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Passion-fruit shell biomass as adsorbent material to remove chromium III from contaminated aqueous mediums

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Abstract. The aim of the study was to evaluate an adsorbent material based on passion-fruit shell biomass (PFSB) for chromium III removal from contaminated aqueous mediums, composed of distilled water and different concentrations of Cr(III), with a dose of 5 g of PFSB per liter. The residual concentration of Cr(III) in the treated mediums was determined by Atomic Absorption Spectrophotometry. A good adsorption process was carried out, achieving removal levels up to 85, 80, and 53% for solutions of 20, 50 and 200 ppm of Cr(III), respectively. The results showed an adequate fit to Langmuir and Freundlich models (R^2 of 0.8864 and 0.7596, respectively), obtaining the following parameters q_{max} : 27.933 mg g⁻¹ and b: 0.029 (for Langmuir model), and k : 1.400 and n : 1.650 (for Freundlich model), with a good adsorbent-adsorbate interaction for Cr(III) according to FT-IR spectra. Therefore, the obtained results suggest that Cr(III) can be removed by more than 50% by using passion-fruit shell, which with a minimum treatment could be used as an adsorbent in the treatment of chromium-contaminated aqueous mediums.

1. Introduction

The study describes the application of passion-fruit shell biomass (PFSB), an agroindustrial waste which with a minimum treatment could be used as a low cost adsorbent material to remove Cr(III) through the mechanism of chemical adsorption, as potential alternative to the physicochemical treatments currently applied for the treatment of industrial effluents with high Cr(III) contents.

In Peru, industrial activities such as mining, leather tanning, paint manufacturing, uses in dyes, metal galvanizing, etc., generate considerable volumes of effluents with high contents of heavy metals, which are discharged into lakes and rivers, exceeding in many cases the maximum permissible limits [1]. Most of these metals cannot be easily degraded or removed from environmental, affecting the biodiversity and producing the mortality of living organisms [2–3]. Moreover, these metals can reach drinking water sources and food crops, affecting humans with severe health consequences when are ingested at high concentrations [2–5].

The leather and tanning industries are among the most important industries in Trujillo, a city located in the north of Peru. Tanning industry is considered the major source of both organic and inorganic pollutants, for example chromium (Cr), considering that the majority of leather produced is tanned using Cr salts.

Chromium is a transition metal that exists in several oxidation states, being trivalent Cr(III) and hexavalent C(VI) the dominant species [2], [6]. Both species show differences in their chemical properties,



and hazards due to environmental contamination depend on its oxidation state, being Cr(VI) more toxic than Cr(III), which precipitates at higher pH [6]. Unlike Cr(VI), Cr(III) cannot cross the cell membrane, however, into the cells Cr(VI) can be reduced to Cr(III), and the latter could react with macromolecules such as DNA, RNA, proteins and lipids [4]. Likewise, although Cr(III) in the tannery effluents is the most expected specie, it can be converted to Cr(VI) by Redox reactions [6]. Therefore, the development of effective and inexpensive procedures for removing Cr(III) from tannery effluents has become crucial.

Several methods are available for the removal metals from wastewaters, including processes as filtration, reverse osmosis, coagulation-flocculation, sorption using activated carbon, use of zeolites, precipitation, ion-exchange, solvent extraction, etc. [7]. Nevertheless these methods have some disadvantages such as the production of secondary wastes, slug formation and high operational costs [2].

The use of alternative materials based on residual biomass from the processing industry of fruits, vegetables, cereals, etc. [2], [8-10] is shown as one of the most promising alternatives due to its availability, low cost and composition. For example, most residual biomass from fruit processing industry is underutilized, which usually leads to economic and environmental issues. Generally, this biomass is discarded as waste.

Passion-fruit (*Passiflora edulis*) is a typical tropical fruit produced in Peru. Generally, this fruit is consumed as fresh fruit, or is processed into juices, jam and frozen pulp. Peru is one of the largest producers of passion-fruit and its main residue, passion-fruit shell, contains approximately 12-15% of pectin (dry basis, [11]). The pectin, due to their content of hydroxyl (OH), carbonyl (CO), carboxyl (COOH) is capable of fixing metal ions through the chemical adsorption mechanism [8], [12]. In a previous paper we reported the feasibility of passion-fruit shell as an alternative adsorbent to remove heavy metals from contaminated aqueous solutions [13].

In this sense, the aim of the study was to evaluate the feasibility of passion-fruit shell biomass (PFSB) as adsorbent material to remove Cr(III) from contaminated aqueous mediums, considering the availability and low cost of these food waste.

2. Materials and Methods

2.1. Adsorbent Material and Aqueous Mediums

The adsorbent material was made from passion-fruit shell biomass (PFSB), which was purchased from the local market in the city of Trujillo, Peru. The biomass was washed with distilled water to remove edible remains and cut into pieces of 1.0 cm x 1.0 cm. Then, it was dried at 60 °C for 48 hours in a forced-air oven (UF-55 model, Memmert, Germany), and ground in a knife mill and sieved through 50-mesh sieves (Tyler series, 300 µm). The adsorbent material was stored and used directly without any later treatment.

2.2. Characterization of the Adsorbent by Fourier Transform-Infrared Spectroscopy

In order to determine the functional groups involved in the metallic ions adsorption, the FT-IR analysis of the PFSB alone and in the presence of Cr(III) were carried out using a Nicolet iS50 FT-IR (Thermo Fisher, Germany), with Attenuated Total Reflectance (ATR) device. The analyses were conducted from 3000 to 500 cm⁻¹, with a resolution of 2 cm⁻¹ and 20 scans.

2.3. Adsorption Experiments

Aqueous mediums composed of distilled water and chromium (as basic chromium sulfate Cr(OH)SO₄ from commercial CUIREXTAN B33) were prepared.

In a first stage, different values of pH (3.0-7.0) and biomass concentration (1.0-10.0 g l⁻¹) were tested, in order to determine the optimal operation values of these parameters.

Once these parameters were defined, the adsorption of Cr(III) was carried out using solutions at different initial concentrations (10, 20, 50, and 200 ppm), with a dose of 5 g of PFSB per liter of medium, at constant pH 3.0, in 500 ml flask at 25 °C, and agitation speed 300 rpm. Aliquots of the slurries were extracted at 5,

10, 15, 30, 45, 60, 90, and 120 min, and filtered in order to separate the adsorbent (PFSB) from the aqueous supernatant.

25 ml of each supernatant was added to a digestion vessel together with 3 ml of nitric acid (HNO₃) and 1 ml of hydrochloric acid (HCl). The samples were heated at 140 °C in a digestion system (DigiPrepJr, SCP Science, Canada), and then, the digested samples were analyzed by Atomic Absorption Spectrophotometry (Agilent Technologies 200 Series AA, USA) [13]. All experiments were conducted in triplicate.

The amount of Cr adsorbed per gram of PFSB (q , mg/g) and the percent metal removal were calculated according to equations 1 and 2 [2]:

$$q = V \frac{(C_0 - C)}{m} \quad (1)$$

$$\% \text{removal} = \frac{(C_0 - C)}{C_0} \times 100 \quad (2)$$

Where V is the solution volume (l), m is the PFSB dose (g), and C_0 and C are the initial and final Cr concentrations in solution respectively (mg l⁻¹).

Additionally, to describe the system behavior and to determine the adsorption capacity of the adsorbent based on PFSB, the isotherm models of Langmuir and Freundlich were fitted, judging the coefficients of determination in order to find the applicability of the developed models. The Langmuir model suggests a monolayer adsorption on a homogenous surface. For its part, the Freundlich model explains the interaction adsorbate-adsorbent with multilayer adsorption on heterogeneous surfaces [14].

2.4. Statistical Analysis

Analysis of variance (ANOVA) and Fisher's LSD (Least Significant Difference) test at a 5% significance level ($p < 0.05$) were performed with Statistica software version 7.0 (Statsoft, Oklahoma, USA), in order to identify significant differences.

3. Results and Discussion

3.1. Effect of pH and Adsorbent Dose on Cr(III) Removal

The effect of pH on Cr removal is shown in Figure 1. One of the more important factors in adsorption processes is the acidity of the medium, because hydrogen ions could compete with metallic ions to active sites on the adsorbent surface [15]. According to Fahim et al. [16], there are different forms of Cr(III) in solution as a function of pH. The form Cr³⁺ predominates at pH values <2.0, the forms Cr³⁺ and Cr(OH)²⁺ at pH values of 3.0-6.0, and the species Cr(OH)₃ at pH values >6.50. The results showed in the Figure 1 indicate that between pH values of 3.0 and 5.0, Cr(III) is adsorbed principally as Cr(OH)²⁺ on PFSB, since the surface of adsorbent becomes negatively charged (carboxylic acids COO⁻ of pectins). Taking in account the wastewater of the tanneries has a pH around 3.0, this value was chosen as the optimum for subsequent tests.

Regarding to adsorbent dose, a Cr(III) solution 10 ppm having pH 3.0, was treated with 1.0-10.0 g l⁻¹ adsorbent (PFSB) separately in five flasks (500 ml) for 60 min (Figure 1). The increase in PFSB dose increases the number of available binding sites for the contact adsorbent-adsorbate, and the results show an increase in the removal of Cr(III) as the adsorbent dose increases, especially up to 5 g l⁻¹ (percent removal of 88.5 %). The Cr(III) adsorption doesn't increase considerably by further increasing the PFSB dose because the metal ions are already adsorbed by the adsorbent [15].

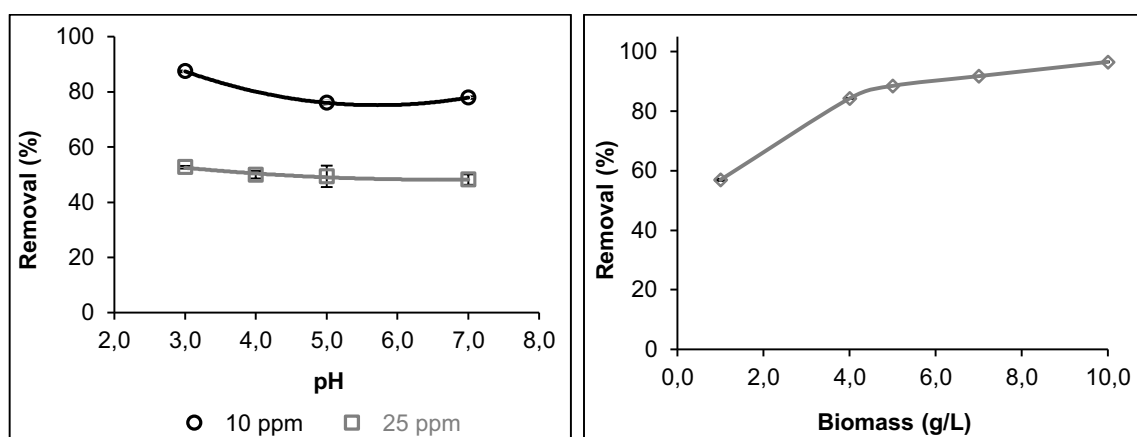


Figure 1. Effect of different pH values (a) and adsorbent doses (b), on Cr removal from aqueous mediums at 25 °C, agitation speed 300 rpm, and contact time 60 min.

3.2. Adsorption Isotherms

In the Figure 2 are shown the amount of Cr(III) absorbed per gram of PFSB (q , [2]). A contact time of 90 minutes was necessary to reach the equilibrium adsorbent-adsorbate, that is, the PFS biomass is no longer able to adsorb further metal ions from that moment, since no statistically significant differences (LSD Fisher, $p < 0.05$) were evidenced with the values of q obtained at higher contact times.

Respect to percent removal, values around 85, 80, and 53% were achieved for solutions of 20, 50, and 200 ppm, respectively, after 90 minutes of treatment. The percent removal of Cr(III) at a low concentration (20 ppm) was high due to a larger number of sites available for adsorption, while a lower adsorption at high concentrations of Cr(III) (200 ppm) may be due to that the available sites for adsorption on the surface of PFSB are saturated [17].

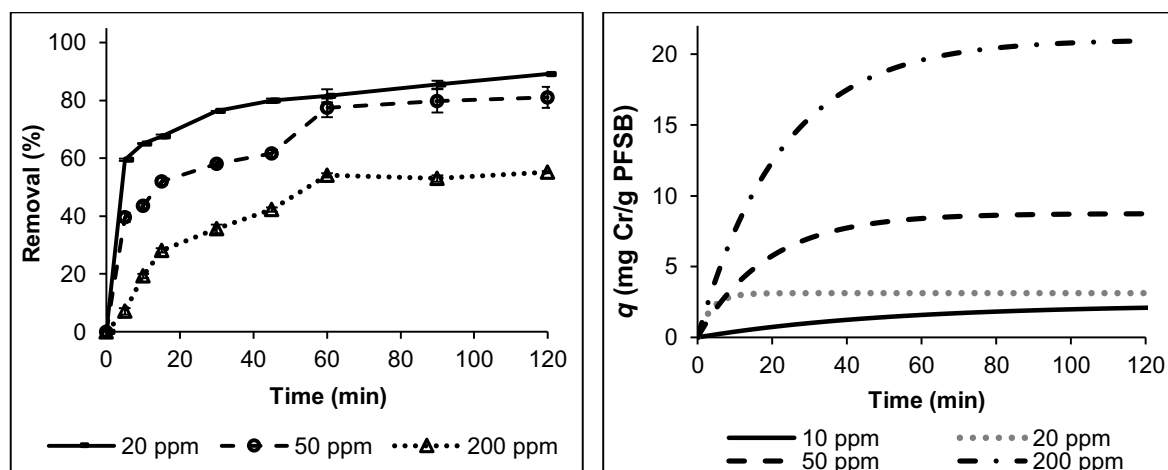


Figure 2. Percent Cr(III) removal (%) and amount of Cr absorbed per gram of PFSB (q) at different contact times. Solutions at initial concentrations of 10, 20, 50 and 200 ppm of Cr(III).

These results indicate a good affinity between Cr and the polymers present in the PFSB, mainly pectin, which contains functional groups as carboxyl (COOH), hydroxyl (OH) and carbonyl (CO), which would be the sites to metal ions fixation [8], [12], and the decrease in the percent removal at high metal ion

concentrations would indicate the saturation of these chemical groups (COOH, OH, and CO) in the pectin, i.e. that the adsorbent-adsorbate equilibrium is reached. For example, in the solution of 20 ppm, the equilibrium is reached after 30 minutes of treatment (value of q around 3.125).

Respect to equilibrium studies, Langmuir and Freundlich models were developed. By analyzing the values of Table 1, it can be seen that the Langmuir model was suitably fitted for Cr(III) adsorption. The maximum adsorption capacity (q_{max}) for the PFSB was 27.933 mg g⁻¹. The capacity of adsorption of Cr increases while the initial concentration of Cr increases, a phenomenon attributed to the competition for the available binding sites. A high concentration provides the necessary strength to overcome the resistance in the mass transfer of the metal ion between the medium and the adsorbent [18].

Based on the coefficient of determination ($R^2 = 0.8864$), the Langmuir model allow an adequate prediction of the concentration of Cr(III) in a range of 10-200 mg l⁻¹, which implies that homogeneous conditions predominate in the experiments. In a previous study of Cr(III) removal with passion-fruit peel, Jacques et al. [15] obtained a q_{max} of 85.1 mg g⁻¹, although the authors used 10 g l⁻¹ of adsorbent and solutions prepared from pure Cr(III), whereas in our study the commercial salt CUIREXTAN B33 was used, which also contains glucose, sodium sulfate, and other impurities (product data sheet), which may have caused interference in the adsorption process.

For its part, the parameters of the Freundlich model, k and n , indicate the capacity and the intensity of adsorption, respectively [10]. The PFSB showed a good adsorption capacity for the Cr ($k = 1.400$), which would indicate a greater number of binding sites Cr-PFSB (adsorbent-adsorbate). Likewise, a high adsorption intensity ($n = 1.650$) was obtained, so it can be considered as a favorable adsorption process ($n > 1$, [19]), in addition to showing an adequate coefficient of determination ($R^2 = 0.7596$).

Table 1. Models for adsorption process of Cr(III) by passion-fruit shell biomass (PFSB)

Langmuir Model	R^2	q_{max}	b
$C_e/q_e = 0.0358 C_e + 1.2382$	0.8864	27.933	0.029
Freundlich Model	R^2	k	n
$Ln q_e = 0.6060 Ln C_e + 0.3366$	0.7596	1.400	1.650

Additionally, in the case of Langmuir model, the dimensionless parameter R' was calculated, which describes the type of isotherm, that according to Weber and Chakraborti [20] is defined by the equation:

$$R' = \frac{1}{1 + b \cdot C_0} \quad (3)$$

Where b is a Langmuir constant, which indicates the nature of adsorption and indicates the shape of the isotherm accordingly. R' -values calculated of 0.7178, 0.6343, 0.4108, and 0.1459 for solutions of 10, 20, 50, and 200 ppm of Cr(III) indicate that the adsorbent-adsorbate system shows a favorable adsorption process ($R' < 1$), in concordance with Fahim et al. [16].

3.3. Characterization of the Adsorbent by FT-IR

A FT-IR analysis was performed on the PFSB, whose spectra were obtained before and after the adsorption process (Figure 3). The spectra display several vibrational bands, indicating the complex nature of the passion-fruit shell.

According to Minamisawa et al. [21], the presence of a CO stretching of carboxylic acid or pectin ester is confirmed by the bands observed at 1700-1750 cm⁻¹, while the bands at 1600-1650 cm⁻¹ were attributed to CO stretching of carboxylic acid with intermolecular hydrogen bond. For its part, the bands in the 1000-1070 cm⁻¹ might be attributed to the CO of alcohols and carboxylic acids [22]. Given spectra of Figure 3, the intensity of the carboxylic bands of pectin in the PFSB after adsorption process (green and blue lines)

presented a small decrease compared to the control (black line), suggesting the participation of the functional groups in the adsorption of Cr(III). Thus, these results indicate a good affinity between Cr and the polymers present in the PFBS, mainly pectin, which contains functional groups as carboxyl (COOH), hydroxyl (OH) and carbonyl (CO), which would be the sites to Cr ions fixation [8], [12].

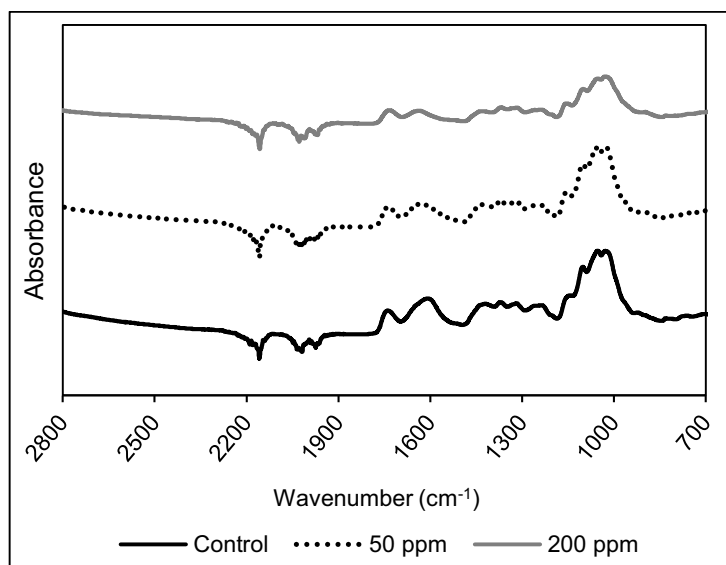


Figure 3. FT-IR spectra of adsorbent based on passion-fruit shell biomass (PFBS) alone (control) and in the presence of Cr(III) at 50 and 200 ppm.

4. Conclusion

The feasibility of passion-fruit shell biomass (PFBS) as adsorbent to remove Cr(III) from contaminated aqueous mediums was evaluated. According to the results, a good adsorption capacity was exhibited by this adsorbent, achieving removal levels up to 85, 80, and 53% for solutions of 20, 50, and 200 ppm of Cr(III), respectively. It was also determined that a contact time of 90 minutes would be necessary to reach the adsorbent-adsorbate equilibrium, showing an adequate fit to the Langmuir and Freundlich models (R^2 of 0.8864 and 0.7596, respectively), with a good adsorbent-adsorbate affinity for Cr(III), according to FT-IR spectra. Therefore, the obtained results suggest that Cr ions can be removed by more than 50% by using passion-fruit shell, which with a minimum treatment could be used as a low cost adsorbent for the ecofriendly removal of this metal from contaminated waters, as a potential alternative to traditional methods nowadays used.

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