

ADSORPTION HEAVY METALS THROUGH THE USE OF A NATURAL BIOPOLYMER, (COCOA SHELL). FRON CONTAMINATED WATERS

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ABSTRACT

The heavy metals found in contaminated waters are dangerous for the environment and human health, so it is necessary to seek and apply techniques to remove these pollutants, using adsorption techniques with natural biopolymers such as cocoa shells, characterizing the adsorption by infrared spectroscopy, obtaining values of (k) Freundlich's constant whose highest value is for the lead cation and the lowest for the more hydrated cation such as copper, presenting an opposite behavior for the exponent "n" of Freundlich's equation. The use of the cocoa shell as an adsorbent is an alternative to remove these contaminants from the water.

keywords

Biopolymer, Adsorption, Hydration energy, Selectivity, cocoa shell.

INTRODUCTION.

In wastewater treatment process, absorption and liquid-liquid extraction operations are applied, generally using different types of molecules that have the property of adsorbing metal cations, in most of the times the most used are those derived from naturally occurring macrocyclic ligands such as clays, amino acid cyclodextrins, activated carbon. These substances are prepared based on their properties and chemical structure that these adsorbents possess as well as the physical-chemical properties of metal cations.

The waters of the Inner Bay of Lake Titicaca, is the area of greatest contamination due to the accumulation of heavy metals mainly from the tributary rivers of the lake that come from mining areas such as the Ramis River, which currently exceed the limits allowed by regulatory bodies, which is necessary to decontaminate them either using conventional or natural techniques, hence the need to seek clean decontamination technologies such as the use of natural biopolymers. Among them application of a natural product from the area such as roasted cocoa shell, a residue in the cocoa paste production.

Liquid solid extraction includes all forms of absorption¹ such as adsorption, ion exchange and other techniques that involve separations of a solute dissolved in a solvent by a solid, in this type of extraction the adsorbent material must have certain characteristics and properties in accordance to the properties of the solute to be separated². It is an extraction technique that is beginning to have a boom in desalination of salt water, purification of wastewater, WB. Aparicio³ cites a calixarene-derived phosphorous amino polymer as an extracting agent for the selective extraction of mercury (II) from contaminated water, Meunier *et al*⁴ used the cocoa shell in a process of adsorption of heavy metals from acidic waters, using ion exchange methods as a modified chitosan exchange resin, Dabrowski *et al*⁵ reported as a technique for the selective removal of heavy metals from industrial waters and waters. At the School of Agricultural Technology in Greece, Manios *et al*⁶ uses a plant called *Typha latifolia* to remove heavy metals from a ferruginous water solution, also Gulay Bayramoglu⁷ reports work done at the University of Kirikkale, Turkey, a bioadsorption technique using a plant called *Lentinus sajor-caju* as a treatment technique of wastewater.

Pure water is not found naturally, it is normally contaminated by domestic and industrial effluents. Impurities can be organic and inorganic either dissolved, or in the form of particulate matter. These impurities can come from the degradation of inorganic substances that are found as a component of soil and air, or also from waste from metallurgical tailings, such as toxic metals, particulate matter such as clays and sediments and from microorganisms such as bacteria, viruses and protozoa.

The common chemical contaminants in water are heavy metals such as iron, manganese, lead, mercury, arsenic, copper, zinc, sodium, potassium, lithium, etc. nitrogenous compounds such as ammonia, nitrite and nitrate, calcium and magnesium carbonate or bicarbonate, anions such as chloride, fluoride, sulfate and silicates and the aforementioned, organic substances. Apart from these substances, there are other anthropogenic contaminants such as cyanides, phenols, chromium and detergents.

Of all these pollutants, the most dangerous for animal life are heavy metals, such as cadmium is carcinogenic, lead produces lead poisoning, etc., which is why many studies such as those mentioned above try to create new technologies to remove these heavy metals from waters and industrial waters.

EXPERIMENTAL PART

Reagents.

Methanol, CH₃OH, (Fisher Reagent, 99%), Water, distilled and deionized, Acetone, CH₃COCH₃, (analytical grade, Aldrich). Potassium Chloride, KCl, (99% Pure, Fisher), Hydrochloric Acid HCl, (33%, Aldrich), Metal salts as nitrate, (analytical grade, Aldrich), Calcium Chloride, CaCl₂, (98%, Fisher) , Sodium hydroxide, NaOH, (Fisher), , Etylen

diamino tetra acetic acid, (Fluka, analytical grade), Ammonia solution, (analytical grade, Aldrich), Buffer solution pH 10, Erio cromo negro T, (indicador).

TREATMENT OF NATURAL BIOPOLYMER (COCOA SHELL) FOR ADSORPTION

Cocoa shell biopolymer was ground and sieved to 100 mesh. They were used with: (1) chemical activation by adding 6.0 M HCl, keeping it for a period of 24 hours, and washed for several times with water until neutral pH, (2) without chemical activation, both samples were used for the different tests.

Heavy metal standard solution.

In order to determine the extraction data for heavy metal cations such as lead, cadmium, copper, zinc, as nitrate, standard solutions of these metals were prepared in distilled water with a concentration $\sim 7 \times 10^{-3} \text{ mol dm}^{-3}$ approximately, which in each case to determine the exact concentration were standardized with EDTA 0.0148 M as detailed in the following sections, these standard solutions were used for adsorption tests.

Infra-red studies

Infra-red measurements were recorded at 298 K using a Perkin Elmer spectrometer, Spectrum 65, for Fourier transform (FIRT). Typical operating conditions for routine determination functional organic groups of natural biopolymers involved the range to determination at 400 to 4000 cm^{-1} the frequency of vibration. Samples of the natural biopolymer ($\sim 0.05 \text{ g}$) were dissolved in KCl and placed in the optical lent.

Extraction experiment

In order to investigate the extraction ability of the natural biopolymeric, (cocoa sell), was check of extraction process by filtered a solution of heavy metal as (Pb^{2+} , Cd^{2+} , Cu^{2+} and Zn^{2+} as nitrate into of a column contained biopolymer ($\sim 1.0 \text{ g}$), the remain solution is analyse for determine concentration of heavy metal cations, as nitrate by use a Perkin Elmer 5000 atomic absorption spectrophotometer.

RESULTS AND DISCUSION

In Fig. 1 you can see the results of infrared analysis in a graph of % of Transmitting versus the vibration frequency in cm^{-1} the different signals of the functional groups that are identified below, following the recommendations of C. N. Banwell⁹ and O. Popovych¹⁰ the following functional groups were identified that is made up of a carbonated family of aliphatic and aromatic by the identified absorbance frequencies, so the phenolic group has a vibration frequency approximately 3060 cm^{-1} , which in Figure 1 is overlapped under the frequency of vibration of the amino group ($-\text{NH}_2$), the primary, secondary and tertiary carbon groups are also forming this wide vibration band between 2800 to 3392 cm^{-1} frequency, other important groups identified are between 1000 and 1800 cm^{-1} frequency

comprising the carbonyl, (-C=O) and thiocarbonyl, (-C=S) groups in addition to the carbon, nitrogen carbon and single-link carbon-carbon-carbon groups.

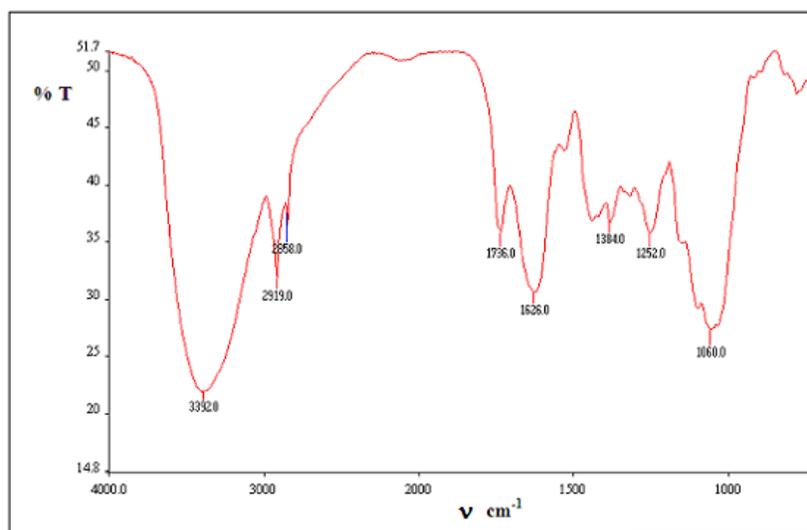


Fig. 2: Percentage of transmission versus vibration frequency in cm^{-1} for the absorption of different organic compounds found in the cocoa shell.

The presence in the chemical structure of an adsorbent of functional groups containing amino groups and groups involving double bonds determines the selectivity of an adsorption^{11,12}. Based on this postulate cited by Izatt and collaborators, we can conclude that the natural biopolymer selected for this study as the cocoa shell due to the presence of the amino groups, the carbonyl and thiocarbonyl groups are responsible for the formation of dipolar moments with the respective formation of negative temporal charges in the oxygen or nitrogen atoms which are in charge of coordinating and immobilizing the metal cation

Figs. 2 and 3 show the infrared absorption spectra of the natural biopolymer, (cocoa shell) after the adsorption of lead and cadmium respectively, as the % Transmittance peaks shown in Fig. 1 are distorted around the vibration bands of the amino group, ($\sim 3060 \text{ cm}^{-1}$), and carbonyl and thiocarbonyl group, (1000 to 1800 cm^{-1}) in the case of lead adsorption with more intensity compared to the cadmium spectrum, indicating that the natural biopolymer has a higher preference for lead adsorption which is a hard cation with slightly basic properties that has an affinity to form complexes with oxygen and nitrogen donor atoms.

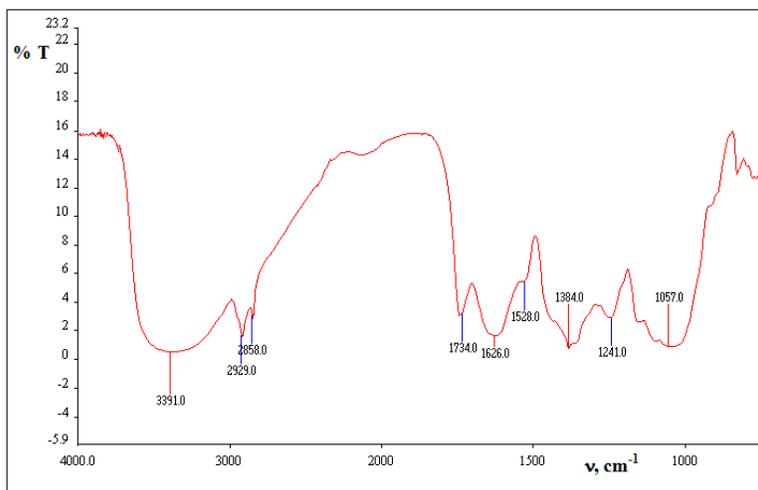


Fig. 2 Percentage of transmittance versus vibration frequency in cm^{-1} for the absorption bands of the different compounds found in the cocoa shell after lead nitrate adsorption

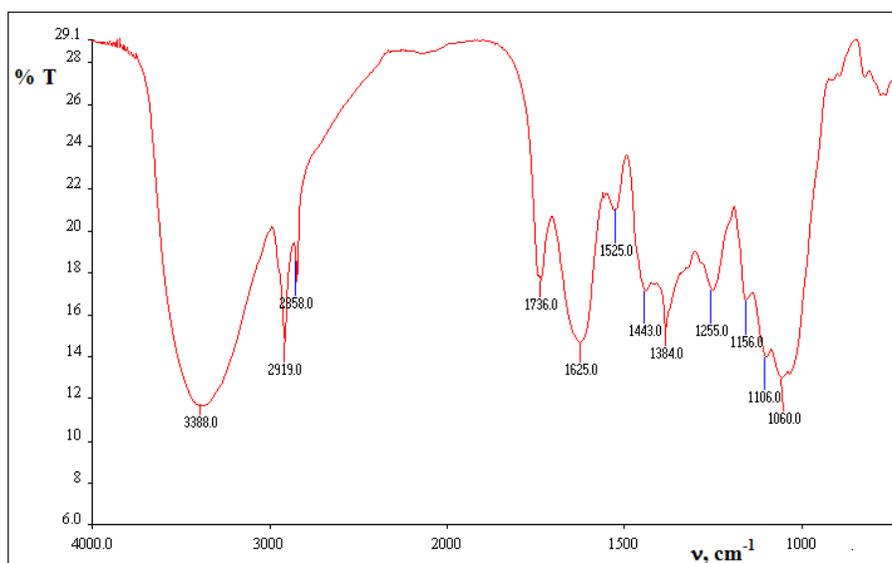


Fig. 4: Percentage of transmittance versus vibration frequency in cm^{-1} for the absorption bands of the different compounds found in cocoa shells after adsorption of cadmium nitrate

ADSORPTION OF HEAVY METALS BY NATURAL BIOPOLYMER, (COCOA SHELLS)

From the adsorption results analysed taking into account the values of the initial and final concentration of the heavy metal solution retained per gram of adsorbent biopolymer, it can be clearly seen that the adsorption increases when the initial concentration increases. Using these data, the adsorption isotherm for the extraction of heavy metals is determined, which

is shown in Fig. 4, where it can clearly be seen that the adsorption isotherm conforms to the Freunlich isotherm as:

$$\frac{X}{M} = k \left(\frac{X}{L} \right)^{\frac{1}{n}} \quad \dots\dots \text{Eq. 1}$$

In Eq. 1: X, M, L, k and n, represent the moles of lead, the grams of natural biopolymer, the litres of solution and the characteristic constants for each type of element respectively.

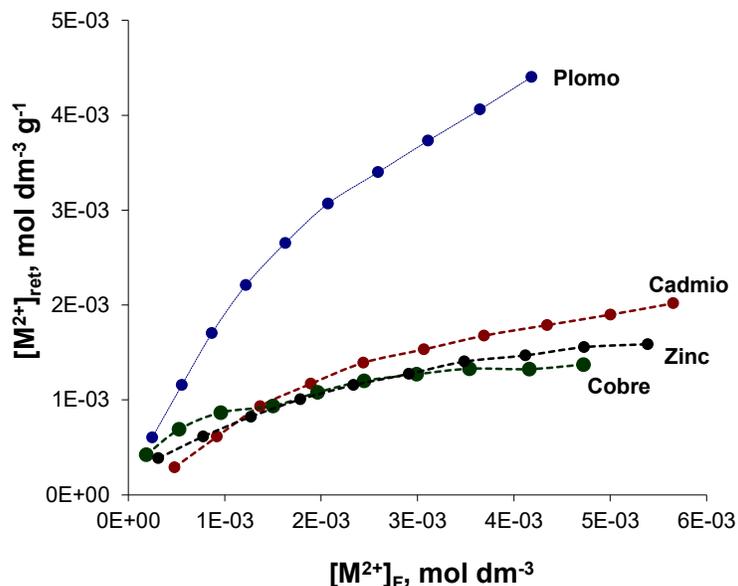


Fig. 4, Isotherms of heavy metal adsorption, (nitrate as anion) through the use of natural biopolymer, cocoa shell at 25 °C.

ANALYSIS OF THE SELECTIVITY OF ADSORPTION

From the analysis of the adsorption results and the respective calculations performed on the Freunlich adsorption isotherms, which are summarized in Table 1 at 25 °C, it is clear that the Freunlich constants increase upwards from a minimum of 0.0246 for the constant k corresponding to the copper cation to a maximum of 0.2243 for the lead cation, correlating these values with the size of the ionic radius of each metal ion shows no correlation so these k values were correlated with the free hydration energies of these heavy metals. In the figure, the affinity of the natural biopolymer to adsorb these cations is related to the hydration capacity of these metals with water, which is clearly seen in figure 5, where it can be seen that the less hydrated cation, such as lead, has a greater affinity to be adsorbed by the cocoa shell, while the more hydrated cation, copper, is less likely to be adsorbed following that sequence for the other intermediate cations whose adsorption varies between these two extremes.

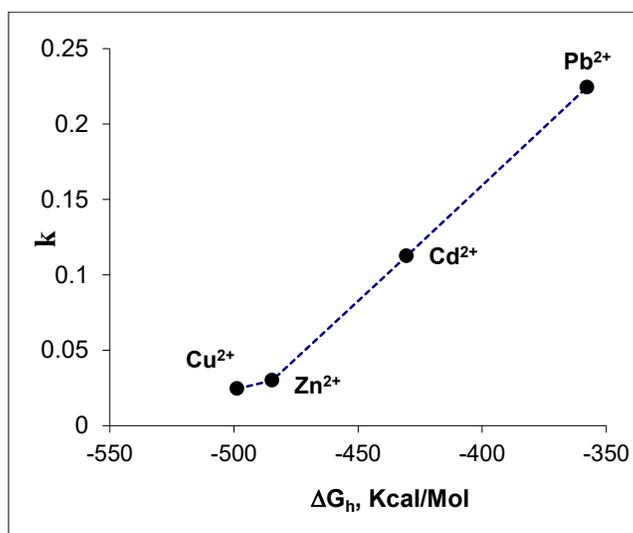


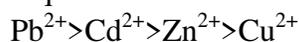
Fig. 5, Freunlich Constant, (k) versus the free energy of hydration of heavy metals, (Kcal/Mol) at 25 °C

TABLE N^o. 1 CORRELATION OF THE FREE ENERGY OF HYDRATION OF HEAVY METALS WITH THE FREUNLICH CONSTANTS

Cation	ΔG_h , Kcal/mol ¹³	k	n
Cu^{2+}	-498.7	0.0246	1.6592
Zn^{2+}	-484.6	0.0301	1.6396
Cd^{2+}	-430.5	0.1126	1.4825
Pb^{2+}	-357.8	0.2243	1.4267

CONCLUSIONS

The natural biopolymer characterised before and after adsorption by means of infrared spectroscopy clearly shows by the distortion of the Transmittance peaks after adsorption that the natural biopolymer traps metal cations because of its chemical structure with double bonds and donor atoms, which are responsible for immobilizing the metal cations when they come into contact, whose isotherms conform to the Freundlich isotherms presenting a selectivity for the metal cation that has less hydration free energy compared to that which has more hydration free energy the adsorption presents the following sequence.



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