RESEARCH ARTICLE

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USE OF LIGNIN GENERATED IN THE BIOETHANOL PRODUCTION PROCESS FOR BIOSORPTION OF LEAD IONS IN AQUEOUS SOLUTION

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ABSTRACT

Lignin contained in the black liquor generated during alkaline delignification of cellulose for bioethanol production was precipitated with H_2SO_4 and evaluated as biosorbent of Pb(II) ions in aqueous solution. Experimental design (DOE) and response surface methodology (RSM) were carried out in order to reduce the number of experiments and achieve the best conditions for biosorption procedure. Three factors at three levels were studied: initial pH (3; 4 and 5), biosorbent mass (50 mg; 100 mg and 150 mg), and initial Pb(II) concentration (40 mg L^{-1}; 60 mg L^{-1} and 80 mg L^{-1}). The kinetic parameters were also evaluated using the biosorption measurements. The results indicated that the higher the metal concentration, the lower was the required amount of biosorbent in Pb(II) removal. Pb(II) amount adsorbed by lignin was 60.4 mg g^{-1} and corresponded to its 75.5% removal. The kinetic model that best fit was the pseudo-second order.

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INTRODUCTION

Most of heavy metals present in aquatic environments due to, mainly, an increase on industrial and agricultural activities cause severe damage to human and aquatic life and can bioaccumulate in these organisms (Wang *et al.,* 2015). They are considered not biodegradable and must be removed from polluted water streams in order to meet increasingly stringent environmental quality standards (Vasconcelos *et al.,* 2009). Lead is one of the most widespread toxic heavy metal contaminants in the environment and its contamination in drinking water is a major source of concern due to its detrimental effect on human health. It can also cause a range of negative effects, from behavioural problems and learning disabilities to death (Yadav *et al.,* 2014). Such effects are mainly associated to their bioaccumulation in bones

(half-time over 20 years) and enzymes inhibition, which results in a probable carcinogenic agent (Morosanu *et al.,* 2017). The highest amount of pollution with Pb(II) comes from textile dyeing, ceramic and glass industries, as well as electroplating, metallurgy, petroleum refining, plastic and battery manufacture and mining operations (Farooq *et al.,* 2010). Thus, it is extremely important to reduce Pb(II) concentration in industrial effluents before their discharge into the environment. Several processes of heavy metals elimination, mainly lead, are used: precipitation, electro-precipitation, electro-coagulation, cementing and separation by membrane, solvent extraction and exchange of ions on resins (Naima *et al.,* 2013). Since the conventional methods for heavy metals removal are either too expensive or create large amounts of toxic sludge, attention has been paid to biosorption, technology that use microorganisms (Golab *et al.,* 1991) or cheap, abundant, organic waste for

sequestering pollutants from contaminated environments (Sadeek *et al.,* 2015). Recent studies showed that common agricultural waste products or natural polymers could be used as potential biosorbents to remove heavy metals from wastewater (Sadeek *et al.,* 2015). The use of lignocellulosic biomass is an interesting and innovative adsorption process. This fact happens due its major constituents, which offer a large variety and abundance of functional groups that can act out as active sites on the biomaterialsurface (Morosanu *et al.,* 2017). Lignin is one of the world's most abundant natural polymeric material, just like cellulose and chitin. It is a polymer of aromatic subunits usually derived from phenylalanine, such as coniferyl alcohol and other monolignols. It serves as a matrix around polysaccharide components of some plant cell walls, providing additional rigidity and compressive strength as well rendering the walls hydrophobic and water impermeable (Whetten and Sederoff, 1995). Lignin-related studies have revealed that it is a promising material to be used as an adsorbent, consequently it can remove heavy metal ions from wastewater (Yao *et al.,* 2014). Several processes including ion exchange, surface adsorption, and complexation have been suggested by several researchers to explain the mechanisms of metal adsorption by lignin. However, detailed studies on understanding the exact mechanism of adsorption are yet to be reported (Ahmed and Ahmaruzzaman, 2016). Chemical modification of lignin, including crosslinking and functionalization, has been necessary to improve its adsorptive properties (Yao *et al.,* 2014; Yan and Li, 2016). However, most of the existing studies have utilized lignin directly as an adsorbent material (Yao *et al.,* 2014).

Currently, lignin is mainly obtained as a by-product of the papermaking industry and often directly burned as a fuel for energy generation (Barana *et al.,* 2016). Large amounts of lignin are expected to be produced in future biorefineries as a by-product of biofuel production, which is stimulating new emerging applications, mainly as sustainable alternatives to non-renewable products such as polyurethanes, thermoplastic polymers, epoxy and phenolic resins as well as corrosion inhibitors (Brosse *et al.,* 2011). Along the last few years, experimental design (DOE) and response surface methodology (RSM) have been employed to optimize heavy-metals biosorption. The factorial experimental design involves using independent variables such as pH, initial metal concentration and biosorbent dosage and varying them from one experiment to the next, while response surface methodology involves a collection of mathematical and statistical techniques useful for analysing the effects of several independent variables on the response (Martin-Lara *et al.,* 2011). Therefore, besides this methodology demands a reduced number of experimental trials to evaluate multiple parameters and their interactions, it plays a key-role in the process design and optimization, as well as the improvement of existing design (Tabaraki *et al.,* 2014). Thus, the use of lignin recovered from delignification step of biomass during bioethanol production process as biosorbent for heavy metals may represent an important contribution to the industrial implementation of bioethanol, mainly regarding lignin valorisation, as well as to minimize residues and environmental impacts of these chemical bio-industries. Although lignin extracted from black liquor of paper and pulp-manufacturing industry has been investigated for heavy metals sequestration in aqueous solutions, there are no reports in the literature, on the characterization and use of bioethanol-derived-lignin for this purpose. Therefore, the present research aimed at

investigating lignin resulting from alkaline delignification of sugarcane bagasse during ethanol production as biosorbent of Pb(II) ions in aqueous solutions. Experimental design and RSM were used to study the effect of pH, initial Pb(II) concentration and lignin mass on biosorption. The kinetic parameters were also evaluated using the biosorption measurements. FTIR analysis was conducted to identify the functional group involved in the biosorption process.

MATERIAL AND METHODS

Preparation of Biosorbent: The lignin used as adsorbent came from a study on bioethanol production of sugarcane bagasse. Firstly, the bagasse was submitted to acid hydrolysis treatment, using 1% H_2SO_4 (w/v), solid-liquid ratio of 1:10, at 121 °C for 20 minutes. After separation of hemicellulosic hydrolysate by filtration using filter paper, the solid mass (cellulignin) was delignified using 1.5% (w/v) NaOH, 1:20 solid-liquid ratio, at 100 °C for an hour. The obtained black liquor was separated from the solid mass (cellulose residue) by filtration using filter paper. For the recovery of lignin from black liquor, different acids such as acetic, chloridric and sulfuric and pH values were tested, and the best result was obtained with H_2SO_4 at pH 2. After acidification, lignin was separated by centrifugation in 50 mL tubes for 15 minutes at 2050 x g and the supernatant was discarded. The precipitated lignin was resuspended in distilled water, centrifuged again, and process was repeated for three times. The resulting lignin was oven dried at 60 °C for 6 hours.

Lignin Characterization by Infrared Spectroscopy: Fourier transform infrared (FTIR) spectroscopy analyses (Shimadzu Prestige-21) were used to determine the major functional groups present on biosorbent structure. The lignin samples were pre-dried, mixed with KBr and compacted under high pressure to obtain some pellets. Spectra were recorded with a 2 cm^{-1} resolution in 400-4000 cm^{-1} range, with 128 acquisition scans.

Preparation of Pb(II) Solution: A stock solution of Pb(II) (1.0 g L^{-1}) was prepared by dilution of Titrisol (Merck) flasks with distilled water. The stock solution was further diluted to obtain the desired initial concentrations (40-80 mg L^{-1}). NaOH and HCl solutions of 0.1 mol L^{-1} were used to adjust initial pH to the required value of each test solution before mixing the biosorbent. All chemical reagents were of analytical grade.

Batch Biosorption Experiments of Pb(II): For biosorption experiments under batch operation, 125-mL Erlenmeyer flasks containing 50 mL of aqueous solution with biosorbent quantity and Pb(II) concentration ranging from 50 to 150 mg and from 40 to 80 mg L^{-1}, respectively, were used. The initial pH varied from 3 to 5 and was adjusted with NaOH and HCl solutions, both of them at 0.1 mol L^{-1}. The experiments were carried out in a shaker incubator at 25 °C and constant stirring at 200 rpm for a pre-determined time interval. The pH was not controlled during the experiments. All tests were prepared in triplicate to check reproducibility of the results and the average values were reported. The experiments were carried out by suspended determined amount of biosorbentin Pb(II) solutions. The suspension was taken, filtered using filter membrane (0.45 μm) and analyses of residual Pb(II) concentrations were determined by flame atomic absorption spectrometry (FAAS), using Shimadzu AA-6300 equipment. The amount of adsorbed Pb(II)

ions at equilibrium per unit mass of adsorbent (q_e) was calculated based on the difference between the initial and equilibrium concentrations of this metal in the solution volume, according to Equation 1:

$$q_e = \frac{(C_i - C_e) * V}{W} \qquad (1)$$

Where C_i and C_e are the initial and equilibrium concentration of metal ion (mg L^{-1}) in the solution, respectively, V is the volume of aqueous solution (L) and W is the weight of adsorbent (g).

Experimental Design and Optimization: A three-factor (X_1, X_2, and X_3) and a three-level (-1, 0, and +1) experimental design (DOE) were used in this trial in order to achieve maximum information about Pb(II) biosorption process by lignin. The studied factors (independent variables) were initial pH (X_1), biosorbent mass (X_2, g), and initial Pb(II) concentration (X_3, mg L^{-1}) to evaluate lead biosorption response (mg g^{-1}). Each variable was coded at one of three levels, -1, 0, and +1. The minimum and maximum levels (Table 1) given to each factor were chosen based on preliminary experiments. Each experiment was carried out in triplicate and the average values were taken as the response (Y).

Experimental data were fitted to the first-order polynomial model and regression coefficients were obtained. The main effects and variables interactions, their respective coefficients for the mathematical model as well as the analysis of variance (ANOVA) were calculated to determine the model validity. Variable effects were described by the difference among the average response at the upper level and the average response at the lowest one. The optimal values concerning the selected variables were analysed by RSM. The adjustment quality of polynomial equation was evaluated by determining R^2 coefficient. The significances of all terms in the polynomial equation were analysed statistically by computing F-value at 0.05 probability (p).

Batch Biosorption Kinetics: After the experimental design of adsorption conditions, experiments were carried out to evaluate kinetic behaviour of Pb(II) ions biosorption process by lignin. Erlenmeyer flasks containing 50 mL of solution at best values for initial pH, lignin mass and Pb(II) concentration were stirred for 10 hours. Aliquots of 500 µL supernatant were withdrawn at different time intervals (0, 15, 45, 60,120, 240, 300, 360 and 600 minutes) and diluted in volumetric flask. Metal concentrations could be measured through FAAS.

RESULTS AND DISCUSSION

Characterization of Lignin by Infrared Analysis: The FTIR spectrum of lignin recovered from black liquor resulting from alkaline delignification step of bioethanol production process is shown in Figure 1. It is possible to observe absorption bands typical of functional groups expected from lignin, such as aldehyde, carboxyl, methoxy and phenolic groups. The broad bands ranging from 3600 to 3300 cm^{-1} were assigned to the stretching vibrations of aromatic and aliphatic O-H groups. The peaks at 2920 and 2830 cm^{-1} were attributed to the asymmetric and symmetric C-H tensile vibration of methylene. The weak band and shoulder at about 1711 and 1630 cm^{-1}, respectively, were attributed to the conjugated carboxyl and carbonyl

stretching. The peaks at 1590, 1500 and 1420 cm^{-1} contributed to the aromatic skeletal vibrations, indicating the aromatic structures of lignin. Absorption at 1462 cm^{-1} indicates aromatic methyl group vibrations. The bands at 1324 and 1210 cm^{-1} depict syringyl ring C-O stretching vibration. Absorption at 1117 cm^{-1} was due to the C-O stretching of alcohol group. The peaks at approximately 1020 and 828 cm^{-1} further indicate the presence of syringyl units. As lignin has different functional groups and properties depending on lignin source, processing and pre-treatments, Sahoo et al. (2011) characterized different kinds of lignin produced from paper pulp industries and one from cellulose bioethanol refinery for its utilization in the future added composite products. The FTIR analyses of bioethanol lignin revealed that its chemical composition was very similar to Protobind 1000 from paper industry, which was taken as base material for the comparison of lignin functionalities. It is important to note that the infrared absorption values, found out in this study for lignin obtained from bioethanol, are in accordance with those ones already recorded in studies that used lignin obtained from the paper industry (Yan and Li, 2016; Sahoo *et al.,* 2011; Guo *et al.,* 2008).

Biosorption Studies of Pb(II): Table 2 shows the real and coded (in parentheses) values of the independent variables and the adsorbed amounts of Pb(II) by lignin achieved in each trial. The results showed a variation in adsorption values that can be explained as a function of adsorptive capacity of the used biomass (chemical structure, functional groups) and the availability of active sites, since contact time and temperature, which can also influence the results, were the same for all trials. It was observed that overall average for Pb(II) biosorption by lignin was 21.0 mg g^{-1}. The lowest obtained value corresponded to trial 3, whose value was 8.4 mg g^{-1}. Trial 6 presented the highest value (41.8 mg g^{-1}), indicating that the best adsorption condition for Pb(II) ion occurred at higher value of initial pH and metal concentration with a lower amount of biomass. For Martín-Lara et al. (2011)*,* the lowest dosages of biosorbent are ideal for lead ions biosorption. Guo et al. (2008), investigated the heavy metal adsorption of ions Pb(II), Cu (II), Cd (II), Zn (II) and Ni (II) on lignin isolated from black liquor from the paper industry.

These authors observed better affinity for Pb(II), with an initial adsorption rate (v_0) and amount of metal adsorbed on lignin (q_e) of 162 mg (g min)$^{-1}$ and 63 mg g^{-1}, respectively. Moreover, the adsorption mechanism involved two main types of acid sites attributed to carboxylic- and phenolic-type surface groups, the latter with higher affinity for metal ions than carboxylic sites. In order to increase the adsorption capability to heavy metals by lignin, Geet al. (2016), prepared a new type of lignin microspheres (LMS) from a lignin obtained from a pulp mill. LMS showed high adsorption capacity to Pb(II) of 33.9 mg g^{-1}. However, this value was lower than the maximum q_e obtained in this work (41.8 mg g^{-1}), showing the importance of a DOE planning in order to determine the best Pb(II) adsorption conditions by lignin and better exploit the potential of this biosorbent. A green porous lignin-based sphere (PLS) manufactured by a feasible gelation-solidification method from lignosulfonate cross-linked with sodium alginate and epichlorohydrin showed an excellent adsorption efficiency (95.6 ± 3.5%) for lead ions at an initial concentration of 25.0 mg L^{-1}, that suggested the possibility of PLS to be applied for the continuous treatment of wastewater rich in heavy metals at the industry (Li *et al.,* 2015).

Table 1. Coded and uncoded levels of the independent variables

Independent variable	Factor	Coded levels		
		-1	0	+1
Initial pH	X_1	3	4	5
Biosorbent mass, M (mg)	X_2	50	100	150
Initial Pb(II) concentration, C_i (mg L^{-1})	X_3	40	60	80

Table 2. Experimental design used in this study with results for lead uptake by lignin

Trials*	Initial pH	M (mg)	C_i (mg L^{-1})	q_e (mg g^{-1})§
1	3 (-1)	50 (-1)	40 (-1)	19.4 ± 1.2
2	5 (+1)	50 (-1)	40 (-1)	25.8 ± 2.0
3	3 (-1)	150 (+1)	40 (-1)	8.3 ± 1.6
4	5 (+1)	150 (+1)	40 (-1)	8.4 ± 2.1
5	3 (-1)	50 (-1)	80 (+1)	25.1 ± 1.8
6	5 (+1)	50 (-1)	80 (+1)	41.8 ± 1.1
7	3 (-1)	150 (+1)	80 (+1)	14.9 ± 1.0
8	5 (+1)	150 (+1)	80 (+1)	20.2 ± 1.7
9	4 (0)	100 (0)	60 (0)	21.6 ± 0.2
10	4 (0)	100 (0)	60 (0)	22.5 ± 1.0
11	4 (0)	100 (0)	60 (0)	23.3 ± 0.6

* The number of each trial does not mean the order it was carried out. § Results are average of triplicate analysis for Pb biosorption ± standard deviation.

Table 3. ANOVA of variable effects of lead biosorption by lignin

Source	Sum of Squares	Degrees of Freedom	Mean Square	F-value	p<0.05
Model	823.85	5	164.77	56.99	0.002
Residue	14.46	5	2.89		
Lack of fit	13.01	3	4.34	5.99	0.15
Pure error	1.45	2	0.72		
Total	838.31	10			

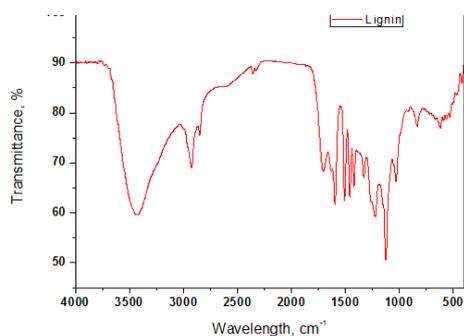Determination coefficient ($R^2 = 0.9828$)

Figure 1. FT-IR spectrum of the lignin precipitated from black liquor resulting from bioethanol production

Schafhauser *et al*. (2015), reported the use of a modified lignin from the corn residue as a lead ion biosorbent, whose removal capacity was 98.87% of an initial solution containing 10 mg L^{-1}. According to Zakzeski *et al*. (2010), lignin structure is highly functional and containsalcohol, aldehyde, ether or acid substituents groups. These monomeric compounds are susceptible to a wide range of transformations, mainly whether reductive in nature, forming simple hydrocarbons, or oxidative in nature, with an increase of aromatic compounds or specifically for the desired functionality. The values obtained by the trials (9, 10 and 11) at the central points showed small variations (Table 3), indicating a good reproducibility. Pareto chart was drawn to analyse significant effects of independent variables and their interactions (Fig. 2a). When analysing the influence of each independent variable alone on Pb(II) ions adsorption, it was observed that the amount of adsorbent mass was statistically significant and showed a marked negative effect.
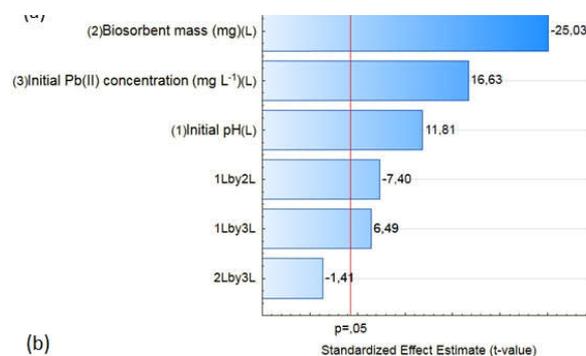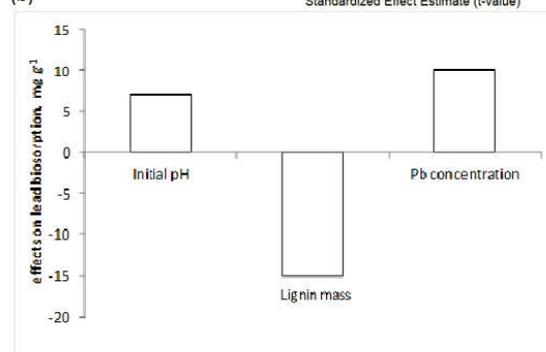

Figure 2.(a). Pareto chart of the standardized effects (t-value) for lead biosorption capacity (mg g^{-1}), α=0.05 and (b) Linear effects (absolute values) of initial pH, lignin mass and lead concentration on biosorption capacity of lead ions

That is, the larger the mass of adsorbent the lower the adsorption of this ion. The other two independent variables (initial pH and metal concentration) showed positive effects and were also statistically significant.
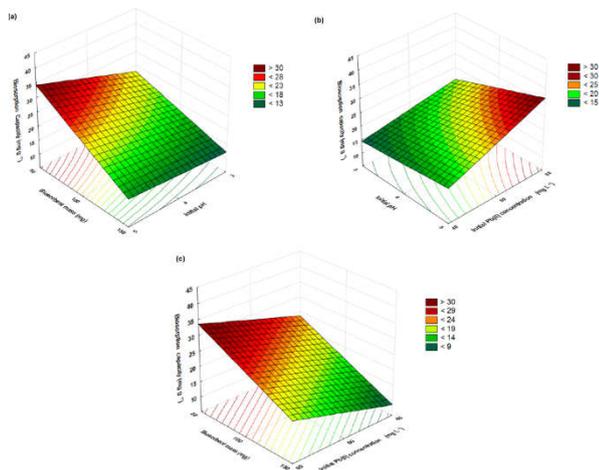
Figure 3. Response surface plots for the effect of (a) initial solution pH and lignin mass (mg); (b) initial solution pH and lead ion concentration (mg L^{-1}) and (c) lead ion concentration (mg L^{-1}) and lignin mass (mg) on the lead biosorption capacity (mg g^{-1})
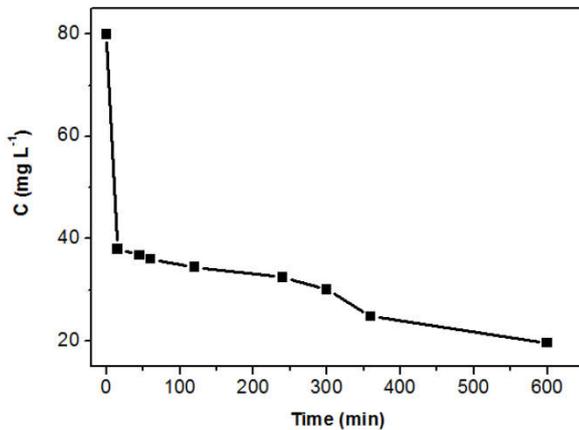

Figure 4. Kinetics of Pb (II) ion adsorption by lignin [Pb^{2+}] = 80 mg L^{-1}; pH 5; lignin mass = 50 mg; T = 25 ^{o}C; stirring = 200 rpm
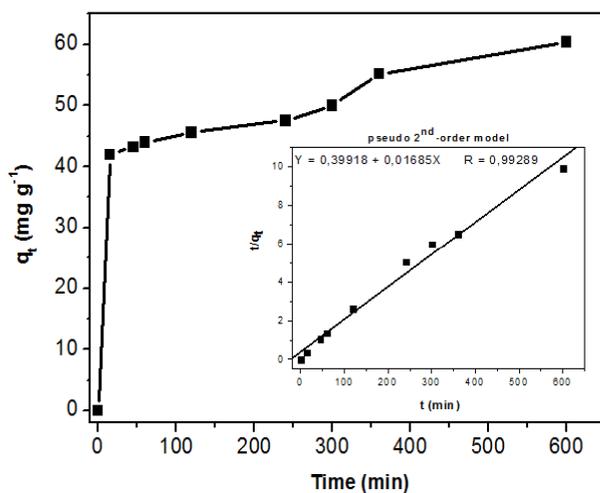

Figure 5. Amount of Pb (II) ions adsorbed by lignin as function of time and the pseudo second-order model graph (insert)

Thus, for the interaction between the variables, due to the simultaneous analysis of the effects of these interactions, the only positive and significant effect on Pb(II) ions adsorption was observed when the initial pH and metal concentration variables were combined, which means that the adsorption of

this ion increased. There was a negative and significant effect for the interaction between initial pH and adsorbent mass, which resulted in lower adsorption of Pb(II) ions. However, the effect of interaction between adsorbent mass and metal concentration did not show a significant answer. Figure 2b shows the effects of initial pH, lignin mass and Pb(II) ions concentration on the ability of Pb(II) biosorption by lignin. It was observed a 7.1 mg g^{-1} increase in adsorption with an increase of initial pH from 3 to 5. This improvement in adsorption was possibly due to the reduction of H$_3$O$^+$ ions concentration and, consequently, there was less competition between protons and Pb(II) for lignin binding sites. The increase in lignin mass from 50 mg to 150 mg provided a reduction of 15.0 mg g^{-1} in the adsorbed amount of Pb(II). This can be explained by the fact that the decrease of lignin mass induces a greater competition of Pb(II) ions for active sites present in lignin superfine available for cation binding (Chen *et al.*, 2011). The increase in Pb(II) concentration from 50 mg L^{-1} to 150 mg L^{-1} increased 10.0 mg g^{-1} in the adsorbed amount of Pb(II) by lignin. This can be explained by the greater availability of Pb(II) ions present in solution to bind the lignin active sites. Experimental values were predicted with empirical equations adjusted by analysis of variance in order to carry out an integral study of the independent variables influence on Pb(II) adsorption (Table 3).

Thus, the equation obtained to predict the response variables $Y(mg\ g^{-1}) = 21.04 + 3.55X_1 - 7.53X_2 + 5.00X_3 - 2.23X_1X_2 + 1.95X_1X_3$ is presented as a function of coded terms of the independent variables, indicating the statistically significant values, at 95% confidence level. The empirical model to describe Pb(II) adsorption by lignin showed a value for determination coefficient (R^2) equal to 0.98, which is considered of high quality because it indicates that only 0.02% of the response variability could not be explained by the model, confirming the quality of the adjustment. Thus, a plot of normality residues was generated to check efficiency of Pb(II) removal in order to analyze the residual values distribution, defined as the differences between predicted and observed (experimental) models.

The correlation validity, found out by the statistical analysis, which points out linearity and absence of trend in the studied data, revealed a model that does not lack a significant adjustment. The graph representation of the response surface, corresponding to the parameter lead biosorption, is shown in Figure 3. It can be observed that the use of lower biosorbent mass (50 mg) with a higher initial pH (5) resulted in higher adsorption (Fig. 3a). The same results can be observed in Figures3b and 3c, respectively, with a higher initial pH and a higher concentration of Pb(II) (80 mg L^{-1}) and with lower biosorbent mass (50 mg) and a higher concentration of Pb(II). The solution pH is one of the most important parameters in heavy metals biosorption from aqueous solutions, since it can influence on the nature of biomass binding sites and metal solubility and affect the solution chemistry of the metals, the activity of the functional groups in biomass and competition of metallic ions (Salman *et al.*, 2014). Adsorption studies with lignin isolated from black liquor of the paper industry revealed that by increasing pH, sorption edges were reached for Pb(II). When pH was higher than 6, more than 85% of metal ions were adsorbed on surface efficiently from a starting solution of 41 mg L^{-1}. Precipitation may also have occurred at higher pH (Guo *et al.*, 2008).

Adsorption Kinetics: The kinetics of Pb(II) ion adsorption by lignin is represented in Figure 4. The kinetics curve shows that Pb(II) ion concentration drops rapidly during the first 15 minutes, of about 53%, which can be attributed to an excess of biosorbent that involves sites available on the adsorbent surface, able to bind lead ions. The equilibrium was reached in approximately 360 minutes and remained constant up to 10 hours. The removal percentage of Pb(II) ions, after reaching the equilibrium, was 75.5%. Figure 5 shows the amount of Pb(II) ions adsorbed by lignin at time t (q_t). A good correlation of kinetics data can indicate the mechanism of metal ion adsorption to the solid phase. Thus, pseudo first-order and second-order models were used to fit the experimental data in order to identify the kinetics mechanism controlling Pb(II) ions adsorption process. These models present lower mathematical complexity when compared to other kinetic models, such as homogeneous surface diffusion, pore diffusion and heterogeneous diffusion. The validity of pseudo first-order and second-order models can be analysed through the linear graphs of log (q_e- q_t) versus t and (t/q_t) versus t, respectively. The pseudo first-order model gives a linear correlation coefficient (R) of 0.772 and a q_e value of 35.0 mg g^{-1}, which differed from the q_e value obtained experimentally (60.4 mg g^{-1}) by 42.1%, indicating that this model is inappropriate for an interpretation of the adsorption kinetics data. It is important to highlight that Pb(II) ions adsorption kinetics data were better fitted when the pseudo second-order kinetics model was applied, providing a better correlation coefficient (R = 0.993). In addition, this indicated that chemisorption is the rate-limiting step during adsorption mechanism (Fig. 5). This model provided a k_2 rate constant of 7.12×10^{-4} g(mg min)$^{-1}$. The q_e value obtained from the slope of equation was 59.3 mg g^{-1}, so it was under an excellent agreement with the experimental q_e value with only a 1.8% deviation. From k_2 and q_e, the initial adsorption rate (h) for Pb(II) ions was calculated by Eq. 2, whose value was 2.5 mg(g min)$^{-1}$.

$$h = k_2 * q_e^2 \qquad (2)$$

Conclusion

This study has concluded that lignin obtained from alkaline delignification step of bioethanol production from sugarcane bagasse can be used as Pb(II) ions biosorbent. The experimental design and RSM were important tools for determining the best Pb(II) biosorption conditions in aqueous solutions, revealing more efficiency with higher metal amounts and smaller adsorbent quantities. The pseudo second-order model showed the best adjust in kinetic studies concerning Pb(II) adsorption by lignin. Considering that this is the first study on heavy metal adsorption by lignin recovered from the bioethanol production, further studies are suggested to verify the removal of other metals.

Acknowledgements

REFERENCES

Ahmed, M.J.K., and Ahmaruzzaman, M. 2016. A review on potential usage of industrial waste materials for binding heavy metal ions from aqueous solutions. Journal of Water Process Engineering. 10:39-47.

Barana, D., Salanti, A., Orlandi, M., Ali, D.S., and Zoia, L. 2016. Biorefinery process for the simultaneous recovery of lignin, hemicelluloses, cellulose nanocrystals and silica from rice husk and Arundodonax. Industrial Crops and Products. 86:31-39.

Brosse, N., Mohamad Ibrahim, M.N., and Abdul Rahim, A. 2011. Biomass to Bioethanol: Initiatives of the Future for Lignin. ISRN Materials Science, http://dx.doi.org/10.5402/2011/461482.

Chen, X., Chen, G., Chen, L., Chen, Y., Lehmann, J., McBride, M.B., and Hay, A.G. 2011. Adsorption of copper and zinc by biochars produced from pyrolysis of hardwood and corn straw in aqueous solution. *Bioresource Technology*. 102 19:8877-8884.

Farooq, U., Kozinski, J.A., Khan, M.A., and Athar, M. 2010. Biosorption of heavy metal ions using wheat based biosorbents – A review of the recent literature. *Bioresource Technology*. 10114:5043-5053.

Ge, Y., Qin, L. and Li, Z. 2016. Lignin microspheres: An effective and recyclable natural polymer-based adsorbent for lead ion removal. *Materials & Design*. 95:141-147.

Golab, Z., Orlowska, B. and Smith, R.W. 1991. Biosorption of lead and uranium by Streptomyces sp. Water, Air, & Soil Pollution. 601-2:99-106.

Guo, X., Zhang, S. and Shan, X.Q. 2008. Adsorption of metal ions on lignin. *Journal of Hazardous Materials*. 1511:134-142.

Li, Z., Ge, Y. and Wan, L. 2015. Fabrication of a green porous lignin-based sphere for the removal of lead ions from aqueous media. *Journal of Hazardous Materials*. 285:77-83.

Martín-Lara, M.A., Rodríguez, I.L., Blázquez, G., and Calero, M. 2011. Factorial experimental design for optimizating the removal conditions of lead ions from aqueous solutions by three wastes of the olive-oil production. Desalination. 278 1-3:132-140.

Morosanu, I., Teodosiu, C., Paduraru, C., Ibanescu, D., and Tofan, L. 2017. Biosorption of lead ions from aqueous effluents by rapeseed biomass. *New Biotechnology*. 39 A:110-124.

Naima, A., Mohamed, B., Hassiba, M., and Zahra, S. 2013. Adsorption of lead from aqueous solution onto untreated orange barks Chem. *Chemical Engineering Transactions*. 32:55-60. Doi:10.3303/CET1332010.

Nguyen, T.A.H., Ngo, H.H., Guo, W.S., Zhang ,J., Liang, S., Yue, Q.Y., Li, Q., and Nguyen, T.V. 2013. Applicability of agricultural waste and by-products for adsorptive removal of heavy metals from wastewater. *Bioresource Technology*. 148:574-585.

Sadeek, S.A., Negm, N.A., Hefni, H.H.H., and Wahab, M.M.A. 2015. Metal adsorption by agricultural biosorbents: Adsorption isotherm, kinetic and biosorbents chemical structures. *International Journal of Biological Macromolecules*. 81:400-409.

Sahoo, S., Seydibeyoğlu, M.Ö., Mohanty, A.K., and Misra, M. 2011. Characterization of industrial lignins for their utilization in future value added applications. *Biomass and Bioenergy*. 3510:4230-4237.

Salman, H.A., Ibrahim, M.I., Tarek, M.M., and Abbas, H.S. 2014. Biosorption of heavy metals: A review. *Journal of Chemical Science and Technology*. 34:74-102.

Schafhauser, B.H., Gonçalves, T.R., Consolin, M.F.B., Almeida, V.C., Pineda, E.A.G., and Consolin Filho, N. 2015. Study of adsorption of lead II in lignin modified

from corn waste. *Brazilian Journal of Food Research.* 61:16-25.

Tabaraki, R., Nateghi, A., and Ahmady-Asbchin, S. 2014 Biosorption of lead II ions on Sargassumilicifolium: Application of response surface methodology. *International Biodeterioration & Biodegradation.* 93:145-152.

Vasconcelos, H.L., Guibal, E., Laus, R., Vital,i L., and Fávere, V.T. 2009. Competitive adsorption of CuII and CdII ions on spray-dried chitosan loaded with Reactive Orange 16. Materials Science and Engineering: C. 292:613-618.

Wang, J., and Chen, C. 2015. The current status of heavy metal pollution and treatment technology development in China. *Environmental Technology Reviews.* 41:39-53.

Whetten, R., and Sederoff, R. 1995 Lignin Biosynthesis. The Plant Cell. 7:1001-1013.

Yadav, S.K., Singh, D.K., and Sinha, S. 2014. Chemical carbonization of papaya seed originated charcoals for sorption of PbII from aqueous solution. *Journal of Environmental Chemical Engineering.* 21:9-19.

Yan, M., and Li, Z. 2016. Microwave-assisted functionalized lignin with dithiocarbamate for enhancing adsorption of PbII. Materials Letters. 170:135-138.

Yao, Q., Xie, J., Liu, J., Kang, H., and Liu, Y. 2014. Adsorption of lead ions using a modified lignin hydrogel. *Journal of Polymer Research,* https://doi.org/ 10.1007/s10965-014-0465-9.

Zakzeski, J., Bruijnincx, P.C.A., Jongerius, A.L., and Weckhuysen, B.M. 2010. The catalytic valorization of lignin for the production of renewable chemicals. *Chemical Reviews.* 1106:3552-3599.

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