Available online www.jocpr.com

Journal of Chemical and Pharmaceutical Research, 2019, 11(5):55-62

Research Article

ISSN: 0975-7384
CODEN(USA): JCPRC5

Removal of Pb^{2+} ions from Aqueous Solutions by Adsorption on the Raw Beet Pulp

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ABSTRACT

The present work concerns the removal of Pb^{2+} ions from aqueous solutions diluted by adsorption on raw beet pulp (BP). The adsorption kinetic at pH=5.5 shows that the adsorption equilibrium is reached at 80 min. But the kinetic of desorption of metal ions on the acid solutions is very fast, and we have about ten minutes of agitation of systems to achieve the equilibrium. The maximum adsorption capacity of Pb^{2+} by BP is of the order of 2.55 mg/g. The effect of the temperature on the adsorption shows the adsorption of Pb^{2+} ions is endothermic in nature. The treatment of a mixture of metals shows that the BP presents the sequence of following selectivity: $Pb^{2+}>Cd^{2+}>Zn^{2+}>Cu^{2+}>Co^{2+}$. The study of the regeneration of this material, after desorption of the metal ions by bringing it into contact with dilute acid solution shows that this material has good mechanical properties, and can be regenerated and repeatedly reused in the process of treating the metal solutions.

Keywords: Removal of Pb^{2+}; Raw beet pulp; Adsorption; Desorption; Regeneration

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INTRODUCTION

The use of adsorbents of natural origin has emerged in the last decade as one of the most promising alternatives to conventional heavy metal management strategies. The adsorption is a fast and reversible reaction of the heavy metals with biomass. The by-products obtained from biomaterial production are a cheap source of biosorbents. Also, these biosorbents have in their composition a variable amount of cellulose, hemicelluloses, lignins and pectins, which have of hydroxyl, carboxyl, and metoxi groups, determine of retention of metal ions by complexation mechanisms [1-6].

We chose the lead as metal to removal from aqueous solutions, because of its massive use in several industrial fields [7,8]. It is also, the lead is known to be one of the heavy metals most toxic to living organisms and it is one of the more widespread heavy metal contaminants of the environment [9].

Several agricultural waste materials have been studied and developed for the effective removal of heavy metals [10-18].

In this work, we studied the adsorption and the desorption of the Pb^{2+} ions in solution by the raw beet pulp.

MATERIAL AND METHODS

Biomass Preparation

The beet pulp (BP) is the residue which remains after the extraction of sugar contained in beet of sugar; it was dried with the air, under the action of the solar rays, then crushed and tamised so as to obtain homogeneous materials for the experimental achievements, and the fraction of granularity of very low diameter.

Preparation of Adsorbate Solutions

The metal solutions of Pb^{2+} ions are prepared by dissolving of the lead chloride salt hydrated ($PbCl_2$, $3H_2O$) in distilled water. The pH of each solution was adjusted by hydrochloric acid (HCl) and the sodium hydroxide (NaOH) using a glass electrode combined with a pH meter type EUTECH: pH510 instrument.

Adsorption Experiments

The process of the removal of Pb^{2+} ions by adsorption on beet pulp was carried out by contacting a volume of 100 ml of the aqueous phase, of concentration equal to 20 ppm, with a mass of 0.5 g of BP stirred in beakers at 25°C until adsorption equilibrium. The pH of each solution is adjusted to 5.5. The adsorbent was previously introduced into a small sachet of filter paper closed by a wire. The homogenisation of the aqueous solutions is ensured by an agitator magnetic with a constant agitation.

Analysis Method

In this work, the dosage of metal solutions of Pb^{2+} ions realized at Laboratory of the National Office of Hydrocarbons and Mines (ONHYM), by the technique of the Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES).The spectrometer used is of type JY-38.

Percent Removal and Adsorption Capacity

The amount of metal ion adsorbed per unit mass of the biosorbent was evaluated by using following equations:

The amount of adsorption at time t (min), q_t (mg g^{-1}), was calculated by:

$$q_t=(C_o - C_t)\ V/m$$

The amount of adsorption at equilibrium was calculated by:

$$q_e=(C_o - C_e)\ V/m$$

Where, C_0 is the initial metal ion concentration and C_e is the metal ion concentration at equilibrium, C_t is the metal ion concentration at time t, and V is the volume of metal ion solution in liter, m is the mass of adsorbent in grams.

The percent of metal ion removal was evaluated from the equation:

$$(\%)\ \text{Removal}=\frac{Co - Ce}{Co} \times 100$$

RESULTS AND DISCUSSION

In this work, we have studied some physicochemical parameters (equilibrium time, pH of solutions, temperature, concentration of adsorbate and quantities of adsorbent) that can influence the maximum adsorption capacity of Pb^{2+} ions in solution on the beet pulp.

Effect of Contact Time

The kinetic curve of the transfer of the Pb^{2+} ions from the aqueous medium to the adsorbent, under our experimental conditions is illustrated in Figure 1.

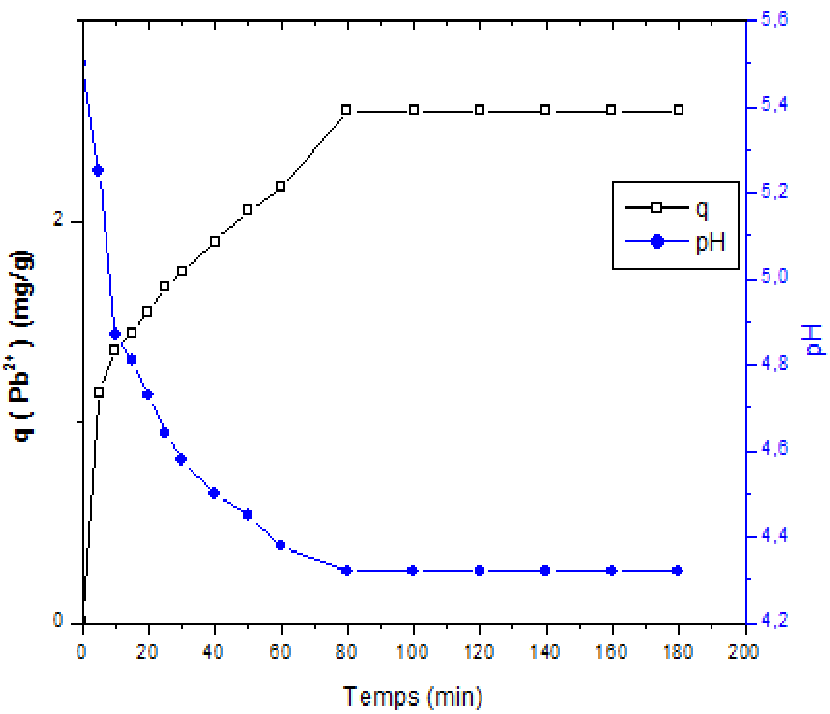

Figure 1. kinetics of adsorption of Pb^{2+} ions on BP

V_{aq}=100 ml, $[Pb^{2+}]$=20 ppm, pH_i=5.5, m (BP)=0.5g

The results obtained during this study, clearly show the increase in the quantity of metal ions fixed on the solid phase. This increase is accompanied by a drop in the initial pH of the aqueous solution, which went from 5.5 to 4.35. The decrease in pH shows that the adsorbent equilibrates with the metal solution by releasing the H^+ protons from hydroxyl sites, hydroxides of phenols and carboxylic sites to aqueous solutions, and consumes the metal ions Pb^{2+} according to a cation exchange mechanism following:

$$Pb^{2+} \text{(solution)} + 2H^+ \text{(solid)} \leftrightarrow Pb^{2+} \text{(solid)} + 2H^+ \text{(solution)}$$

The adsorption equilibrium is reached at 80 min and the percent removal is 64%, and the adsorption capacity is q=2.5 mg/g.

Effect of pH

The pH plays an important role in the adsorption process by affecting the surface charge of adsorbent, the degree of ionization and speciation of the adsorbate. Thus the effect of pH in the solutions on the removal efficiency of Pb^{2+} was studied at different pH ranging from 2.0 to 7.50. The results are shown in Figure 2.

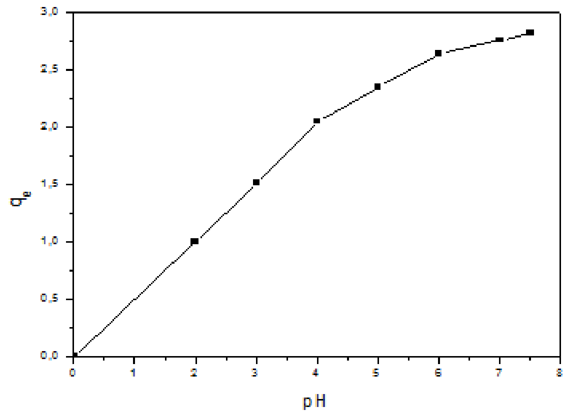

Figure 2. Effect of pH$_i$ on the adsorption capacity

It was observed that a sharp increase in the adsorption capacity from 1.1 mg/g 2.82 mg/g occurred when the pH values of the solutions changed from 2.0 to 7.50. The low removal efficiency at low pH is apparently due to the presence of higher concentration of H^+ in the solution which competes with the Pb^{2+} ions for the adsorption sites of The BP. With the pH increasing, the H^+ concentration decreases leading to increased of Pb^{2+} ions.

Effect of Temperature

The effect of the temperature on the adsorption capacity was investigated for Pb^{2+} ions solutions at initial concentration 20 ppm and amount of biosorbent 0.5 g. Three different temperatures of 25, 36 and 45 ºC were considered. From Figure 3, the amounts of adsorbed lead onto the BP increase with an increase in the temperature of metal solution. The adsorption capacities obtained at temperatures of 25°C, 36°C and 45°C respectively are as follows: 2.55 mg/g, 2.752 mg/g et 2.868 mg/g. These results indicate that adsorbent was suitable for heavy metals removal from aqueous media and the adsorption of Pb^{2+} ions is endothermic in nature.

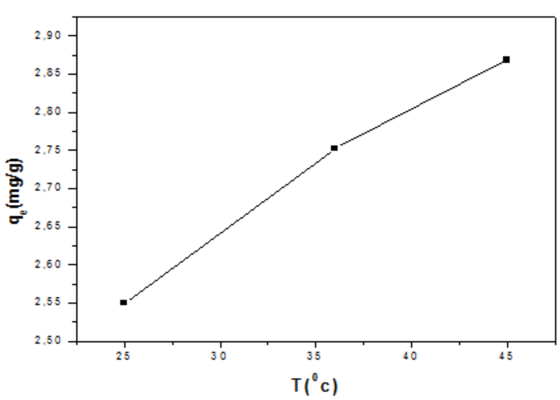

Figure 3. Effect of temperature on the adsorption capacity

Effect of Initial Metal Ion Concentration

The effect of the initial concentration of Pb^{2+} on the adsorption capacity was studied by varying the initial concentrations of the metal ions Pb^{2+} between 20 ppm and 400 ppm. The Figure 4 shows the evolution of the adsorption capacity of Pb^{2+} ions as a function of the initial concentration of metal. The amount of Pb^{2+} fixed to the

BP increases with the increase of the initial concentration and reached a maximum value of 2.87 mg/g at a concentration of 250 ppm of Pb^{2+}.

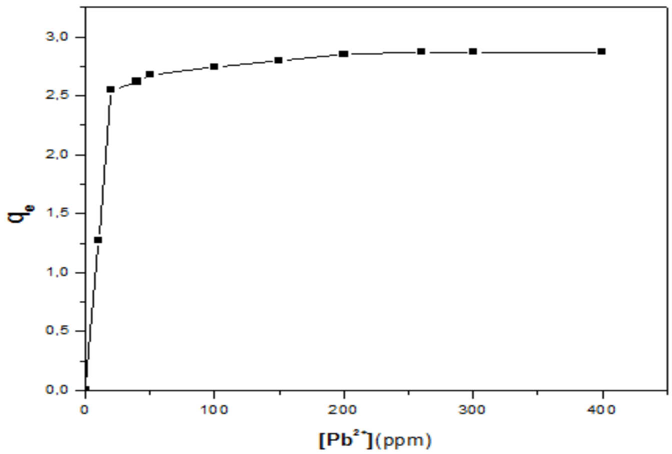

Figure 4. Effect of initial metal ion concentration on the adsorption capacity

Effect of the Material Mass

The effect of the BP dose on the removal of metal ions is shown in Figure 5. According to these results, we note that the percent removal of Pb^{2+} ions increases with increasing the mass of adsorbent brought into contact with the metal solution. Indeed, the increase in the percent removal can be explained by the fact that, as the mass increases, the contact surface offered for the adsorption of metal ions becomes large. This leads to an increase in the availability of the active sites (-OH, COOH...) Responsible for the complexation of the metal ions.

The dosage of the metal solutions of the Pb^{2+} ions shows that a mass of 0.9 g of the BP is sufficient to purify a metal solution of Pb^{2+} with a concentration of 20 ppm.

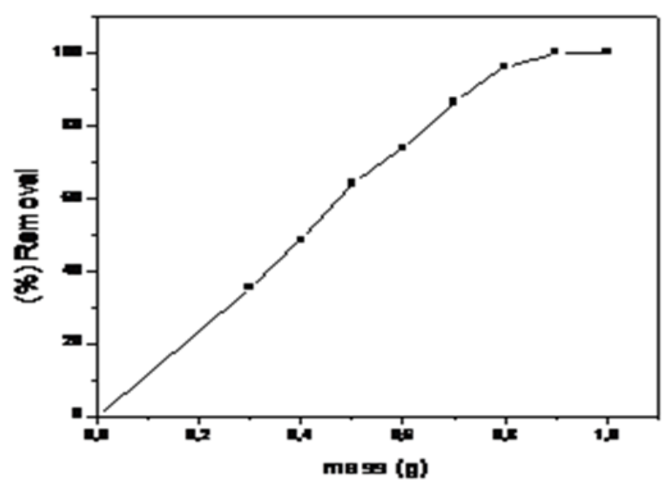

Figure 5. Effect of material mass on the adsorption

Adsorption of a Mixture of Metals

The study of competitive adsorption was carried out using a mixture of metal ions ($Pb^{2+,}$ Cd^{2+}, Zn^{2+}, Cu^{2+}, Co^{2+}) in equimolar concentration.

The Table 1 summarizes the initial and final concentrations, percent removal and adsorption capacity of Cd^{2+}, Cu^{2+}, Zn^{2+}, Co^{2+} et Pb^{2+} ions during the adsorption of a mixture of these metals from the beet pulp.

Table 1. Selectivity of adsorption by BP from of mixture (Pb, Co, Cd, Cu, Zn)

Metal ions	Pb^{2+}	Cd^{2+}	Zn^{2+}	Cu^{2+}	Co^{2+}
$[M^{2+}]_i$ (ppm)	19.91	10.98	6.35	6.19	5.58
$[M^{2+}]_f$ (ppm)	6.968	4.062	2.618	2.599	2.566
q (mg/g)	0.517	0.501	0.483	0.463	0.428
(%) Removal	65	63	60.5	58	54

According of the results of the adsorption of this mixture of metals by BP, we note that the elimination efficiencies of the metal cations of Pb^{2+}, Cd^{2+}, Zn^{2+}, Cu^{2+} and Co^{2+} Are classified in the following order: R (Pb^{2+})>R (Cd^{2+})>R (Zn^{2+})>R (Cu^{2+})>R (Co^{2+}), Therefore it can be concluded that the selectivity of these metals is in the following order: Pb^{2+}>Cd^{2+}>Zn^{2+}>Cu^{2+}>Co^{2+}.

Desorption and Regeneration

Effect of the concentration of mineral acid on deextraction: In this part, we have prepared of dilute solutions of the hydrochloric acid (HCl) of different concentrations (0.1 mol/l, 0.15 mol/l, 0.2 mol/l). In 100 ml of each solution, a bag of filter paper containing the BP loaded with lead. The curve of variation of the concentration of the lead in the acid solutions as a function of time is shown in Figure 6.

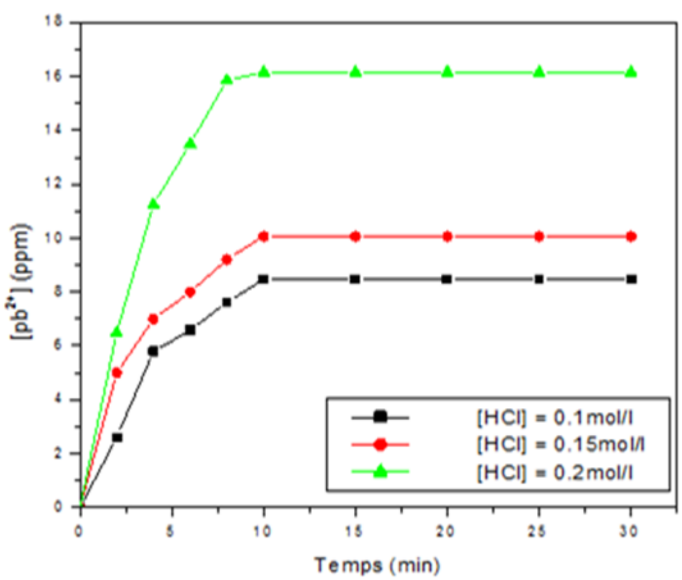

Figure 6. Desorption of lead fixed on the BP as a function of time for different concentrations of HCl

These results show that the release of the Pb^{2+} ions fixed on the BP depends on the concentration of the acid solution and that the more the concentration of the mineral acid increases the more the liberation of the metal ions fixed on the material increases. For a concentration of 0.1 mol/l of the acid solution, we have about 60% of Pb^{2+} was recovered, and for a concentration of 0.15 mol/l we have 86% Pb^{2+} was recovered, and the BP is completely emptied of metal for a concentration 0.2 mol/l of HCl. Also, the kinetics of desorption of metal ions on the acid solutions is very fast, and we have about ten minutes of agitation of systems to achieve the equilibrium.

Effect of cycles of reuse of the material on the percent removal: To carry out this study, we used a solution of HCl of concentration 0.2mol/l as a desorption agent because the latter offers a better metallic recovery. Three consecutive cycles of adsorption/desorption are carried out for the BP loaded with Pb^{2+}. The Table 2 summarizes the variation of extraction yields of Pb^{2+} by the BP respectively as a function of the reuse cycles.

Table 2: Percent removal of Pb^{2+} ions in function of reuse cycles of BP.

Nombre du cycle	1	2	3
Removal (%)	100	99.5	99.4

CONCLUSION

The study of the removal of Pb^{2+} ions in solution by adsorption on raw beet pulp was studied. The operating conditions used during the process of this work are: T=25°C, pH=5.5, Pb^{2+} ions concentration is equal to 20 ppm, Vaq=100 ml. The results obtained give the following conclusions:

- The adsorption kinetic shows that the adsorption equilibrium is reached at 80 min. But the kinetic of desorption of metal ions on the acid solutions is very fast, and we have about ten minutes of agitation of systems to achieve the equilibrium.
- The percent of removal ions is all the more important as the pH imposed on the solution is high.
- The maximum adsorption capacity of Pb^{2+} by BP is of the order of 2.55 mg/g.
- Under the operating conditions used, a mass of 0.9 g of the BP is sufficient to completely purify at 20 ppm of Pb^{2+} ions.
- The effect of the temperature on the adsorption shows the adsorption of Pb^{2+} ions is endothermic in nature.
- The treatment of a mixture of metals shows that the BP presents the sequence of following selectivity: $Pb^{2+}>Cd^{2+}>Zn^{2+}>Cu^{2+}>Co^{2+}$.
- The study of the regeneration of this material, after desorption of the metal ions by bringing it into contact with dilute acid solution shows that this material has good mechanical properties, and can be regenerated and repeatedly reused in the process of treating the metal solutions.

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