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Research Article

Design of Bio-adsorbents of Heavy Metals from Waste of the Productive Chain of Banana

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Abstract: The design of bio-adsorbents of heavy metals from waste of the banana production chain is the answer to the problem of toxic waste generated by companies that become a high source of contamination and put human health at risk; so it is necessary to look for alternatives to end this type of contamination. This way, heavy metal adsorbents were prepared using as a starting material *Musa paradisiaca* husks from waste from the plantain production chain in Quindío; the removal capacity of these metals was evaluated through a phenol-formaldehyde polycondensation process in acid medium at different concentrations, in order to obtain low cost and highly efficient adsorbents for the treatment of wastewater contaminated with heavy metals. The resulting adsorbents showed a high effectiveness (>80%) in the removal of Cu (II) and Cr (III) ions from diluted aqueous solutions at different concentrations, attributable to their porous structure and the presence of phenolic groups on their surface. The adsorption isotherms of the Cu (II) and Cr (III) ions for the prepared adsorbents were satisfactorily adjusted by the Freundlich model. In addition, it was found that the adsorbents have a greater capacity to retain the Cu (II) ion than the Cr (III) ion. Therefore, it can be observed through the results obtained that the plant material used is a viable alternative for water decontamination.

Keywords: Colloidal aggregation, fractal dimension, protein adsorption, static and dynamic light scattering

INTRODUCTION

The discharge of industrial effluents contaminated with heavy metals in watercourses is a serious problem that must be resolved, since their presence and accumulation cause toxic effects in living species. Adsorption has proven to be an effective method for the removal of heavy metals from water, when they are presented in low concentration (Cooney, 1998).

The technique of adsorption of heavy metals is of great importance in the sanitation of water discharges resulting from industrial activities. However, the use of this technique requires large amounts of money due to the high cost of adsorbents that are in the market, therefore, the development of new adsorbents from biomass, has a special interest.

One of the alternatives that is very useful for obtaining heavy metal adsorbents is the use of lignocellulosic residues (Grotewold, 2006), which in many cases have a high tannic content (Riedl and Hagerman, 2001). The benefit of tannic content is derived from the known capacity of these chemical species for the formation of heavy metal complexes. Among the new technologies, the sequestration of heavy metals by chelating functional groups can be favorable in the processes of heavy metals elimination in bodies of wastewater. However, we must highlight the progress in the study of lignocellulosic and tannic materials as the main chelating molecules presented in ethanol extractions with the use of a defined organic material, which enables the decontamination of these residues as a renewable source.

Obtaining bio-adsorbents of heavy metals from waste products, such as banana peel, have a great interest in the technological, environmental and economic sense (Otles, 2013) and that in obtaining this type of adsorbents, the possibility of improving lignocellulosic residues of banana production that is now presented as a source of contamination of the environment is raised (García *et al*., 2009). The use of this product as a raw material for obtaining bio-adsorbents, has a dual purpose, from a waste product, this would generate a useful product for the decontamination of wastewater and on the other hand this product would be revalued (Martínez *et al*., 2004). In this way, bio-adsorbents were developed that are used as raw material or precursor, green plantain husks of the Musaceae family a plant easily propagated in agricultural areas from Quindío Colombia.

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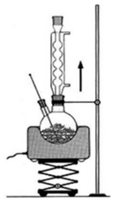

Fig. 1: System reflux for obtaining adsorbents banana peel (CP)

EXPERIMENTAL METHODOLOGY

This project was developed in the laboratories of the Faculty of Sciences of the University of Quindío, located in the city of Armenia in the period 2014-2016.

Obtaining bio-adsorbents: The bio-adsorbents were prepared from green banana peels which were dried in an oven at 80°C for 24 h. A grinding was carried out and subsequently separated in a sieve and a particle size of 3 mm was chosen.

Obtaining bio-adsorbents is based on the polycondensation product of phenol formaldehyde in acid medium. For this, aqueous solutions of phenol, formaldehyde and hydrochloric acid were prepared in appropriate concentrations. To the reaction solution the barks were added in a distillation flask which was refluxed for one hour at 60°C. Subsequently, the barks were washed with distilled water to completely eliminate the chloride ions. The obtained barks were dried at 80°C for 24 h and stored for further analysis. These barks were called CP. The concentrations obtained were 0.5, 2, 5, 10, 15 and 20% of formaldehyde and 1 and 2% of hydrochloric acid. Figure 1 shows the reactor where the polymerization process was carried out to obtain bio-adsorbents from the banana peel.

Characterization of Bio-adsorbents: The chemical characterization of the bio adsorbents was carried out by means of tests of apparent density, degree of swelling, percentage of moisture, number of functional groups and infrared spectroscopy using the DRIFT technique (infrared spectroscopy of diffuse reflectance) (Fig. 2) (Geckeler, 2001).

Degree of swelling and percent moisture: These measurements were made from the amount of water retained by the bio-adsorbents. In this sense, 0.1 g of bio-adsorbent was taken, which was moistened for 24 h, then the wet bio-adsorbents were weighed and subsequently dried at 80°C until a constant weight was obtained. The following formulas were used to calculate the degree of swelling and moisture content:

$$H_p = \frac{W_{Hinc} - W_{\sec}}{W_{\sec}} x100 \tag{1}$$

$$100 - \left(\frac{100}{W_{AdsH}} * W_{Ads.S} \right) = \%moisture \tag{2}$$

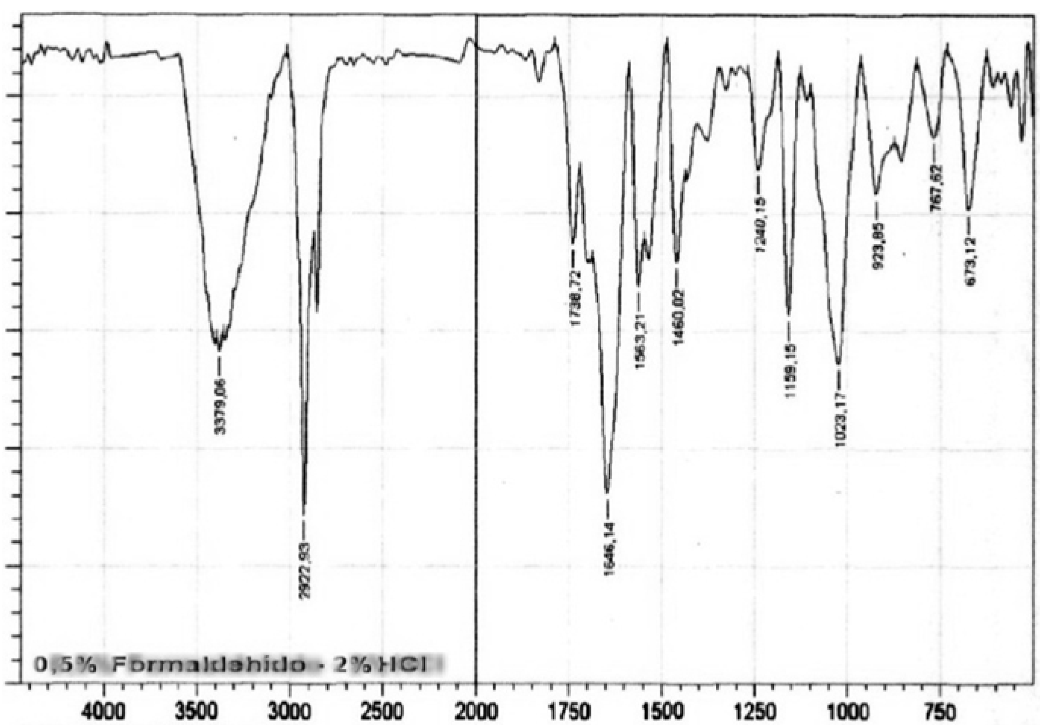

Fig. 2: Infrared spectrum of CP adsorbent 0.5-2%

where,

H_P = The degree of swelling
W_{AdsH} = The weight of the swollen adsorbent
$W_{Ads.S}$ = The weight of the dry adsorbent

Bulk density: This was calculated by introducing a quantity of bio-adsorbent into a test tube which occupied a volume of 10 mℓ in this case:

$$\frac{W_{Ads.}}{V.} = D \tag{3}$$

where,

D = The apparent density
V = The volume occupied by the adsorbent
W_{Ads} = The weight of the adsorbent

Number of functional groups: These measurements are based on the trimetric method of Boehm, which allows to calculate the number of groups presented on the surface of an absorbent element by acid-base and the groups are selected according to their different acid strength. In this case, one gram of bioadversion is taken and placed in 50 mℓ of a basic solution of NaOH (0.1 N) for 10 min and titrated back with hydrochloric acid (0.1N) using phenolphthalein as an indicator. For the calculation of the amount of phenolic groups presented on the surface of the bioadditives, the following formula was used:

$$\frac{Eq.OH}{gAds.} = \frac{[NaOH]*Vol_{NaOH} - [HCl]*Vol_{HCl}}{Wsample} \tag{4}$$

where,

Eq.OH = The OH equivalents
gAds = The grams of adsorbent
Vol = The volumes that are measured for each concentration of acid and base

Infrared analysis by diffuse reflectance DRIFT: For the analysis of the bio-adsorbents, it was necessary to use the DRIFT technique (Aparicio, 2002), as it was interesting to characterize the surface of the bio-adsorbents. The bio-adsorbents were duly dried and analyzed by DRIFT (FTIR spectrophotometer) without causing disruption to them.

Testing metal absorbents: For the comparison test of the bio-adsorbents with the metals Cu (II) and Cr (III) was done by lot tests in order to find the most effective bio-adsorbent for these ions. Subsequent to the practice of the adsorption of metals in the presence of the biopolymer, these solutions are filtered for subsequent colorimetric procedures.

RESULTS AND DISCUSSION

Table 1 shows the results of the proposed analyzes for the characterization of synthesized bio-adsorbents.

According to this analysis, it can be deduced that the adsorbents are not homogeneous, bio-adsorbent that has less moisture content and the degree of swelling is # 8 with a value of 55.57% moisture and swelling of 1.23% and the highest moisture and degree of swelling corresponds to # 3 with values of 39.24% and 79.554% respectively.

Both for the degree of swelling and moisture it can be clearly seen that all the adsorbents show a statistically significant difference that allows us to deduce that the water content they are able to retain is different, this may be due to the different concentrations.

The moisture and the degree of swelling are calculated because if an adsorbent is able to retain or adsorb enough water, it is possible that a greater amount of metals are trapped by the sorbent.

The table also shows that the highest number of bio-adsorbents containing OH equivalents are 7, 9 and 10, with values of (1.1138, 1.4531, 1.8341), respectively, if analyzing the greater number of OH groups that are present in the molecules of this resin there is a greater chance that the ion or ions can chelate; In this way it gives us an idea of what type of bio-adsorbents may have a greater adsorption capacity.

The characterization of adsorbents by Diffuse Reflectance Infrared Spectroscopy (DRIFT) was used to characterize the surface of each of the bio-adsorbents synthesized, 12 spectra were obtained; since the spectra are similar, because the components are the same, there was only change in the concentrations here we only show one of the spectra.

We found in the region between 3370-3600 cm^{-1} typical absorption of phenolic compounds. Bands

Table 1: Physico-chemical characteristics of bio-adsorbents

Bio-adsorbents	Bulk density (g/mL)	% Moisture	Degree of swelling	No. Eq. OH/g Ad.
CP 0,5-1	0,273	65,14	1,85	0,162
CP 2,0-1	0,25	71,52	2,51	0,475
CP 5.0-1	0,257	79,55	3,92	0,563
CP 10-1	0,271	77,44	3,47	0,597
CP 15-1	0,252	69,63	2,26	0,265
CP 20-1	0,224	72,65	2,66	0,673
CP 0,5-2	0,256	64,9	1,83	1,113
CP 2.0-2	0,246	55,57	1,23	0,086
CP 5.0-2	0,233	63,24	1,72	1,453
CP 10-2	0,177	64,75	1,84	1,834
CP 15-2	0,174	66,55	1,95	0,182
CP 20-2	0,225	64,65	1,83	0,245

between 2922-2924 cm^{-1} are attributed to CH aldehyde connections. There may also be frequencies between 1730-1740 cm^{-1} characteristic of the carbonyl groups presented. The bands that are between 1640-1650y1560-1565cm^{-1} cm^{-1} are due to C = C of the aromatic compounds.

The bands that appear between 1455-1461 cm^{-1} are typical of the deformed methylene vibrations (-CH2-) of the phenolic resins. Between1237-1240 cm^{-1} there are bands that are typical of (-OH) phenol. The peaks between 1156-1160 cm^{-1} are assigned to the CO bonds of aliphatic ethers. Finally, the bands between 1020-1040 cm^{-1} refer to the stretching of the CO group (-CH2OH) (Martínez *et al*., 2004). The results of the characterization, confirm that all the bio-absorbent was synthesized by polycondensation due to a band that appears between 1455-1461 cm^{-1} which indicates the presence of methylene bridges (-CH2), obtaining what was expected.

The Freundlich model was used in this analysis because it conforms to the experimental conditions in which this process is carried out, since this model is only valid when the adsorption is a physical process and there are no changes in the configuration of the molecules when they have adsorbed. This model adequately represents the sorption at low metal concentrations as there are no saturation phenomena. (Fiol and Villauscusa, 2001):

$$q_e = K * C_e^{1/n} \tag{5}$$

where, K is a constant of the adsorption capacity expressed in mg.g-1.El-1, n is a constant related to the affinity or adsorption energy between adsorbent and adsorbate and CEQ is the final equilibrium concentration of the expressed metal in mg/L.

This equation can be linearized from its expression in logarithmic form:

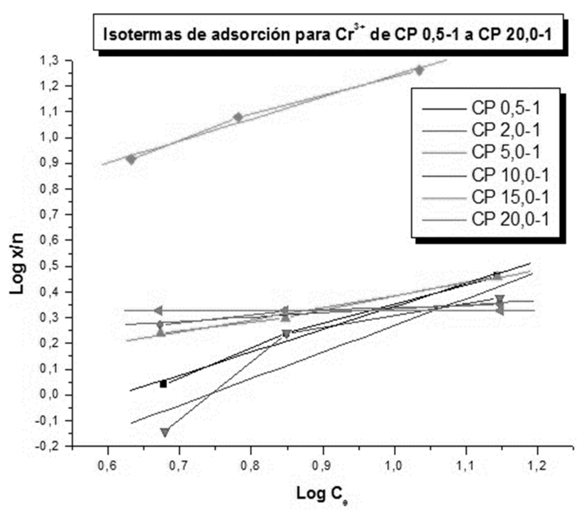

Fig. 3: Freundlich Cr^{+3} adsorption isotherms (CP 0.5-1 to CP 20-0.1)

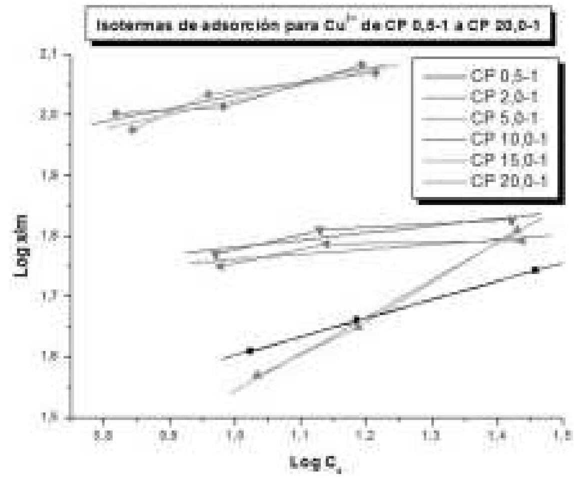

Fig. 4: Freundlich Cu^{+2}adsorption isotherms (CP 0.5-1 to CP 20-0.1)

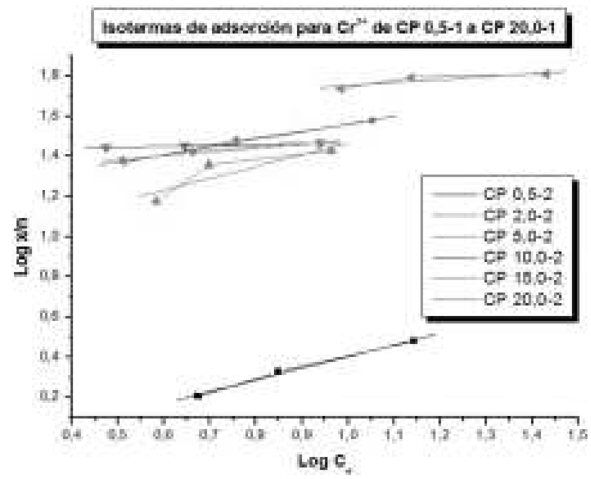

Fig. 5: Freundlich adsorption isotherms for Cr^{+3} (CP 0.5-2 to CP 20-0.2)

$$\log q_e = \log K + \frac{1}{n}\log C_e \tag{6}$$

Figure 3 to 6 show all the graphs of the Freundlich adsorption isotherms obtained for each of the concentrations of the bio-adsorbents.

The results show that the best retention capacity with respect to copper was for bio-adsorbent # 11 (CP 15-2), with an adsorption capacity of 70,762 mg Cu + 2 adsor./gr.Ads and for chromium the bio-adsorbent # 12 (CP 20-2), with an adsorption capacity of 39,418 mg Cr + 3 adsor./gr.Ads.

We can clearly see that the bio-adsorbent retained copper (II) more effectively than chromium (III). With respect to the concentration of CP 20-2 both have the same capacity of adsorption, in addition the statistical data show that this bio-adsorbent has a greater selectivity for copper than for chromium.

It was possible to analyze that for both ions there is a higher adsorption capacity at higher concentrations of formaldehyde and hydrochloric acid, that is to say, that

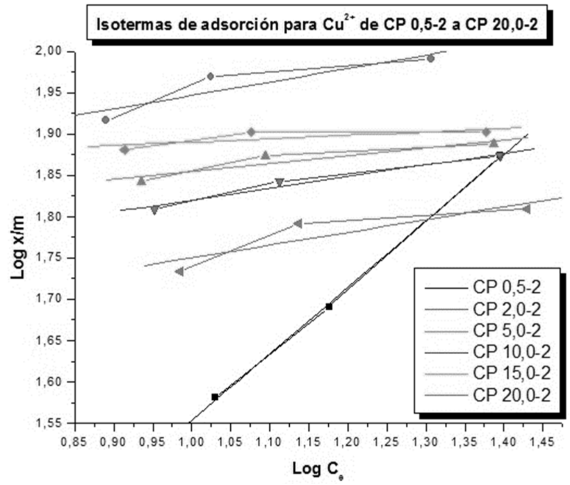

Fig. 6: Freundlich adsorption isotherms for Cu^{+2} (CP 0.5-2 to CP 20-0.2)

for concentrations of 2% hydrochloric acid it showed a better retention.

Regarding related research work, the present research project is presented as an innovative analysis when banana peels are used as starting material, unlike other researches that have used another type of polymeric matrix in adsorption processes, which takes on a vital because it revalues a waste and provides a solution to the environmental problem of the contamination of bodies of water and discharges, in addition that the production of this product is very economical and efficient thus providing the possibility of obtaining an organic decontaminant and Low cost.

CONCLUSION

For the polycondensation reaction of phenol-formaldehyde carried out for banana peels at different concentrations of formaldehyde and hydrochloric acid, twelve amorphous, porous adsorbents were obtained which were used for further analysis.

Through the characterization of bio-adsorbents, there was a clearer idea of their behavior in presence with metals. In the determination of functional groups presented in the bio-adsorbents, it was possible to establish which of them could have a better retention of the ion.

As for the infrared spectroscopy technique used, it provided information on polymerization through the appearance of a methylene band in the region between 1455-1461 cm^{-1}.

The Freundlich adsorption isotherms determined the retention capacity of the Cu + 2 and Cr + 3 ions, thus establishing that the biopolymer obtained is more selective for the Cu + 2 ion than for the Cr + 3 ion, using the concentrations Higher hydrochloric acid and formaldehyde.

It was proved that this technique of retention of heavy metals is a good alternative for the decontamination of wastewater containing this type of heavy metals that are harmful to health and endanger life.

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