XANTIZAÇÃO DE RESÍDUOS DE SAWDUST PARA ADSORÇÃO DE ÍONS DE CHUMBO A PARTIR DE SOLUÇÕES AQUOSAS

XANTHATION OF SAWDUST WASTE FOR ADSORPTION OF LEAD IONS FROM AQUEOUS SOLUTIONS

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RESUMO

Metais pesados em efluentes industriais tenham contaminado águas naturais comprometendo a saúde dos seres humanos e animais. Os métodos tradicionais eliminam estes metais de águas residuais, mas eles são dispendiosos ou ineficaz em baixas concentrações de metais para os quais são necessários métodos alternativos. Nós investigamos a absorção de chumbo na serragem xanthated (tratamento CS₂). testes de cinética e de pH, isotérmicas de adsorção e espectroscopia de infravermelho foram realizadas. Estudos cinéticos indicaram que a adsorção equilibrada a 120 minutos a seguir uma cinética de pseudo-segunda ordem. A capacidade de adsorção foi de 72 mg Pb²⁺ g⁻¹ (máxima em pH 5, Freundlich tipo isotérmica, 98% de adsorção). Este produto obtido de matérias-primas sem valor comercial, pode ser usado para recuperação ambiental como alternativa ao dumping sua caros em aterros sanitários.

Palavras-chave: Estudos cinéticos; metais pesados; trocador catiônico; curva isotérmica

ABSTRACT

Heavy metals in industrial effluents have contaminated natural waters compromising the health of humans and animals. Traditional methods eliminate these metals from wastewater but they are costly or ineffective at low metal concentrations for which alternative methods are required. We investigated the adsorption of lead on xanthated sawdust (CS₂ treatment). Kinetic and pH tests, adsorption isotherms and infrared spectroscopy were performed. Kinetic studies indicated that adsorption equilibrated at 120 min following a kinetic model of pseudo-second order. The adsorption capacity was 72 mg Pb²⁺ g⁻¹ (maximum at pH 5, Freundlich type isotherm, 98% adsorption). This product obtained from raw materials without commercial value, can be used for environmental remediation as an alternative to its expensive dumping into landfills.

Keywords: Kinetic studies; contamination; heavy metals; cation exchanger; isotherm

1. INTRODUCTION

The disposal of heavy metals through industrial effluents has led to contamination of natural water bodies. This has endangered the health of humans and animals because, as metals are not biodegradable, they can accumulate in living tissues causing various diseases and disorders by their toxic and carcinogenic effects (Ngah and Hanafiah, 2008). To remove heavy metals from wastewater, various conventional methods have been used; however, these methods are not economical or effective when metal concentration is in the 1-100 mg L⁻¹ range (Torres-Blancas *et al.*, 2013). Different biomass residues, such as orange peels (Liang *et al.*, 2009), de-oiled allspice husk (Torres-Blancas *et al.*, 2013), and other biomass types (Patriota *et al.* 2016) have been used as bioadsorbents for the removal of heavy metals in wastewater. Carboxylic and phenolic groups are the main active sites for metal removal onto native agricultural waste (Pagnanelli *et al.*, 2003).

Adsorbents are chemically modified by addition of different chelating groups to increase their adsorption capacity. Sulfur groups as sulfides, thiols, dithiocarbamates, dithiophosphates and xanthates have also been used to increase the adsorption capacity of agricultural waste (Torres-Blancas *et al.*, 2013; Liang *et al.*, 2009; Chakraborty and Tare, 2006; Kumar *et al.*, 2000; Pillai *et al.*, 2013). These groups are characterized by a high affinity for heavy metals but a low affinity for the light ones. Xanthates are formed by reacting an organic substrate containing hydroxyl groups, with carbon disulfide under basic conditions according to equation 1 (Liang *et al.*, 2009):

Sawdust is mainly composed of cellulose, hemicellulose and lignin, and is an ideal substrate for the synthesis of xanthates due to its high content of hydroxyl functional groups. In this study, we prepared an adsorbent by incorporation of xanthate groups to the sawdust surface and evaluated its capacity to adsorb Pb²⁺ from aqueous solutions through adsorption, kinetic and optimum adsorption pH studies.

2. METHODOLOGY

2.1 Instrumental

Metal concentrations were determined by flame atomic absorption spectrometry (ICE 3000, Thermo Scientific, Zeeman correction). Other parameters were measuring time: 4.0 s and number of replicate analyses, 3. Solutions were prepared with a sodium acetate/acetic acid buffer and the ionic strength was adjusted with NaCl. Infrared spectra of the adsorbents were obtained by mixing one mg of sample with 100 mg of KBr, compressing to obtain a pellet that was analyzed on a FTIR (SHIMADZU-8400) in the 4000-400 cm⁻¹ range, to identify the functional groups involved in the adsorption of heavy metals.

2.2 Xanthation of Sawdust

Carito wood sawdust (*Enterolobium cyclocarpum*) was obtained from a local sawmill (Cartagena, Colombia), washed with distilled water and dried at 70° C for 24 h. Subsequently, it was milled in a ball mill, sieved to a 0.225 mm particle size, washed with 0.1 N HCl and distilled water to neutral pH; then, it was dried at 70° C for 24 h to remove colored substances and contaminants. The product obtained was named S. Later, xanthation was performed according to equation 1: twenty five grams of sawdust were put in a polyethylene vial mechanically stirred, 500 ml of a 4 M NaOH solution were added using a 0.33 sawdust/NaOH w/w ratio stirring for 3 hours and, finally, 30 ml of CS₂ with a 1.12 CS₂/sawdust w/w ratio stirring for 4 hours. The mixture was allowed to stand for 16 hours, filtered, washed several times with deionized water and dried at 70°C (Chakraborty and Tare, 2006). This product was named XS.

2.3 Effect of pH

The effect of pH on Pb²⁺ adsorption was examined by mixing 50 mg of XS or S with 10 ml of 100 ppm of Pb²⁺ at 25°C at pH values of 3 to 5 adjusted by adding 0.1 M HNO₃ and 0.1 M NaOH solution. After 3 h stirring, the solutions were filtered and Pb²⁺ was determined in the filtrate.

2.4 Kinetic Study and Adsorption Experiments

500 mg of adsorbent were mixed with 100 ml of 100 ppm of Pb²⁺ at pH 5 for 2.2 h and 25° C. Samples were extracted at different time inter-

vals, and filtered to determine their concentrations. In the adsorption experiments, 50 mg of adsorbent were mixed with 10 ml of 25, 50, 100, 200 or 400 ppm of Pb^{2+} at pH 5 for 2 h and 25° C. The amount of adsorbed metal, q_e , was determined using:

$$q_e = \frac{C_0 V_0 - C_e V_0}{m} \quad (Eq. 2)$$

Where C_0 is the initial concentration of Pb^{2+} in $mg\ L^{-1}$, V_0 the initial volume in liters, C_e the equilibrium concentration of Pb^{2+} in $mg\ L^{-1}$ and m the mass of adsorbent in grams.

3. RESULTS AND DISCUSSION

3.1 pH Effect

Figure 1. Effect of the exchange solution pH on Pb^{2+} adsorption on S (■) and XS (◆). Adsorbent dose: 50 mg/10 ml, concentration: 100 ppm of Pb^{2+} , contact time: 3 h. The optimum adsorption pH was 5.

pH affects Pb^{2+} adsorption from aqueous solutions on S and XS (Figure 1). A poor Pb^{2+} adsorption was observed at acid pH because of strong electrostatic repulsion between H^+ and metal ions on the sawdust surface, preventing metal ions from interacting with the adsorbent (Jiang *et al.*, 2009). This type of competition has been described with metal biosorption onto olive pomace waste (Pagnanelli *et al.*, 2003). The greater adsorption at lower pH for XS than for S was due to the higher nucleophilicity of xanthate groups than that of the original oxygen groups in S; therefore, even at low pH, XS showed a high

adsorption of Pb^{2+} . By increasing pH, the repulsion force becomes weak favoring Pb^{2+} diffusion to the adsorbent surface, increasing adsorption (Acar and Eren, 2006). Figure 1 shows that the maximum adsorption on S and XS was obtained at pH 5 with adsorptions of 89% and 98% of Pb^{2+} from 100 ppm solutions and 50 mg/10 ml doses of adsorbent, respectively. The main advantage of XS over S was that Pb^{2+} adsorption was higher for XS at all pH values, especially at low pH. This is consistent with Torres-Blancas *et al.* (2013) who evaluated the adsorption of lead on pepper peel and xanthated pepper peel. They observed that at acid pH, adsorption on pepper peel was poor as a result of the strong electrostatic repulsion, while the adsorption of lead was high at all pH for XS; similar results were obtained by Liang *et al.* (2009) and Taty-Costodes *et al.* (2003)

3.2 Adsorption Kinetics

One important property of adsorbents is the speed with which the adsorbate is adsorbed and reaches equilibrium. The mathematical model that describes the amount of Pb^{2+} adsorbed at a zero time and at a specific time, is given by:

$$\left(\frac{mg\ Pb^{2+}}{g} \right)_n = \frac{[(CV)_{n-1} - (CV)_n]}{g} + \left(\frac{mg\ Pb^{2+}}{g} \right)_{n-1}$$

Where C is the remaining concentration of Pb^{2+} at time t in $mg\ L^{-1}$ (calculated with Equation 2), V the volume of the remaining solution at time t in liters, and n the number of data taken in time t . Using the graph of Pb^{2+} adsorbed as a function of time, we identified the time the equilibrium was reached and the corresponding adsorption capacity, q_e (Silgado *et al.*, 2014). To assess the rate of Pb^{2+} adsorption on S and XS, two kinetic models were considered. The model of pseudo-first order was proposed by Lagergren (Tseng *et al.*, 2010; Lagergren, 1898):

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t$$

Where q_e and q_t are the adsorption capacities ($mg\ g^{-1}$) at equilibrium and time t , respectively, and k_1 is the rate constant model (min^{-1}). k_1 values were obtained from the intercept and

slope of the graph of $\log (q_e - q_t)$ vs. t . The kinetic model of pseudo-second order is given by:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$

Where q_e and q_t were defined in the model of pseudo-first order, and k_2 is the rate constant model of pseudo-second order ($\text{g mg}^{-1} \text{min}^{-1}$) (Torres-Blancas *et al.*, 2013). k_2 and q_e values were obtained from the intercept and slope of the graph of t/q_t vs. t (Silgado *et al.*, 2014). The fact that S and XS fit a pseudo-second-order kinetics shows that the limiting-speed step can be caused by chemical sorption or chemisorption involving valence forces through the exchange of electrons between sorbent and sorbate (Ho and McKay, 1999; Ho, 2006). Xanthate groups allow SX to adsorb metal ions by ion exchange or complexation, or a combination of both

processes. By ion exchange, two sulfur atoms, negatively charged, capture Pb^{2+} , while complex formation occurs between the sulfur atoms and Pb^{2+} , which is characterized by empty orbitals that can be occupied by the xanthate free electrons to form a complex (Torres 2013). This model also assumes that the initial rate of adsorption, h_0 , ($\text{mg g}^{-1} \text{min}^{-1}$) is proportional to the square of the number of remaining free surface sites, and is defined by:

$$h_0 = k_2 q_e^2$$

Where q_e and k_2 are the adsorption capacity (mg g^{-1}) and the pseudo-second order model rate constant ($\text{g mg}^{-1} \text{min}^{-1}$), respectively. The results obtained for each model are described in Table 1.

Table 1. Kinetic parameters for S and XS. Pb^{2+} concentration: 100 ppm, adsorbent dose: 500 mg/100 ml, pH: 5, contact time: 140 min. Adsorbents S and XS followed a pseudo second-order kinetics.

Adsorbent	q_e (exp)	Kinetic Model						
		Pseudo first order			Pseudo second order			
		q_e model (mg g^{-1})	k_1 min^{-1}	R^2	q_e model (mg g^{-1})	k_2 ($\text{g mg}^{-1} \text{min}^{-1}$)	R^2	h_0 (mg g^{-1})
S	17.8	17.0	0.045	0.972	17.6	0.047	0.999	14.8
XS	19.3	16.6	0.027	0.967	19.2	0.095	0.999	35.6

q_e (exp): experimental q_e

From the data, it follows that, for the pseudo-first order kinetic model, the theoretical values of q_e for S and XS differ from the experimental q_e , as evidenced by the regression coefficients of 0.972 and 0.967 for S and XS, respectively, but they agree on the model of pseudo-second order with a regression coefficient of 0.999 for both S and XS. Therefore, the mechanism of adsorption of lead ions on S and XS is represented by the pseudo-second order kinetic model, and this agrees with the (Liang *et al.*, 2011; Liang *et al.*, 2009; Torres-Blancas *et al.*, 2013). This indicates that chemical adsorption was the mechanism of speed control. As for the initial velocity h_0 , this was faster for XS than for S, confirming that xanthation increases the adsorbent affinity towards metals.

3.3 Adsorption Isotherms

Adsorption isotherms are mathematical models used to estimate the maximum amount of contaminant that an adsorbent can remove from an aqueous solution. The adsorption isotherms were evaluated using the Langmuir and Freundlich models. The Langmuir isotherm is given by:

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m}$$

Where q_e is the amount of material retained by a specific amount of adsorbent (mg g^{-1}), C_e the equilibrium concentration (mg L^{-1}), q_m the amount of metal or contaminant necessary to form a monolayer on the adsorbent surface (mg g^{-1}) and expresses its maximum adsorption capacity, and b the Langmuir constant (L mg^{-1}) (Silgado *et al.*, 2014; Sciban *et al.*, 2006). The es-

sential characteristics of the Langmuir isotherm can be expressed in terms of a constant dimension known as the separation factor RL given by:

$$RL = \frac{1}{1 + bC_0}$$

Where, b is the Langmuir constant and C_0 the initial concentration of adsorbate in the solution. We used RL to obtain the shape of the isotherm and the favorability of adsorption, according to the following criteria: if $RL > 1$ adsorption is unfavorable, $RL = 1$ linear, $0 < RL < 1$ favorable, and $RL = 0$ the adsorption is irreversible (Memon *et al.*, 2007).

Unlike the Langmuir isotherm, that assumes a homogeneous surface, the Freundlich isotherm considers a heterogeneous surface and is used at low pressures:

$$\log q_e = \log KF + \frac{1}{n} \log C_0$$

Where q_e is the amount of material adsorbed by a specific amount of adsorbent (mg g^{-1}), C_e the equilibrium concentration (mg L^{-1}) in the liquid phase, KF the Freundlich constant ($\text{mg}^{1/n} \text{L}^{1/n} \text{g}^{-1}$) and n the heterogeneity factor which depends on the substance (Liang *et al.*, 2009). Figure 2 shows the Langmuir and Freundlich isotherms for Pb^{2+} adsorption and Figure 3 the separation factors for S and XS.

Figure 2. Langmuir and Freundlich isotherms for Pb^{2+} adsorption on S (left) and XS (right). Adsorbent dose: 50 mg/10 ml, metal concentration: 100 ppm of Pb^{2+} , contact time: 120 min. pH: 5. Sand XS fit the Freundlich isotherm; q_e is the sawdust adsorption capacity of Pb^{2+} and C_e the equilibrium concentration of Pb^{2+} .

The isotherms in Figure 2 show that the adsorption capacity in the equilibrium, C_e , increases as a function of concentration in solution, q_e , while Figure 3 confirms that the adsorption of Pb^{2+} on S and XS was favorable because the RL values for all metal concentrations were in the range 0 -1. According to Kumar *et al.* (2000) this means that adsorption is more favorable at high concentrations. Table 2 shows the values of the isotherm parameters for S and XS, determined by least squares.

Table 2. Langmuir and Freundlich isotherm parameters for Pb^{2+} adsorption on S and XS.

Adsorbent	Kinetic Model						
	Pseudo first order				Pseudo second order		
	q_m $mg\ g^{-1}$	b $L\ mg^{-1}$	R^2	RL	K_f $L\ g^{-1}$	n	R^2
S	64.5	0.069	0.938	0.062	7.04	2.20	0.997
XS	72.0	0.109	0.977	0.115	9.02	2.07	0.981

Figure 3. Separation Factors (RL) in the adsorption of Pb^{2+} on S (left) and XS (right). Adsorption was favorable because $0 < RL < 1$. C_0 is the initial concentration of Pb^{2+} .

To determine which of the two isotherm models was best suited to Pb^{2+} adsorption, we evaluated correlation coefficients that measure how well the experimental values were adjusted to theoretical ones (Panda *et al.*, 2008). Table 2 shows that the correlation coefficients with respect to lead adsorption on S were 0.938 and 0.977, and for XS, 0.997 and 0.981, for the Langmuir and Freundlich models, respectively. This means that, for both adsorbents, the Freundlich model gave the best fit; that is, lead adsorption occurred due to the energy distribution of the active sites for adsorption and the absence of monolayers. These results agree with those reported by Torres-Blancas *et al.* (2013) who established that the adsorption of lead on xanthated and untreated pepper peel follows a Freundlich isotherm type. Our results also partially agree with Liang *et al.* (2009) who studied the adsorption of lead on untreated orange

peel, and concluded that it follows a Freundlich isotherm type, but once xanthated follows a Langmuir type. This means that the type of adsorption isotherm depends on the nature of adsorbent used.

3.4 Infrared Spectroscopy Analysis

The FTIR spectra of S and XS are shown in Figure 4. In the spectrum of S, broad, intense absorption peaks around $3442\ cm^{-1}$ correspond to OH stretching vibrations due to inter and intra macromolecular hydrogen bonds of molecular associations such as alcohols and phenols (Torres-Blancas *et al.*, 2013), and at $2923\ cm^{-1}$ due to CH groups stretching vibration produced by alkanes and $-OCH_3$ $-CH_2OH$ groups, in cellulose and lignin (Liang *et al.*, 2011). The peak at $1739\ cm^{-1}$ was the result of stretching vibrations of carbonyl groups in lignin. The peaks at 1645, 1514, 1503,

1463 and 1425 cm^{-1} are due to stretching vibrations of C = C bonds of aromatic groups in lignin. The peaks at 1040, 1050, 1160, 1242 and 1368 cm^{-1} were assigned to torsion or deformation and O-H stretching vibrations of C-O of primary and secondary alcohols, and phenolic groups, and that at 667 cm^{-1} to balancing of C-H groups. Some changes were observed in the spectrum of XS with respect to S. For example, the peaks due to stretching vibrations of OH, CH_2 and CH_3 groups were weaker and more elongated than in S because hydroxyl groups reacted with CS_2 . Xanthate groups in XS were identified by the appearance of new peaks at 612, 899 and 1237 cm^{-1} that correspond to $\gamma\text{C-S}$, $\gamma\text{C=S}$ and $\gamma\text{S-C-S}$ vibrations. This is consistent with reports by Panda *et al.* (2008) who identified xanthate groups in *Lathyrus Sativus* peel, a legume from Asia and East Africa, by peaks appearing at 661 and between 1200 -1250 cm^{-1} ; Pillai *et al.* (2011) who associated sulfur groups to peaks at 538, 1020 and 1151.5 cm^{-1} corresponding to $\gamma\text{C-S}$, $\gamma\text{C=S}$ y $\gamma\text{S-C-S}$ vibrations; and Mustafa *et al.* (2004) who indicated that xanthate groups are found at 800-1200 cm^{-1} .

Figure 4. FTIR spectra of S and XS

4. CONCLUSION

Xanthated sawdust has a great potential as an efficient adsorbent for heavy metals. Its adsorption capacity was 72 $\text{mg Pb}^{2+} \text{g}^{-1}$, following the Freundlich isotherm. The optimal pH for adsorption was ≥ 5 with 90% adsorption and equilibrium was reached in about 120 minutes following a pseudo-second order kinetics.

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