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Lead (II) removal using lignin obtained from processing banana pseudostem

Remoción de plomo (II) usando lignina obtenida a partir del procesamiento del seudotallo de plátano

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Abstract

The adsorption of lead ions (Pb^{2+}) on lignin was investigated. Lignin of black liquor generated in the paper production process from banana stem was recovered, obtaining a recovery efficiency of 82%. Lignin was characterized by infrared spectroscopy to identify suitable active sites for the adsorption of heavy metals. Surface characteristics were determined by adsorption–desorption isotherms of nitrogen (N_2). Recovered lignin showed a surface area of 840 m^2/g and a total pore volume of 0.30 cm^3/g. After that, solutions of Pb^{2+} at 0.6, 0.8 and 1.0 mM were prepared to evaluate the adsorption capacity of lignin with respect to initial concentration of the ions. The final concentration of Pb^{2+} was determined by Atomic Absorption Spectroscopy (AA) achieving removal efficiencies of 55%.

Key words: Adsorption, residual liquor, lignin, pseudostem

Resumen

Se evaluó la adsorción de iones plomo (Pb^{2+}) sobre lignina recuperada del licor residual generado en el proceso de producción de papel a partir de seudotallos (vástago) de plátano. La eficiencia de recuperación encontrada fue de aproximadamente 82%. La lignina fue caracterizada mediante espectroscopia de infrarrojo con el objeto de identificar sitios activos adecuados para el proceso de adsorción de metales pesados. Sus características de superficie se determinaron mediante isotermas de adsorción – desorción de nitrógeno (N_2). La lignina recuperada después de su uso en adsorción mostró un área superficial de 840 m^2/g y un volumen total de poros de 0.30 cm^3/g. Para evaluar la capacidad de adsorción de la lignina respecto de la concentración inicial de los iones, se prepararon soluciones de Pb^{2+} 0.6, 0.8 y 1.0 mM. Finalmente, se determinó la concentración final de Pb^{2+} por medio de espectroscopia de absorción atómica, encontrando remociones de 55%.

Palabras clave: Adsorción, plomo, licor residual, lignina, seudotallo de plátano.

Introduction

In recent years it has increased the control of pollution caused by heavy metals in the water. In particular is of great importance the removal of metal ions such as Pb (II), Hg (II) and Cd (II) which have harmful effects on human health when present above the limits set by regulatory agencies (Basso *et al.,* 2000). One of the most harmful metals is lead resulting from the processing industries dedicated to the processing of batteries, manufacture of tetraethyl lead, petrochemical, refineries, ceramic and glass industries, electroplating, among others (Goel *et al.,* 2005).

The main techniques used to remove heavy metals in water include chemical precipitation, membrane filtration, ion exchange and adsorption on activated carbon (Gabaldón *et al.,* 1996). However, these methods have limitations such as high operating costs, in the case of the activated carbon adsorption, and difficulties in meeting regulatory requirements, in the case of chemical precipitation. According to the World Health Organization (WHO) for water purification has established a guideline value for lead concentration of 0.010 mg/l (FAO, 2004). For the foregoing reasons at present pursuing the development of adsorbent materials that allow removing metal contaminants efficiently and at low cost is ongoing. These materials are agro-industrial waste (Basso *et al.,* 2002), fly ash, pine bark and lignin. According to Mazzeo *et al.* (2010) 79% of plantain pseudostem stands in the field, 6% is deposited as residue and only 15% is used for animal feed or as fertilizer. This residue is lignocellulose source so it can be used as raw material for paper production; also it contains about 60% cellulose, 16% lignin, and 23% hemicellulose and minerals.

Lignin is also the main component of the waste liquor generated in the paper industry. According Guo *et al.* (2007) this industrial activity annually produce 500,000 tons of this product and only 2% have some use, while the remaining 98% is solubilized and forms part of the pollution load. However this high contaminant load is retrievable, since the solubility of the lignin in an alkaline medium and insolubility in acid medium permits their recovery by physical processes such as filtration or centrifugation.

Furthermore, lignin has chemical properties as dispersant, adsorbent, binder, emulsifier and stabilizer of emulsions (Gilarranz, 1998), properties that have not been fully developed. The main functional groups in lignin include phenolic hydroxyl, aliphatic hydroxyl, methoxyl, carbonyl, carboxyl and sulfonate (Mansouri, 2006) and its structure may vary from plant source material, so it is necessary to identify the carboxyl and phenolic groups in the lignin molecule. The study by Guo *et al.* (2007) showed that due to the presence of these active sites, the lignin molecule has a higher affinity to metal ions, which can be used in the adsorption of heavy metals such as Pb (II), Cu (II), Cd (II), Zn (II), and Ni (II) in wastewater treatment. This work aimed to evaluate the usefulness of the pseudostem of banana, an agro-industrial waste, in the absorption of lead.

Materials and methods

Obtaining cellulose and waste liquor with lignin

Banana pseudostem with a moisture content of 71.1% were subjected to an initial treatment to remove the bark and reduce its size. The size was reduced by 0.5 mm cross-sections and the resulting material was subsequently liquefied. Then the delignification process was performed by alkaline treatment with a solution of sodium hydroxide (NaOH) 30% w/v with temperature below 60 °C for 30 min. The extraction was performed at room temperature for 3 h. Finally, filtration was performed to separate the solid material (cellulose), which was used in papermaking, and the residual liquid or liquor with pH 13 where the lignin and other components of the pseudostem were found.

Lignin recovery for this treatment were evaluated with sulfuric acid (H2SO4) and hydrochloric acid (HCl) (Abarca and Blanco, 2003).

Adsorption assay

Lead solutions at 0.6, 0.8 and 1.0 mM where prepared using lead nitrate ($Pb(NO_3)$), according to the recommendations by Guo *et al.* (2007), in order to have comparison points between the obtained results vs. other studies results.

Lignin characterization

The recovered lignin was characterized by near-infrared spectroscopy (NIR) and structural analysis. The purpose of the NIR characterization was to identify the active sites of the lignin obtained experimentally (Figure 1). The NIR spectrum of lignin has a very broad band between 3500 - 3100/cm, assigned to O-H tension due to the formation of hydrogen bonds (Bykov,

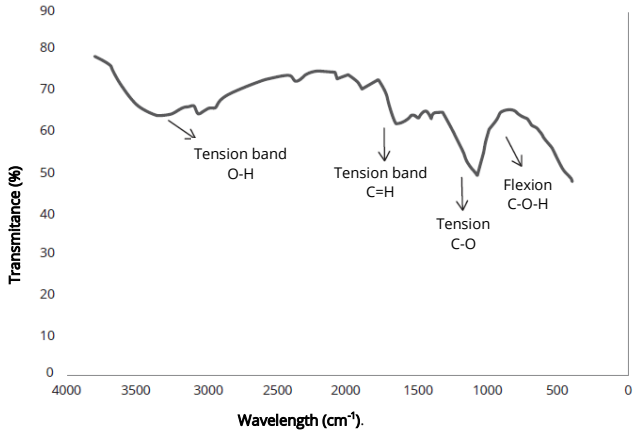

Figure 1. Identification of the active sites in lignin recovered from waste liquor.

2008). Additionally, to ensure the presence of the carbonyl group, the tensions associated to C=O (1730 – 1700/cm), C–O 211 (1320 – 1200/cm) bonds and a flexion in C–O–H that forms a bell shape band at 900/cm are identified (Fernández, 2013).

The structural analysis was performed based in nitrogen adsorption-desorption isotherms at 77.3 K. The superficial area was obtained with the model proposed by S. Brunauer, P. Emmett and E. Teller (BET) (Castellar, 2012) and in the same manner the total pore volume was obtained. The isotherms were taken in 45 points but, only the measurements with relative pressures in the range of applicability of the BET method (0.05 – 0.30) were taken into account (Castellar, 2012). In this case the assay was neither done with values lower than 0.05 because of the heterogeneous surface presence, nor above 0.30 due to condensation values (Martín, 1990). Amount of absorbed nitrogen is measured by changes in the pressure at the phase that is absorbed till a monolayer is obtained, from which, and taking into account the area occupied by each molecule, the surface area is calculated (Rodríguez, 2011).

Adsorption assays

As absorbent material the resulting lignin was used. Initially 1 g of lignin was hydrated in 400 ml of 0.01M sodium nitrate ($NaNO_3$) solution and stirred by 2 h. Then, $Pb(NO_3)$ at 0.6, 0.8 and 1.0 mM concentrations was added, according to the type of analysis, and it was in contact with the solution for 30 min at room temperature. The remove the lignin together with the Pb^{2+} ion, the solutions were filtered (Guo *et al.*, 2007). The ions final concentration was determined by atomic absorption spectroscopy. Although generally a graph of absorbance versus concentration of the standards used (known concentration) is developed; in this case, standard solutions with concentrations 0.5, 1.0 and 1.5 mg/l were used. Before the reading, it was determined whether the initial sample (hydrated lignin with $NaNO_3$) had levels of lead ion (Pb^{+2}), for that a blank treatment as control to determine the absorbance was performed. The calculated value was zero. Finally reading of samples in which Pb^{+2} solutions at initial concentrations of 0.6, 0.8 and 1.0 mM were added individually was performed.

The effectiveness of the used method was determined by calculating the absorption capacity of lignin (q), defined in terms of the initial concentration (C_0), final concentration of the solution or equilibrium concentration (C_f), the sample volume (V) and the amount of absorbent material (G) (equation 1) (Suteu *et al.*, 2010).

$$q = \frac{(C_0 - C_f)V}{G} \qquad (1)$$

Results and discussion

Lignin extraction and characterization

In Table 1 is shown that the most effective treatment to recover lignin was the one with sulfuric acid, which recovers the highest amount (82%) of this compound due to the precipitation of the products degraded from polysaccharides; on the opposite, using hydrochloric acid more dirt is generated.

The data showed the best results with the use of sulfuric acid, therefore 3 ml of it were added to reduce the pH of the medium and precipitate lignin, which was recovered in solid by vacuum filtration (0.7 bar), washed with distilled water and dried at 60 °C.

Table 1. Recovered lignin by HCl and H_2SO_4.

Assay	Method	Liquor volume (ml)	Recovered lignin (%)
1	HCl treatment	70	61.4
2	H_2SO_4 treatment	70	82.13

The surface area of lignin was calculated by the BET method (Castellar, 2012) using the equation 2 that correlates the reduced pressure (P_r), the absorbed amount (n^s), the required

amount to form the monolayer (n_m) and a constant (C) that associated the average heat for absorption in the first layer with the liquefying heat of the adsorbate (Martín, 1990).

$$\frac{P_r}{n^s(1-P_r)} = \frac{1}{n_m C} + \frac{C-1}{n_m} P_r \qquad (2)$$

The C and n_m parameters were calculated by lineal regression analysis of the curve showed in Figure 2. The surface area according to BET was evaluated by equation 3, where the n_m parameter, Avogadro number (L) and the transversal area occupied by nitrogen are associated.

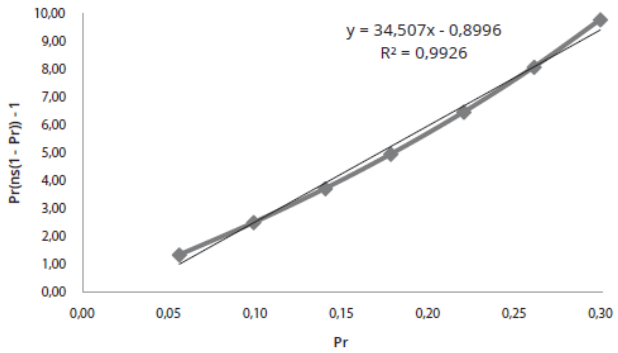

Figure 2. Nitrogen adsorption isotherm at 77 K.

$$a_{BET} = Ln_m a_m \qquad (3)$$

In the Figure 3 and in the Table 4 the volume of absorbed nitrogen (Vads) is displayed in function to the relative pressure according to the most common experimental isotherms classification.

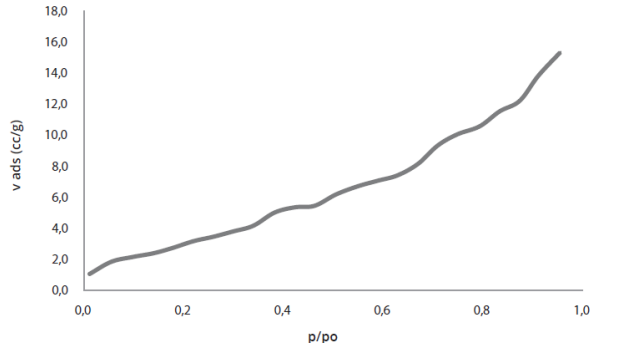

Figure 3. Nitrogen adsorption isotherm on the lignin simple recovered from waste liquor.

Table 4. Results of the characterization by nitrogen adsorption isotherms.

Parameter	Value
C	1.298
n_m	0.0086
a_m (nm^2)	0.162
a_{BET} (m^2/g)	839.04
V_T (cm^3/g)	0.30

In Figure 3 the obtained isotherm is similar to type II and III isotherms, showing that the absorption happens in multilayers in non-porous solids or with multiple micropores that favor the adsorption process (UNAM, 2012).

The total pore volume was calculated by equation 4 that associates the nitrogen molarity (M) and the nitrogen density at 77 K.

$$V = \frac{M n_m}{\rho} \qquad (4)$$

In Table 2 is shown a summary of the structural analysis results.

Table 2. Experimental data for the lignin extraction by alkaline hydrolysis and recovery with H_2SO_4.

Assay No.	Wet raw material (g)	Extracted lignin (%)
1	226.1	82.13
2	237.4	64.53
3	268.4	80.04
4	119.1	79.21
5	246.3	83.05

Lead adsorption with lignin

For the adsorption assay the initial lead concentration were defined according to the information of experimental tests (Guo *et al.*, 2007). According to the data in Table 3, when comparing the adsorption capacity to the initial concentration of the Pb^{+2} ion, it was found that with more concentration in the initial solution the absorption capacity is reduced, since in this cases the solution can saturate the absorbent material.

The efficiency of removal was moderately high (55%). It is important to mention that other absorbents, like activated carbon, have higher

Table 3. Removal efficiencies of Pb^{2+} using lignin as absorbent agent.

C_{ini} (mM)	C_{fin} (mM)	m_{in} (g)	m_{fin} (g)	q (mg /g lignin)	Removal efficiency (%)
0.632	0.2828	0.02619	0.01170	23.27	55.25
0.811	0.5931	0.03361	0.02458	14.58	26.87
1.027	0.9264	0.04128	0.03724	6.70	9.80

Average data of two experiments per each concentration.

removal efficiencies but, the methods to obtain them are more complex and expensive because of they are related to the pyrolysis process in order to get carbon. Moreover, temperatures over 500 °C are required, implicating high energy costs, to activate the carbon chemical compounds are used, normally acid compounds, which are also costly during the process. On the opposite, the treated lignin by the process described in the present research is a result of agro-industrial waste (plantain pseudostem) of low cost and highly available in the agro-industry.

Conclusions

The lignin obtained from the waste liquor generated in the paper processing from plantain pseudostem, has a suitable material for metal absorption since, besides a specific area of 840 m^2/g, there are active sites in its structure.

Efficient methods to extract and recover lignin were established. The treatment with sulfuric acid had an approximate efficiency of 82%.

The absorption tests showed high affinity of the lignin for lead, with a maximum removal of 23.27 mg/g of lignin (55 %).

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