Results and Discussion

3.1 Biomass Characterization

Figure 1 shows the spectrum of banana peels before and after adsorption process in order to identify functional groups affecting chromium ions uptake. It was observed absorption bands around 3600 and 1748 cm^{-1} assigned to hydroxyl and carbonyl groups, respectively, which are widely found in the chemical composition of lignocellulosic materials[18]. After adsorption process, variations in the spectrum are observed around 1000-1800 cm^{-1} confirming the contribution of carbonyl groups. As shown in Figure 2, the stretching of absorption band at 3600 cm^{-1} suggested the interaction of hydroxyl groups with Cr (VI) ions[13].

3.2 Adsorption Experiments

3.2.1 Effect of Particle Size

The influence of particle size on adsorption process was studied by varying particle size in 0.355, 0.5 and 1 mm. As shown in Figure 3, this parameter did not affect significantly the chromium ions uptake. It is well known that small particles exhibit high removal yield because of the increase in active sites. However, the porous capacity may not depend on particle size causing slight variation of adsorption results[19]. Figure 4 shows the adsorption results over different temperature conditions between 40 and 70°C. It was found that this parameter did not influence chromium removal and its increases were not significant over temperature variations. The biosorbent dosage was the parameter that most affected removal yields. As shown in Figure 5, the chromium uptake increased as

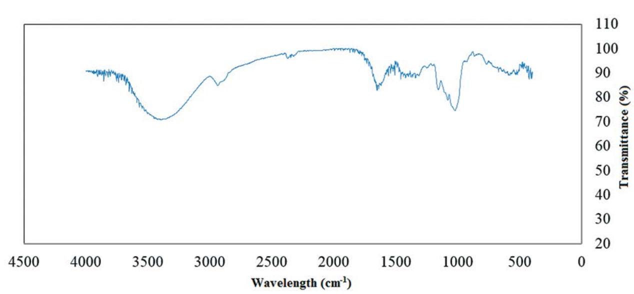

Figure 1. FT-IR spectrum of banana peels biomass.

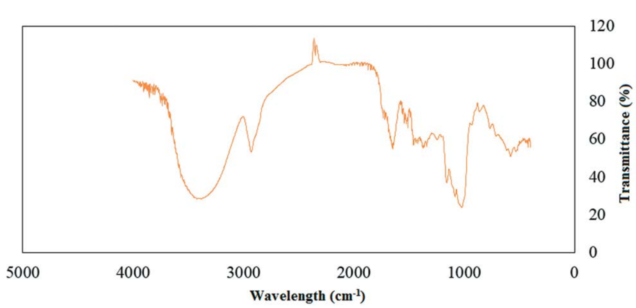

Figure 2. FT-IR spectrum of banana peels biomass after chromium uptake.

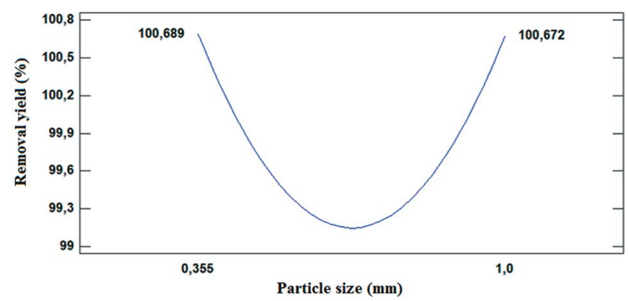

Figure 3. Effect of particle size on Cr (VI) ions removal yield.

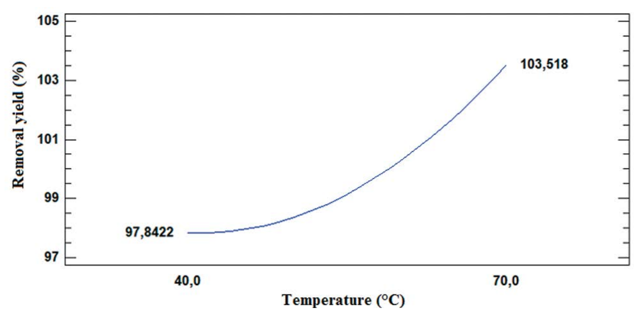

Figure 4. Effect of temperature on Cr (VI) ions removal yield.

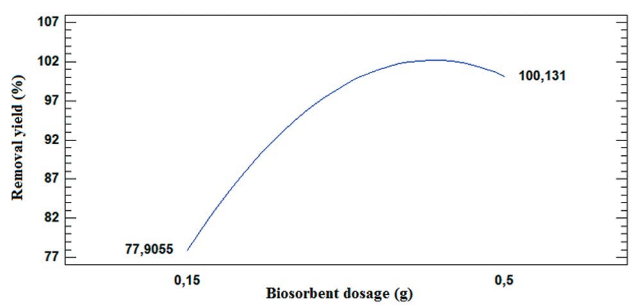

Figure 5. Effect of biosorbent dosage on Cr (VI) ions removal yield.

biosorbent dosage increased due to the presence of more active sites. These results were confirmed by applying Pareto chart shown in Figure 6. As can be observed, the parameter that most contributed to adsorption process was biomass dosage, followed by temperature and particle size[20] pointed out that increasing biomass amount enhances heavy metal ions uptake because of the increase in available active sites.

3.2.2 Adsorption Kinetics

Figure 7 shows the adsorption kinetics considering two different operating conditions that include variations in particle size, biosorbent dosage and temperature. The small-sized particles (0.355 mm) exhibited the highest adsorption at the beginning, similar removal yields were achieved more quickly using particle size of 0.5 mm. Hence, it was selected the following values for temperature, particle size and biosorbent dosage: 25°C, 0.5 mm and 0.67 g, respectively.

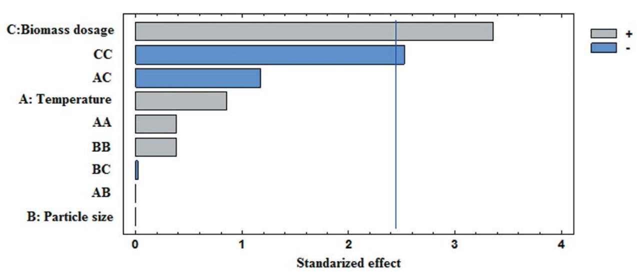

Figure 6. Pareto chart of adsorption parameters.

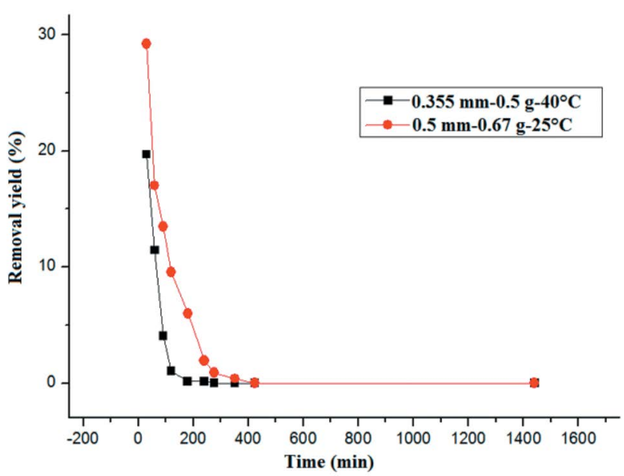

Figure 7. Adsorption kinetics results using banana peels for Cr (VI) ions uptake.

3.3 Adsorption-Desorption Cycles

As shown in Figure 8, banana peels biomass exhibited a reduction in adsorption capacity over the experimental cycles, which is attributed to biosorbent saturation affecting the number of available sites for heavy metal uptake[14]. At the end of the third cycle, removal yield was reduced by 30% suggesting a short useful life for this biomass. In addition, these results can be also explained by the effects of desorbing agents on the biosorbent that are employed to prepare the biomass for other adsorption cycle[21, 22] reported a reduction in removal yield around 13.3% after ten adsorption cycles using activated carbon for copper ions removal.

The desorption process was performed through nitric acid solution, which reported to be non-viable because of the low desorption yield results shown in Figure 9. In[23] also used this desorbing agent for Cr (VI) ions desorption from *Spirulina* sp. and obtained desorption yield of 98%. In[24] pointed out that hexavalent chromium adsorption is an irreversible process due to traces of desorbed metal are insignificant and are not affected by the increase in acid concentration. In[25] reported Cr (VI) ions desorption yield of 98% using mixtures of sodium hydroxide and sodium chloride.

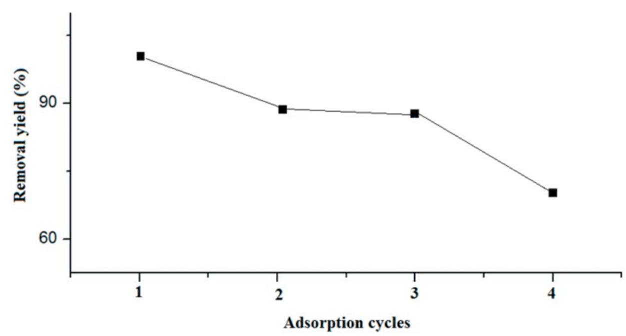

Figure 8. Effect of adsorption cycles on removal yield.

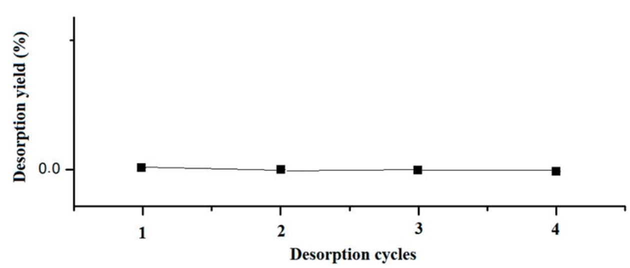

Figure 9. Desorption experimental results.

Table 1. Mechanical resistance of bricks

		Rupture force		Mechanical resistance	
Biomass (%)	**Area (cm^2)**	**lb_f**	**Kg_f**	**Kgf/cm^2**	**Mpa**
5	25	1739.743	789.133507	31.5653403	3.09550244
7.5	25	1584.4012	718.671709	28.7468684	2.81910477
10	25	876.733	397.679075	15.907163	1.5599598

Table 2. Results for leaching tests

Biomass (%)	Leachateconcentration (ppm)
5	0.09009
7.5	0
10	0.9009

3.4 Solidification/Stabilization Immobilization Technique

The bricks were prepared by mixing clay with polluted biosorbent (5, 7.5 and 10% of biomass). The mechanical resistance testing was performed using Soiltest Universal Machine. Table 1 summarizes the results obtained during these experiments. It was found that the bricks with 5 and 7.5 % of biomass obeyed the quality standard of 3-14 MPa reported in the regulation NTC 4017 (Nov. 2005)[26]. The leaching experiments were performed to evaluate the efficiency of solidification/stabilization technique for encapsulating heavy metal ions. As listed in Table 2, the leachate concentrations for all bricks were below 5 mg/L, which is the limit value reported by national environmental regulation (Decree 4741/2015)[27].

4. Conclusions

The solidification/stabilization immobilizationtechnique was applied to encapsulate hexavalent chromium ions in bricks containing polluted banana peels biomass, which obeyed environmental and quality standards. The characterization of banana peels biomass indicated the presence of hydroxyl and carbonyl groups that are recognized to enhance adsorption process.

The biosorbent dosage was identified as the parameter that most affects Cr (VI) ions uptake. The adsorption kinetics reported better results at 25°C, 0.5 mm and 0.67 g of temperature, particle size and biosorbent dosage, respectively. During adsorption-desorption cycles, the biomass reduced its removal capacity by 30%. The bricks prepared with clay and polluted biomass exhibited good resistance to compression above the quality standard using 5 and 7.5 % of biomass. For all bricks, leaching test showed leachate concentration below the environmental regulation indicating the suitability of this heavy metal encapsulation alternative from an environmental viewpoint.

5. Acknowledgement

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