

## Research Article

# Biosorption and Diffusion Modeling of Pb(II) by Malt Bagasse

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Received 24 July 2016; Accepted 11 October 2016

Academic Editor: Evangelos Tsotsas

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The removal of Pb(II) from water by biosorption processes onto malt bagasse was investigated and the kinetic and thermodynamic parameters were obtained; additionally a diffusion modeling was proposed. The characterization of malt bagasse was performed by FTIR and SEM/EDS. The experiments were conducted in batch system and an experimental design based response surface methodology was applied for agitation speed and pH optimization. The kinetics of biosorption followed pseudo-second-order model and the temperature of the process affected the biosorption capacity. Isotherm models of Langmuir, Freundlich, and Elovich were applied and the Langmuir model showed better fit and the estimated biosorption capacity was  $29.1 \text{ mg g}^{-1}$ . The negative values obtained for  $\Delta G^\circ$  and positive values of  $\Delta H^\circ$  confirm, respectively, the spontaneous and endothermic nature of the process. The diffusion modeling was performed based on experiments in the absence of agitation to investigate the influence of the biosorbent on the sorption process of Pb(II) ions.

## 1. Introduction

The pollution of water by toxic elements such as cadmium (Cd), mercury (Hg), and lead (Pb) generally from industrial wastes is potentially harmful to the health of human beings and the ecosystem [1–4]. Considering the contamination of aquatic systems, Pb is one of the most toxic and problematic elements. The effects of Pb on human's health include kidney damage, inhibition of hemoglobin formation, sterility, and mental retardation [5]. Industrial effluent treatment is normally performed by conventional processes such as precipitation and sludge separation, besides some processes including chemical oxidation and/or reduction, electrochemical treatment, ion exchange, and reverse osmosis that can be also performed. However, some of these methods are costly and have poor efficiency of treatments, concerning metal removing [6]. Consequently, alternative methods, such as biosorption process, for metals removal of effluents have been studied [7–11].

Biomaterials from natural resources or from agricultural products have been applied for preconcentration of metals and as sorbents to remove heavy metal effluents by biosorp-

tion process [11]. Examples of biosorbents are natural spider silk [11], olive tree pruning waste [7], red microalgae [9], orange peel [8], and sugarcane bagasse [10]. A potentially new and low cost biosorbent is malt bagasse, the main subproduct obtained from the beer production process; around 14–20 kg of malt bagasse is generally produced for each 100 L of beer [12]. For textile removal from aqueous solution, malt bagasse was found to be a good biosorbent due to the removal capacity, low cost, and possibility of use without previous treatment [13].

From this point of view, the goal of this work is to investigate the efficiency of malt bagasse in lead ions (Pb(II)) removal by biosorption process. The effects of some experimental parameters on the biosorption of Pb(II) onto malt bagasse were evaluated. Furthermore, the thermodynamic and kinetic parameters were obtained and a diffusion study was performed for the biosorption process. Regarding the last point and its influence on the sorption process, we consider the adsorption of Pb(II) ions from the water in the absence of agitation when it is in contact with a surface that was coated with malt bagasse.

TABLE I: Design matrix and experimental results for the central composite factorial design.

Run	Coded variable		Real variable		Dependent variable
	$X_1$	$X_2$	Initial pH	Agitation speed (rpm)	Lead removal (%)
1	$-\sqrt{2}$	0	2.0	100.0	7.9
2	-1	+1	2.4	170.7	26.8
3	-1	-1	2.4	29.3	30.1
4	0	$+\sqrt{2}$	3.3	200.0	73.4
5	0	0	3.3	100.0	73.4
6	0	0	3.3	100.0	73.8
7	0	0	3.3	100.0	75.6
8	0	$-\sqrt{2}$	3.3	0.0	54.7
9	+1	+1	4.1	170.7	89.3
10	+1	-1	4.1	29.3	72.9
11	$+\sqrt{2}$	0	4.5	100.0	91.2

## 2. Materials and Methods

**2.1. Instrumentation.** The malt bagasse was dried in an oven with forced air circulation (Solab). The malt bagasse was characterized before and after biosorption process by Fourier transform infrared (FTIR) spectroscopy (Varian 7000) and scanning electron microscope (SEM) (Tescan, Vega 3 LMU) with energy dispersed spectroscopy (EDS) (Oxford, AZTec Energy X-Act). The biosorption experiments were carried out in bath system using metabolic shaker (Solab) and the pH adjustments were performed in pHmeter (Aaker). After the biosorption process the samples were centrifuged in a centrifuge (Fanem). The remaining Pb concentration in the solutions was measured using an atomic absorption spectrometer (Perkin Elmer) equipped flame atomization. The Pb concentration was monitored at Pb resonance line 283.3 nm and using air-acetylene flame.

**2.2. Reagents and Solutions.** The biosorption experiments were carried out with solutions prepared by adequate dilutions of a stock solution ( $\text{Pb}(\text{NO}_3)_2$ ) (Biotec) containing  $1000 \text{ mg L}^{-1}$ . The calibration standards were obtained from Pb stock solution containing  $200 \text{ mg L}^{-1}$  (Specsol). Nitric acid ( $0.1 \text{ mol L}^{-1}$ ) and sodium hydroxide ( $0.1 \text{ mol L}^{-1}$ ) were used for pH values adjustments. All the dilutions and solutions were prepared using ultrapure water ( $18 \text{ M}\Omega \text{ cm}$  resistivity), purified in a system (Master All 2000, Gehaka).

**2.3. Malt Bagasse Preparation.** The biosorption experiments were performed with malt bagasse samples provided by Beer Company from Ponta Grossa City, Paraná State. The samples were dried at different temperatures (303, 313, and 323 K), crushed, and sieved, and different particle size fractions were separated.

**2.4. Batch Biosorption Experiments.** The experiments were performed in triplicate and the results are shown as mean values. The biosorption process was performed in batch system using a mass of malt bagasse from 30 to 225 mg, directly

weighted in a 50 mL Erlenmeyer flask. Then an aliquot of 25 mL of  $100 \text{ mg L}^{-1}$  Pb(II) solution was added and the pH was adjusted at range of 2.0 to 4.5. The mixtures were agitated at speed range from 0 to 200 rpm, at determined temperature and contact time. After the biosorption process the malt bagasse was separated from the solution by centrifugation at 4000 rpm (3 min) and the remaining concentration of Pb was determined in F AAS spectrometer.

The following equation was applied to obtain the biosorption capacity ( $q_e$ ):

$$q_e = \frac{V(C_i - C_f)}{m}, \quad (1)$$

where  $V$  is the volume of the solution (L),  $C_i$  is the initial concentration ( $\text{mg L}^{-1}$ ) of Pb(II),  $C_f$  can be defined as Pb(II) concentration at equilibrium ( $\text{mg L}^{-1}$ ), and  $m$  is the amount of malt bagasse (g).

**2.5. Experimental Design and Optimization.** The effects of operating parameters on the biosorption of Pb(II) ions on malt bagasse were analyzed using a central composite factorial. The general form of this factorial design is  $2^n$  plus a star configuration  $\pm\alpha = 2^{n^{(1/4)}}$ , with a central point, where  $n$  represents the number of factors and 2 is the two levels of work [23].

The levels are defined as low level (-1), high level (+1), central point (0), and two outer points given by  $\pm\sqrt{2}$ .

The independent variables were  $X_1$  and  $X_2$  representing pH and agitation speed, respectively, while the dependent variable  $Y$  (response variable) was the Pb(II) removal percentage. The minimum and maximum levels of each factor were defined based on the results obtained from previous experiments. The settings for the independent variables (Table 1) were as follows (low/high value): pH from 2 to 4.5 and agitation speed from 0 to 200 rpm. In this work, a  $2^2$  full-factorial central composite design with 4 axial (star configuration) and 3 central points, resulting in 11 experiments, was

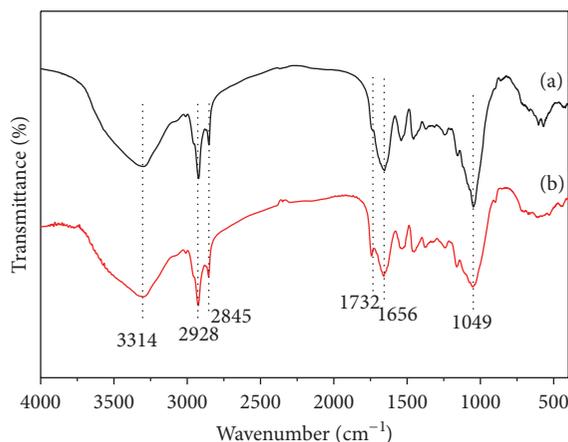


FIGURE 1: FTIR spectra for malt bagasse unloaded (a) and Pb(II)-loaded (b).

applied. Thus, to permit the approximation of the pure error, the central point of the design was performed in triplicate.

Optimal conditions of pH and agitation speed for Pb(II) removal percentage were obtained using the predictive models from response surface methodology (RSM), which is resulting from mathematical and statistical equations applied for process optimization [24].

The response surface was calculated for the two independent factors using the software *Statistica 7.0* from *Statsoft Inc* [25] and the model was evaluated by analysis of variance (ANOVA), verifying if the models reproduced the experimental data in the range studied.

**2.6. Kinetics Studies.** The experiments were performed using 125 mg of biosorbent 25 mL of 100 mg L<sup>-1</sup> Pb(II) solution at pH 4.5 ± 0.1 and agitation speed at 170 rpm with controlled temperature (295, 305, and 315 (±2) K). The samples were collected, centrifuged, and diluted and the Pb(II) concentration was determined at different contact time.

**2.7. Equilibrium Studies.** For equilibrium experiments the biosorbent weight ranged from 30 to 225 mg, using 25 mL of Pb(II) solution 100 mg L<sup>-1</sup> at pH 4.5±0.1 and selected temperature of 305 ± 2 K and 170 rpm of agitation speed for a contact time of 180 min. Then the samples were centrifuged and the Pb(II) concentration in each solution was determined.

**2.8. Diffusion Modeling.** Diffusion studies were performed using 1.25 g of malt bagasse and 250 mL of Pb(II) solution 100 mg L<sup>-1</sup> without agitation. The biosorbent is totally deposited in the end of the recipient which was filled with the Pb(II) solution. The experiments were realized at 303 ± 2 K and aliquots of supernatant solution were taken and the remaining concentration of Pb(II) in the solution was determined at predefined time, during 5990 min.

### 3. Results and Discussion

**3.1. Characterization of Biosorbent.** The malt bagasse unloaded (a) and Pb(II)-loaded (b) were characterized by Fourier

transform infrared (FTIR) spectroscopy; the obtained spectra are presented in Figure 1. As can be observed there are functional groups, indicating the complex nature of biomass [15]. At 3314 cm<sup>-1</sup> a strong absorption peak can be observed for malt bagasse before and after Pb(II) biosorption process, result of the presence of -OH and -NH groups. The absorbance at 2928 and 2845 cm<sup>-1</sup> is attributed to -CH<sub>2</sub> and -CH<sub>3</sub> groups. Bands at around 1732 and 1656 cm<sup>-1</sup> are signatures of C=O stretching vibrations [13]. The peak at 1732 cm<sup>-1</sup> Pb(II)-loaded shows an intensity increase when compared with malt bagasse unloaded. Other peaks were observed in both spectra at 1049 cm<sup>-1</sup> due to C-O stretching of carboxyl groups and bending vibration band of hydroxyl groups [26]. However, for the spectrum Pb(II)-loaded, biomass causes an intensity decrease.

The characterization of malt bagasse was also performed by scanning electron microscopy (SEM) equipped with energy dispersed spectroscopy (EDS). The SEM micrographs and EDSs spectrum (a) unloaded and (b) Pb(II)-loaded are shown in Figure 2. As observed the malt bagasse presents a fibrous morphology (Figure 2(a)) and after biosorption process (Figure 2(b)) there were no significant changes in the malt bagasse morphology. However, an aggregate of small particles can be observed over the surface of biomass with Pb(II)-loaded. The EDS spectrum shows the absence of Pb at unloaded biomass and after biosorption process the signal of Pb can be clearly identified.

**3.2. Particle Size and Malt Bagasse Drying Temperature.** The influence of malt bagasse particle size and drying temperature over the biosorption of ions Pb(II) was investigated. The biosorption capacity was obtained using malt bagasse without any treatment and particle size between 0.12 and 2.00 mm. The removal of Pb(II) ranged from 99.5 to 100%, indicating that the particle size has no significant effect on the Pb(II) biosorption. The effect of drying temperature over the malt bagasse did not affect the biosorbent surface and the Pb(II) removal capacity. The obtained results showed no significant effect in the removal percentages from evaluated temperatures ranging from 91.7 to 97.7%.

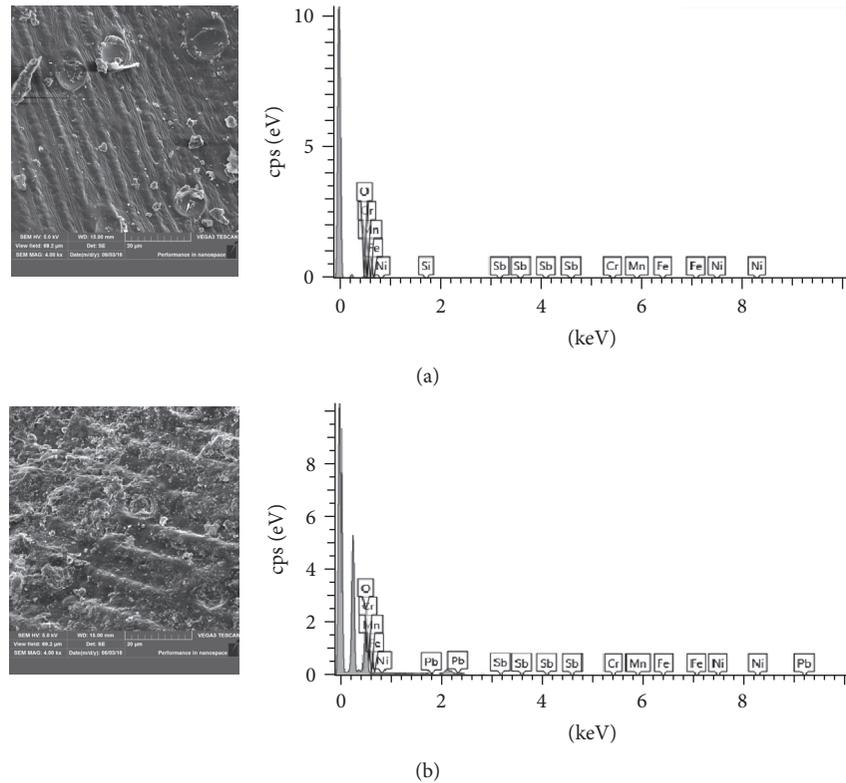


FIGURE 2: SEM/EDS malt bagasse; (a) unloaded and (b) Pb(II)-loaded.

TABLE 2: Regression analysis using factorial central composite design.

	Coefficient estimate <sup>a</sup>	<i>p</i> value
$A_0$	74.27	0.000083
$A_1$	27.88	0.000221
$A_2$	4.94	0.006952
$A_{11}$	-12.86	0.001468
$A_{22}$	-5.62	0.007622
$A_{12}$	4.93	0.013861

<sup>a</sup>Polynomial model ( $Y = A_0 + A_1X_1 + A_2X_2 + A_{11}X_{12} + A_{22}X_{22} + A_{12}X_1X_2$ ), where  $A_0$  is the constant coefficient,  $A_i$  is the linear coefficient,  $A_{ij}$  is the quadratic coefficient, and  $A_{ij}$  is the two-factor interaction coefficient.

**3.3. Experimental Design and Optimization.** The effects of parameters pH and agitation speed on the Pb(II) removal in aqueous solution were investigated using RSM. Table 1 shows experimental results of the independent variables combination obtained by the experimental design. Additionally, the values for coded and decoded variables of each experiment are shown.

As can be observed in Table 1, there is a distinct response in terms of Pb(II) removal of the solution by malt bagasse under different operating parameters combination, reaching maximum value (91.2%) at pH 4.5 and agitation speed 100 rpm. Table 2 presented the statistical significance of the variables and their interactions at different levels of probabil-

ity and regression coefficient of the second-order polynomial models for Pb(II) removal.

The *p* values indicated the interaction strength of each parameter. Considering a confidence level of 95%, a factor can be statistically significant if *p* value < 0.05. From *p* values of each model term (Table 3), it can be determined that the regression coefficients of the constant term  $A_0$ , the linear terms  $A_1$  and  $A_2$ , the quadratic terms of  $A_{11}$  and  $A_{22}$  and two-factor interaction term  $A_{12}$  had significant effect on the Pb(II) removal.

The application of RSM expressed in the regression (2) is an empirical relationship between Pb removal (*Y*) and the tested variables.

$$Y = 74.27 + 27.88X_1 + 4.94X_2 - 12.86X_1^2 - 5.62X_2^2 + 4.93X_1X_2, \quad (2)$$

where *Y* is the response, that is, Pb(II) removal percentage, and  $X_1$  and  $X_2$  are the coded values of pH and agitation speed, respectively.

The statistical significance of the model was evaluated by the analysis of variance (ANOVA) as presented in Table 3. The ratio between the mean square regression ( $MS_R$ ) and the mean square residual ( $MS_r$ ), the *F*-ratio<sub>*R/r*</sub>, was applied to establish the statistical significance of models. The ratio between the mean square lack of fit ( $MS_{LOF}$ ) and the mean square pure error ( $MS_{PE}$ ), the *F*-ratio<sub>*LOF/PE*</sub>, was used to evaluate if the model was well adjusted to the observations.

TABLE 3: Analysis of variance (ANOVA) of Pb(II) removal (%) fitted to (1).

Source of variation	Sum of squares (SS)	Degrees of freedom (DF)	Mean square (MS)	F-ratio	F-value
Regression (R)	7623.955	5	1524.791	144.708	5.050
Residual (r)	52.684	5	10.537		
Lack of fit (LOF)	49.937	3	16.646	12.115	19.164
Pure error (PE)	2.747	2	1.374		
Total (T)	7676.639	10			
$R^2$	0.9931				

The calculated  $F$ -ratio $_{R/r}$  (144.708) was more than twenty-eight times higher than the  $F$ -value $_{R/r}$  at 95% confidence interval ( $F_{0.95;5,5} = 5.050$ ), representing a good agreement with the practical rule, in which the model has statistical significance when the calculated  $F$ -value is at least three-to-five times higher than the listed value [27]. Furthermore, from the ANOVA analysis and the model from experimental data, the calculated  $F$ -ratio $_{LOF/PE}$  (12.115) was lower than the critical  $F$ -value $_{LOF/PE}$  ( $F_{0.95;3,2} = 19.164$ ) in the 95% confidence interval. The quality of the fit of the model was also checked by the multiple correlation coefficient ( $R^2$ ). In this case, the value of  $R^2$  was 0.9931, which revealed that this regression is statistically significant and only 0.69% of the total variations is not explained by the model.

The relationship between the independent and dependent variables is illustrated in a three-dimensional representation of the response surface (Figure 3). The response surface plot was used to determine adsorption percentage of the metal over interactive variables pH and agitation speed. The removal of Pb(II) increased with increase of solution pH ranging from 2.0 to 4.5 as well as with agitation speed ranging from 0 to 200 rpm.

Several papers have reported the negative effect of metal removal by biosorption at low pH values. This behavior may be due to the fact that high concentration and high mobility of  $H^+$  ions lead to the preferential biosorption of hydrogen ions rather than the metal ions. On the other hand, the biosorption efficiency is significantly improved with pH increasing [8]. However, at pH values higher than 5.0, the precipitation of Pb(II) species was observed; thus pH range up to 4.5 was selected in this study in order to avoid the influence of the precipitation process on the biosorption results.

The agitation speed is a significant parameter to be optimized in biosorption processes, since it may have influence on the solute distribution in the solution and the formation of the external boundary layer [28]. The biosorption of Pb(II) by malt bagasse increased with high speed agitation. Thus at pH = 4.5 and speed agitation of 170 rpm, the maximum removal capacity was achieved and these optimum parameters were used for the following biosorption experiments.

**3.4. Kinetics Studies.** The results of the kinetics studies are summarized in Figure 4. In the initial time, a high rate of biosorption was observed at all evaluated conditions. As can be observed, the kinetics curves show that the biosorption process of Pb(II) by malt bagasse is favored with

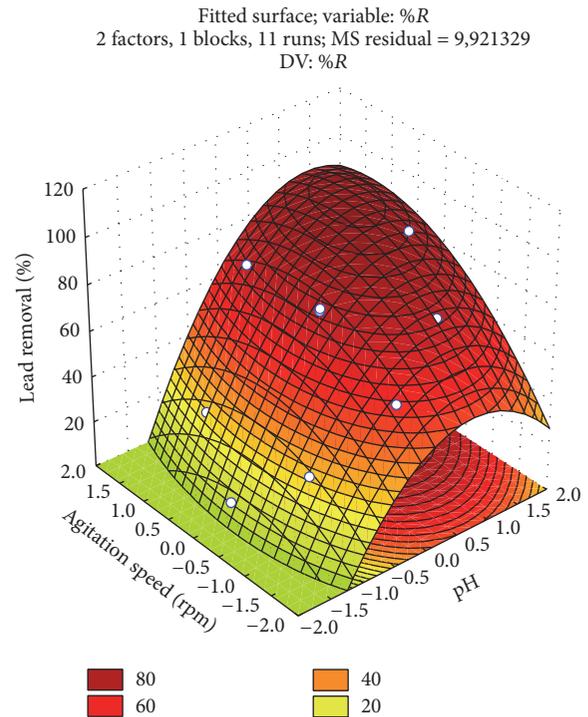


FIGURE 3: Response surface plot for Pb(II) removal by malt bagasse versus pH and agitation speed.

the temperature increasing. The equilibrium was reached in a shorter time (60 min) for the highest evaluated temperature (315 K), indicating the endothermic character of the Pb(II) biosorption process by malt bagasse.

The kinetic behavior of Pb(II) biosorption by malt bagasse was evaluated by means of pseudo-first-order, pseudo-second-order, and Elovich models. Pseudo-first-order model can be given by [29]

$$q_t = q_e (1 - e^{-k_1 t}), \quad (3)$$

where the pseudo-first-order rate constant is given by  $k_1$  ( $\text{min}^{-1}$ ) and the parameters  $q_e$  and  $q_t$  are the adsorbed amounts of Pb(II) ( $\text{mg g}^{-1}$ ) at equilibrium and time  $t$  (min), respectively.

The pseudo-second-order model can be given by

$$q_t = q_e \frac{q_e^2 k_2 t}{1 + q_e k_2 t}, \quad (4)$$

TABLE 4: Kinetics model parameters for the biosorption of Pb(II) by malt bagasse.

	Temperature (K)		
	295 ± 2	305 ± 2	315 ± 2
$q_e$ (exp.) (mg g <sup>-1</sup> )	19.0	20.0	20.0
Pseudo-first-order			
$q_e$ (cal.) (mg g <sup>-1</sup> )	12.5	12.1	18.2
$k_1$ (min <sup>-1</sup> )	0.0234	0.0318	0.0793
$R^2$	0.9624	0.9499	0.9924
Pseudo-second-order			
$q_e$ (cal.) (mg g <sup>-1</sup> )	20.5	20.8	20.6
$k_2$ (g mg <sup>-1</sup> min <sup>-1</sup> )	0.0034	0.0059	0.0104
$R^2$	0.9995	0.9997	0.9994
$h$ (mg g <sup>-1</sup> min <sup>-1</sup> )	1.424	2.539	4.413
Elovich			
$a$ (mg g <sup>-1</sup> min <sup>-1</sup> )	1.703	5.475	1.02
$b$ (g mg <sup>-1</sup> )	0.274	0.312	0.363
$R^2$	0.9696	0.8965	0.8109

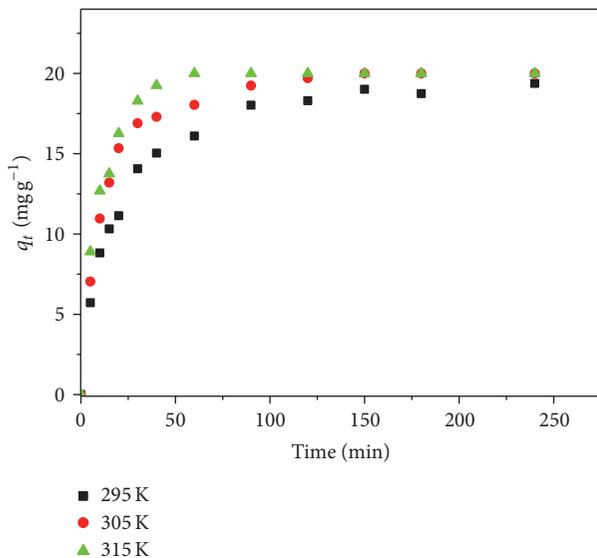


FIGURE 4: Contact time effect at different temperatures for Pb(II) biosorption by malt bagasse.

where  $k_2$  is the pseudo-second-order rate constant (g mg<sup>-1</sup> min<sup>-1</sup>). The initial sorption rate  $h_o$  (mg g<sup>-1</sup> min<sup>-1</sup>) was obtained using the pseudo-second-order rate constant ( $k_2$ ). The initial sorption rate of the process can be expressed as [30]

$$h_o = k_2 q_e^2. \quad (5)$$

The Elovich model is based on a kinetic principle considering a multilayer adsorption [31]. The equation of Elovich can be expressed as [32]

$$q_t = \frac{1}{b} \ln(ab) + \frac{1}{b} \ln(t), \quad (6)$$

where parameters  $a$  and  $b$  are the initial sorption rate (mg g<sup>-1</sup> min<sup>-1</sup>) and the desorption constant (g mg<sup>-1</sup>), respectively.

In Table 4, the parameters and correlation coefficients ( $R^2$ ) for pseudo-first-order, pseudo-second-order, and Elovich kinetic models at evaluated temperatures are presented. The experimental data for the Pb(II) biosorption by malt bagasse were better described by the pseudo-second-order model, as judged by the highest correlation coefficients (>0.999) at evaluated temperatures (Figure 5). Moreover, the  $q_e$  values calculated were in agreement with the experimental  $q_e$  values. Increasing the temperature, the constant pseudo-second-order rate values changed from  $3.4 \times 10^{-3}$  to  $10.4 \times 10^{-3}$  g mg<sup>-1</sup> min<sup>-1</sup>.

During the biosorption process, the ions of Pb(II) of the solution have to overcome an energetic barrier to be adsorbed by malt bagasse; the minimum kinetic energy necessary for this process to occur is defined as activation energy ( $E_a$ ).  $E_a$  can be calculated by fitting the kinetic constant from the pseudo-second-order model at different temperatures to the Arrhenius equation [33]:

$$\ln k_2 = \ln A - \frac{E_a}{RT}, \quad (7)$$

where  $E_a$  (J mol<sup>-1</sup>) is the activation energy,  $A$  (g mg<sup>-1</sup> min<sup>-1</sup>) is the Arrhenius constant,  $R$  (8.314 J mol<sup>-1</sup> K<sup>-1</sup>) is the ideal gas constant, and  $T$  (K) is the temperature of the solution.

$E_a$  for Pb(II) biosorption was evaluated by plotting  $\ln k_2$  versus  $1/T$ . The values from 5 to 40 kJ mol<sup>-1</sup> to  $E_a$  are expected for physical biosorption and from 40 to 800 kJ mol<sup>-1</sup> for chemical biosorption [34]. In the present study, the obtained value of  $E_a$  was 42.2 kJ mol<sup>-1</sup>, and this value is very close to the established limits used for mechanism definition. Thus, the mechanism process of Pb(II) by malt bagasse cannot be defined only by this parameter.

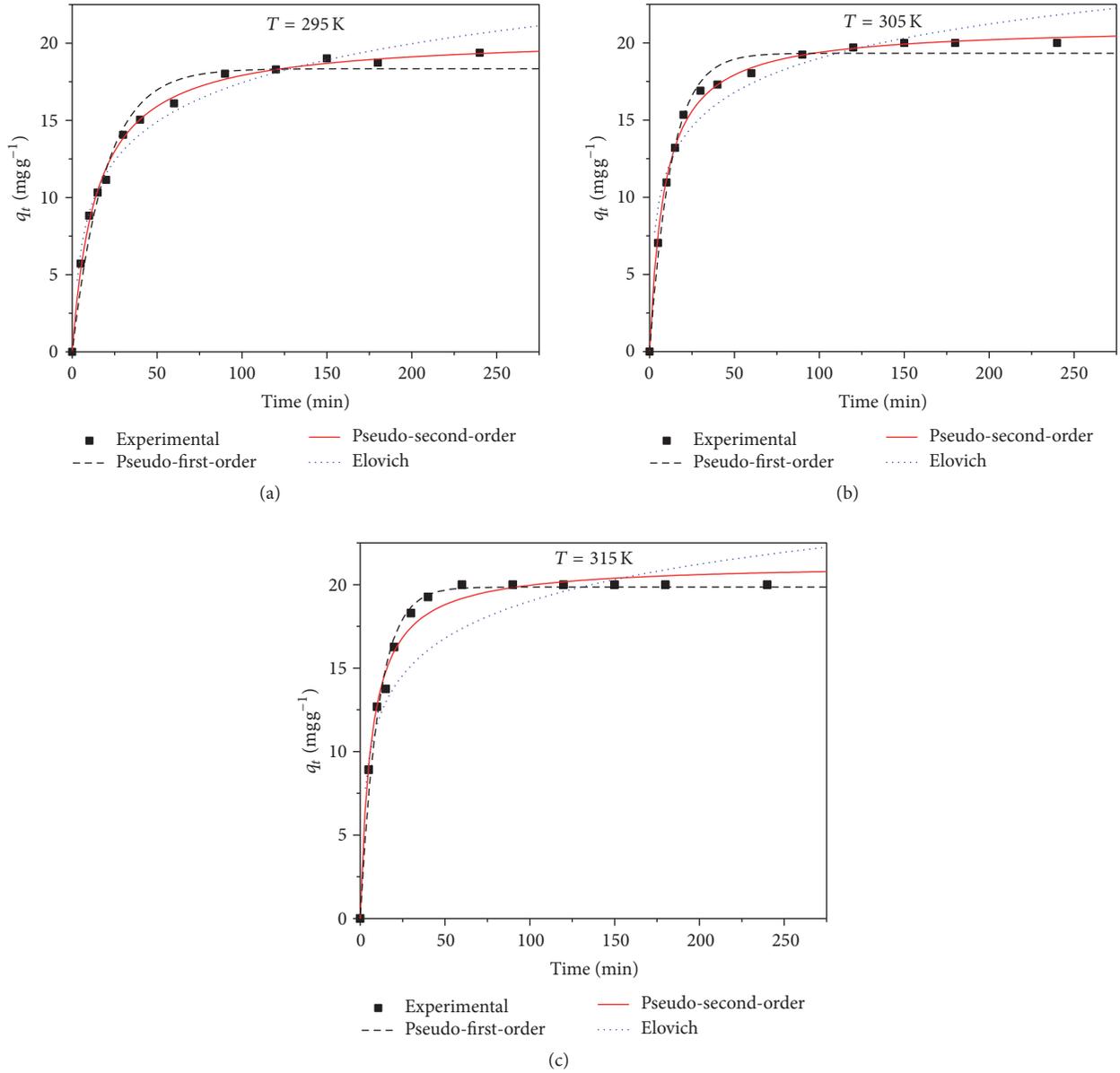


FIGURE 5: Pseudo-first-order, pseudo-second-order, and Elovich models plots at different temperatures for the biosorption of Pb(II) by malt bagasse.

3.5. *Sorption Isotherms.* The Pb(II) biosorption by malt bagasse was evaluated by Langmuir, Freundlich, and Temkin isotherms models.

The Langmuir model is one of the most applied to equilibrium data evaluation and assumes that the biosorption occurs in monolayers [35]. The linear form of the Langmuir isotherm model can be represented by [36]

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{K_L q_{max}}, \quad (8)$$

where  $q_{max}$  is the monolayer biosorption capacity of the biosorbent ( $\text{mg g}^{-1}$ ) and  $K_L$  is the Langmuir constant ( $\text{L mg}^{-1}$ ) related with adsorption energy. The linear plot of  $C_e/q_e$  versus  $C_e$  is used for  $q_{max}$  and  $K_L$  calculation.

The essential quality of the Langmuir isotherm can be obtained by means of dimensionless constant separation factor ( $R_L$ ), which is defined as

$$R_L = \frac{1}{1 + K_L C_0}. \quad (9)$$

$R_L$  value indicates that the biosorption process is favorable ( $0 < R_L < 1$ ), unfavorable ( $R_L > 1$ ), linear ( $R_L = 1$ ), or irreversible ( $R_L = 0$ ) [32].  $R_L$  constant value obtained for biosorption of Pb(II) by malt bagasse was 0.035, indicating that the biosorption process is favorable.

The Freundlich equation is given as [11]

$$\log q_e = \log K_F + \frac{1}{n} \log C_e, \quad (10)$$

TABLE 5: Parameters isotherms models for Pb(II) removal by malt bagasse.

$q_{\max}$ (mg g <sup>-1</sup> )	Langmuir model			Freundlich model			Temkin model		
	$K_L$ (L mg <sup>-1</sup> )	$R_L$	$R^2$	$K_F$ (mg g <sup>-1</sup> )	$n$	$R^2$	$b_T$ (J g mol <sup>-1</sup> mg <sup>-1</sup> )	$K_T$ (L mg <sup>-1</sup> )	$R^2$
29.1	0.277	0.0348	0.9820	12.5	5.107	0.9453	554.7	0.693	0.9179

TABLE 6: Comparison of Pb(II) biosorption capacity of malt bagasse with other biosorbents from literature.

Biosorbent	pH	$T$ (K)	$q$ (mg g <sup>-1</sup> )	Ref.
<i>Bacillus</i> sp.PZ-1	5.0	288	15.38	[14]
<i>C. aphidicola</i>	5.0	303	36.91	[15]
Chaff	—	293	12.5	[16]
<i>Lactarius scrobiculatus</i>	5.5	293	56.2	[17]
<i>Amanita rubescens</i>	5.0	293	38.4	[18]
Sugarcane bagasse	5.0	298	7.297	[10]
Olive tree pruning waste	5.0	333	32.15	[7]
Functionalized cells	7.0	298	116.69	[19]
<i>Agaricus bisporus</i>	5.0	301	33.78	[20]
Natural spider silk	—	—	1.17	[11]
<i>Agave sisalana</i>	7.0	296	1.34	[21]
Coir	5.6	293–298	18.9	[21]
Lichen ( <i>C. furcata</i> )	5.0	293	12.3	[22]
Malt Bagasse	4.5	305	29.1	This work

where Freundlich constants are represented by  $K_F$  and  $n$ , which are defined as biosorption capacity and biosorption intensity, respectively. Plotting  $\log(q_e)$  versus  $\log(C_e)$ , if the Freundlich equation applies, a straight line can be obtained with slope  $1/n$  and  $K_F$  is obtained by the intercept.

The Temkin isotherm model contemplates the effects of indirect interactions between adsorbent and adsorbate on the biosorption isotherms and gives the free energy of sorption to the surface coverage [37]. Temkin model is defined as

$$q_e = \frac{RT}{b_T} \log K_T + \frac{RT}{b_T} \log C_e, \quad (11)$$

where  $K_T$  is the equilibrium binding constant (L mg<sup>-1</sup>) and  $b_T$  (g J mol<sup>-1</sup> mol<sup>-1</sup>) is the Temkin isotherm constant related to the heat of biosorption.

The parameters obtained for the isotherms models applied to the Pb(II) biosorption and the, respectively, linear correlation coefficients ( $R^2$ ) are presented in Table 5.

The poorest fit was given by Temkin isotherms model, confirmed by lowest value of correlation coefficient (0.9179). However, the highest value of correlation coefficient (0.9820) was obtained for Langmuir model, indicating that the this model can accurately describe biosorption Pb(II) by malt bagasse. The obtained maximum biosorption capacity ( $q_{\max}$ ) in this process was 29.1 mg g<sup>-1</sup>; this value is comparable to the biosorption capacity obtained for Pb biosorption at literature, as shown in Table 6.

Comparing to literature,  $q_{\max}$  of malt bagasse was not the highest; however, it should be mentioned that malt bagasse is

TABLE 7: Thermodynamics parameters for Pb(II) biosorption onto malt bagasse.

Temperature (K)	$\Delta G^\circ$ (kJ mol <sup>-1</sup> )	$\Delta H^\circ$ (kJ mol <sup>-1</sup> ) <sup>a</sup>	$\Delta S^\circ$ (kJ mol <sup>-1</sup> K <sup>-1</sup> ) <sup>a</sup>
295	-7.33		
305	-7.86	4.27	0.039
315	-8.13		

<sup>a</sup>measured between 295 and 315 K.

a low cost biosorbent and can be used without previous treatment. Thus, the malt bagasse can be considered an excellent option of biosorbent to remove Pb(II) ions from solution.

**3.6. Thermodynamic Study.** The thermodynamic parameters were applied to determine whether a biosorption process will occur spontaneously. The changes in Gibbs free energy ( $\Delta G^\circ$ ), enthalpy ( $\Delta H^\circ$ ), and entropy ( $\Delta S^\circ$ ) of biosorption process were obtained by the following equations:

$$k_d = \frac{C_a}{C_e} \quad (12)$$

$$\Delta G^\circ = -RT \ln k_d$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ,$$

where  $C_a$  is defined as concentration of Pb(II) adsorbed at equilibrium. The enthalpy ( $\Delta H^\circ$ ) and entropy ( $\Delta S^\circ$ ) can be calculated by the slope and intercept of a Van't Hoff equation of  $\Delta G^\circ$  versus  $T$  [35, 38]. Negative values of  $\Delta G^\circ$  at different temperatures, summarized in Table 7, indicate that

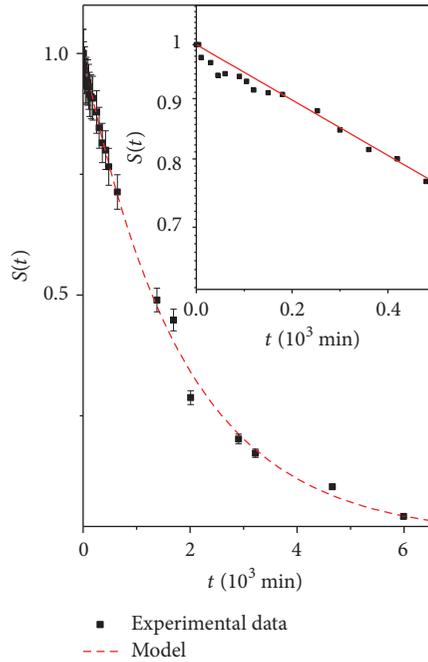


FIGURE 6: Experimental data obtained from the experimental scenario described in Section 2.8 (black squares) and the model discussed in Section 3.7. The best fit is obtained by using  $q(t) = q_e(1 - e^{-k_1 t})$  with  $q_e = C_0 L = 1$  and  $k_1 = 1/1850$ .

Pb(II) biosorption is a spontaneous process. The change in the standard enthalpy,  $\Delta H^\circ$ , is  $4.27 \text{ kJ mol}^{-1}$  and the positive value of  $\Delta H^\circ$  indicates that biosorption of Pb(II) by malt bagasse is an endothermic process. The positive value of  $\Delta S^\circ$  ( $0.039 \text{ kJ mol}^{-1}$ ) indicates that randomness at the interface malt bagasse/solution increases during the biosorption process.

**3.7. Diffusion Modeling.** Now, we consider the Pb(II) uniformly distributed in the bulk and the system in absence of movement. In this manner, we intend to analyze the influence of diffusion on the kinetic process, that is, the sorption process of Pb(II) by the biosorbent present in the end of the recipient. Experimental data were obtained by applying the procedure previously described in Section 2.8 and are shown in Figure 6.

In order to describe the experimental data presented in Figure 5, we consider that the diffusion process of the Pb(II) in the bulk is governed by the diffusion equation [39]:

$$\frac{\partial}{\partial t} C(x, t) = D \frac{\partial^2}{\partial x^2} C(x, t), \quad (13)$$

where  $D$  is the diffusion coefficient,  $C(x, t)$  represents the concentration of Pb(II) in the bulk, and  $S(t) = \int_0^L C(x, t) dx$  gives the quantity of Pb(II) in the bulk as a function of time  $t$ . Equation (13) is subjected to the initial condition  $C(x, 0) = C_0$ , in order to represent the Pb(II) initially

uniformly distributed in the bulk. The boundary conditions, obtained from the experiment, are

$$\begin{aligned} D \frac{\partial}{\partial x} C(x, t) \Big|_{x=0} &= \frac{d}{dt} q(t), \\ D \frac{\partial}{\partial x} C(x, t) \Big|_{x=L} &= 0. \end{aligned} \quad (14)$$

Note that boundary conditions consider that in  $x = 0$  there is a flux of particle of the bulk to the biosorbent and in  $x = L$  the flux is absent. The function  $q(t)$  is connected to the quantity of Pb(II) which is sorbed by the biosorbent.

By solving the diffusion equation with the previous boundary conditions, we get that the solution, in the Laplace space [39], is given by

$$C(x, s) = \frac{C_0}{s} - \frac{\cosh(\sqrt{s/D}(L-x))}{\sqrt{s/D} \sinh(\sqrt{s/D}L)} s q(s) \quad (15)$$

and performing an integration, we get that

$$S(s) = \frac{1}{s} C_0 L - q(s), \quad (16)$$

where  $C_0 L$  represents the initial quantity of Pb(II) in the bulk. In order to determine the time dependence of  $q(t)$  in this scenario, we used the experimental data exhibited in Figure 5. The experimental data presented in Figure 5 is well fitted in terms of the first-order model; that is,  $q(t) = q_e(1 - e^{-k_1 t})$ , as previously discussed. By connecting the quantities of this model with the parameters present in the diffusive model, we obtain  $q_e = C_0 L$  and  $k_1 \sim \sqrt{D/L^2}$ . This connection leads us to observe the influence of the diffusion process on the sorption process of Pb(II) by the biosorbent; that is, the sorption process depends on the diffusive time  $\sqrt{L^2/D}$ . In addition, it is possible to verify that the temperature increasing, since in general  $D \propto T$  (Einstein-Smoluchowski relation) in a diffusive process, implies that  $k_1$  has also an amount and, consequently, the sorption rate increases.

## 4. Conclusion

Malt bagasse was found to be a promising biosorbent for the removal of Pb(II) from aqueous solution, due to the removal efficacy, low cost, and the ability to be used without previous treatment. The Fourier transform infrared spectroscopy confirmed biosorbent-Pb(II) ions interaction. The Langmuir model showed better fit and the estimated biosorption capacity was  $29.1 \text{ mg g}^{-1}$  ( $305 \pm 2 \text{ K}$ ). The temperature change in the range of  $295\text{--}315 \text{ K}$  affected the biosorption capacity. The kinetics of biosorption followed pseudo-second-order model and the negative values of Gibbs free energy,  $\Delta G^\circ$ , indicate a favorable biosorption of Pb(II) by malt bagasse and positive value of enthalpy,  $\Delta H^\circ$ , showed the endothermic nature of biosorption. We investigated an experimental scenario where the diffusion may play an important role, that is, the sorption process in absence of agitation. For this case, we consider that the Pb(II) diffusion in the bulk was governed by (13) and

verified that the sorption process of this substance was well modeled by a first-order model. The relaxation time present in this model was connected to the diffusion time evidencing that in this case the diffusion has a direct influence on the sorption process.

## Nomenclature

$a$ :	Parameter initial sorption rate ( $\text{mg g}^{-1} \text{min}^{-1}$ )
$A$ :	Arrhenius constant ( $\text{g/mg min}$ )
$b$ :	Parameter desorption constant ( $\text{g mg}^{-1}$ )
$b_T$ :	Temkin isotherm constant ( $\text{g kJ mg}^{-1} \text{mol}^{-1}$ )
$C$ :	Concentration ( $\text{mg L}^{-1}$ )
$C_e$ :	Equilibrium concentration of adsorbate in solution ( $\text{mg L}^{-1}$ )
$C_i$ and $C_f$ :	Initial and final concentration of Pb(II) ( $\text{mg L}^{-1}$ )
$D$ :	Diffusion coefficient
$E_a$ :	Activation energy ( $\text{J mol}^{-1}$ )
$h_0$ :	Initial sorption rate
$k_1$ :	Pseudo-first-order rate constant ( $\text{min}^{-1}$ )
$k_2$ :	Pseudo-second-order rate constant ( $\text{g mg}^{-1} \text{min}^{-1}$ )
$k_d$ :	Sorption equilibrium constant ( $\text{L g}^{-1}$ )
$K_F, n$ :	Freundlich constants
$K_L$ :	Langmuir constant ( $\text{L mg}^{-1}$ )
$K_T$ :	Equilibrium binding constant ( $\text{L mg}^{-1}$ )
$L$ :	Length (m)
$q_e$ :	Adsorbed amounts at equilibrium ( $\text{mg g}^{-1}$ )
$q_t$ :	Adsorbed amounts at $t$ time ( $\text{mg g}^{-1}$ )
$q_{\text{max}}$ :	Biosorption maximum capacity ( $\text{mg g}^{-1}$ )
$S(t)$ :	Quantity of Pb(II) in the bulk as a function of time $t$ (mg).
$t$ :	Time (min)
$T$ :	Temperature (K)
$V$ :	Volume of the solution (L)
$\Delta G^\circ$ :	Variation of the Gibbs energy ( $\text{kJ mol}^{-1}$ )
$\Delta H^\circ$ :	Enthalpy variation ( $\text{kJ mol}^{-1}$ )
$\Delta S^\circ$ :	Entropy variation ( $\text{kJ mol}^{-1} \text{K}^{-1}$ ).

## Competing Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

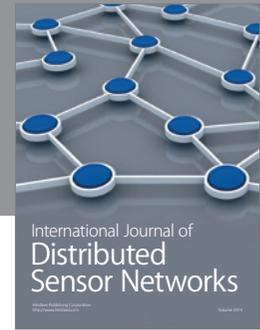
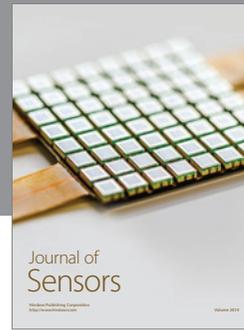
## Acknowledgments

The authors would like to thank Fundação Araucária, Saneapar, and CNPq for the partial financial support and Schultz Bier Microcervejaria for kindly providing malt bagasse.

## References

- [1] Y. Ding, D. Jing, H. Gong, L. Zhou, and X. Yang, "Biosorption of aquatic cadmium (II) by unmodified rice straw," *Bioresource Technology*, vol. 114, pp. 20–25, 2012.
- [2] J. He and J. P. Chen, "A comprehensive review on biosorption of heavy metals by algal biomass: materials, performances, chemistry, and modeling simulation tools," *Bioresource Technology*, vol. 160, pp. 67–78, 2014.
- [3] T. B. Mostafa, "Chemical modification of polypropylene fibers grafted vinyl imidazole/acrylonitrile copolymer prepared by gamma radiation and its possible use for the removal of some heavy metal ions," *Journal of Applied Polymer Science*, vol. 111, no. 1, pp. 11–18, 2009.
- [4] L. Uzun, A. Kara, B. Osman, E. Yilmaz, N. Besirli, and A. Denizli, "Removal of heavy-metal ions by magnetic beads containing triazole chelating groups," *Journal of Applied Polymer Science*, vol. 114, no. 4, pp. 2246–2253, 2009.
- [5] A. Mudipalli, "Lead hepatotoxicity & potential health effects," *Indian Journal of Medical Research*, vol. 126, no. 6, pp. 518–527, 2007.
- [6] B. Volesky, "Advances in biosorption of metals: selection of biomass types," *FEMS Microbiology Reviews*, vol. 14, no. 4, pp. 291–302, 1994.
- [7] G. Blázquez, M. A. Martín-Lara, G. Tenorio, and M. Calero, "Batch biosorption of lead(II) from aqueous solutions by olive tree pruning waste: equilibrium, kinetics and thermodynamic study," *Chemical Engineering Journal*, vol. 168, no. 1, pp. 170–177, 2011.
- [8] N. Feng, X. Guo, S. Liang, Y. Zhu, and J. Liu, "Biosorption of heavy metals from aqueous solutions by chemically modified orange peel," *Journal of Hazardous Materials*, vol. 185, no. 1, pp. 49–54, 2011.
- [9] W. M. Ibrahim, "Biosorption of heavy metal ions from aqueous solution by red macroalgae," *Journal of Hazardous Materials*, vol. 192, no. 3, pp. 1827–1835, 2011.
- [10] M. Á. Martín-Lara, I. L. R. Rico, I. C. A. Vicente, G. B. García, and M. C. de Hocés, "Modification of the sorptive characteristics of sugarcane bagasse for removing lead from aqueous solutions," *Desalination*, vol. 256, no. 1–3, pp. 58–63, 2010.
- [11] L. Pelit, F. N. Ertaş, A. E. Eroğlu, T. Shahwan, and H. Tural, "Biosorption of Cu(II) and Pb(II) ions from aqueous solution by natural spider silk," *Bioresource Technology*, vol. 102, no. 19, pp. 8807–8813, 2011.
- [12] UNEP/IE United Nations Environment Programme/Industry and Environment, "Environmental management in the brewing industry," UNEP Technical Report Series 33, UNEP, Paris, France, 1996.
- [13] K. B. Fontana, E. S. Chaves, J. D. S. Sanchez, E. R. L. R. Watanabe, J. M. T. A. Pietrobelli, and G. G. Lenzi, "Textile dye removal from aqueous solutions by malt bagasse: isotherm, kinetic and thermodynamic studies," *Ecotoxicology and Environmental Safety*, vol. 124, pp. 329–336, 2016.
- [14] G. Ren, Y. Jin, C. Zhang, H. Gu, and J. Qu, "Characteristics of *Bacillus* sp. PZ-1 and its biosorption to Pb(II)," *Ecotoxicology and Environmental Safety*, vol. 117, pp. 141–148, 2015.
- [15] S. Tunali, T. Akar, A. S. Özcan, I. Kiran, and A. Özcan, "Equilibrium and kinetics of biosorption of lead(II) from aqueous solutions by *Cephalosporium aphidicola*," *Separation and Purification Technology*, vol. 47, no. 3, pp. 105–112, 2006.
- [16] R. Han, J. Zhang, W. Zou, J. Shi, and H. Liu, "Equilibrium biosorption isotherm for lead ion on chaff," *Journal of Hazardous Materials*, vol. 125, no. 1–3, pp. 266–271, 2005.
- [17] R. A. Anayurt, A. Sari, and M. Tuzen, "Equilibrium, thermodynamic and kinetic studies on biosorption of Pb(II) and Cd(II)

- from aqueous solution by macrofungus (*Lactarius scrobiculatus*) biomass," *Chemical Engineering Journal*, vol. 151, no. 1-3, pp. 255-261, 2009.
- [18] A. Sari and M. Tuzen, "Kinetic and equilibrium studies of biosorption of Pb(II) and Cd(II) from aqueous solution by macrofungus (*Amanita rubescens*) biomass," *Journal of Hazardous Materials*, vol. 164, no. 2-3, pp. 1004-1011, 2009.
- [19] X. Ma, W. Cui, L. Yang, Y. Yang, H. Chen, and K. Wang, "Efficient biosorption of lead(II) and cadmium(II) ions from aqueous solutions by functionalized cell with intracellular CaCO<sub>3</sub> mineral scaffolds," *Bioresource Technology*, vol. 185, pp. 70-78, 2015.
- [20] R. Vimala and N. Das, "Biosorption of cadmium (II) and lead (II) from aqueous solutions using mushrooms: A Comparative Study," *Journal of Hazardous Materials*, vol. 168, no. 1, pp. 376-382, 2009.
- [21] W. N. L. dos Santos, D. D. Cavalcante, E. G. P. da Silva, C. F. das Virgens, and F. D. S. Dias, "Biosorption of Pb(II) and Cd(II) ions by *Agave sisalana* (sisal fiber)," *Microchemical Journal*, vol. 97, no. 2, pp. 269-273, 2011.
- [22] A. Sari, M. Tuzen, Ö. D. Uluözlü, and M. Soylak, "Biosorption of Pb(II) and Ni(II) from aqueous solution by lichen (*Cladonia furcata*) biomass," *Biochemical Engineering Journal*, vol. 37, no. 2, pp. 151-158, 2007.
- [23] L. P. Tovar, M. R. W. Maciel, A. Winter, C. B. Batistella, R. M. Filho, and L. C. Medina, "Reliability-based optimization using surface response methodology to split heavy petroleum fractions by centrifugal molecular distillation process," *Separation Science and Technology*, vol. 47, no. 8, pp. 1213-1233, 2012.
- [24] S. Chowdhury and P. D. Saha, "Scale-up of a dye adsorption process using chemically modified rice husk: optimization using response surface methodology," *Desalination and Water Treatment*, vol. 37, no. 1-3, pp. 331-336, 2012.
- [25] *Statistic for Windows (Computer Program Manual)*, StatSoft Inc., Tulsa, Okla, USA, 2004.
- [26] S. Qaiser, A. R. Saleemi, and M. Umar, "Biosorption of lead from aqueous solution by *Ficus religiosa* leaves: batch and column study," *Journal of Hazardous Materials*, vol. 166, no. 2-3, pp. 998-1005, 2009.
- [27] S. J. Kalil, F. Maugeri, and M. I. Rodrigues, "Response surface analysis and simulation as a tool for bioprocess design and optimization," *Process Biochemistry*, vol. 35, no. 6, pp. 539-550, 2000.
- [28] A. Esmaeli, M. Jokar, M. Kousha, E. Daneshvar, H. Zilouei, and K. Karimi, "Acidic dye wastewater treatment onto a marine macroalga, *Nizamuddina zanardini* (Phylum: Ochrophyta)," *Chemical Engineering Journal*, vol. 217, pp. 329-336, 2013.
- [29] A. Günay, E. Arslankaya, and I. Tosun, "Lead removal from aqueous solution by natural and pretreated clinoptilolite: adsorption equilibrium and kinetics," *Journal of Hazardous Materials*, vol. 146, no. 1-2, pp. 362-371, 2007.
- [30] M. F. Ahmad, S. Haydar, and T. A. Quraishi, "Enhancement of biosorption of zinc ions from aqueous solution by immobilized *Candida utilis* and *Candida tropicalis* cells," *International Biodeterioration and Biodegradation*, vol. 83, pp. 119-128, 2013.
- [31] M. Yurtsever and I. A. Şengil, "Biosorption of Pb(II) ions by modified quebracho tannin resin," *Journal of Hazardous Materials*, vol. 163, no. 1, pp. 58-64, 2009.
- [32] Y. Tang, L. Chen, X. Wei, Q. Yao, and T. Li, "Removal of lead ions from aqueous solution by the dried aquatic plant, *Lemna perpusilla* Torr," *Journal of Hazardous Materials*, vol. 244-245, pp. 603-612, 2013.
- [33] E. Eren, O. Cubuk, H. Ciftci, B. Eren, and B. Caglar, "Adsorption of basic dye from aqueous solutions by modified sepiolite: equilibrium, kinetics and thermodynamics study," *Desalination*, vol. 252, no. 1-3, pp. 88-96, 2010.
- [34] M. D. Mashitah, Y. Yus Azila, and S. Bhatia, "Biosorption of cadmium (II) ions by immobilized cells of *Pycnoporus sanguineus* from aqueous solution," *Bioresource Technology*, vol. 99, no. 11, pp. 4742-4748, 2008.
- [35] R. Han, H. Li, Y. Li, J. Zhang, H. Xiao, and J. Shi, "Biosorption of copper and lead ions by waste beer yeast," *Journal of Hazardous Materials*, vol. 137, no. 3, pp. 1569-1576, 2006.
- [36] I. Ullah, R. Nadeem, M. Iqbal, and Q. Manzoor, "Biosorption of chromium onto native and immobilized sugarcane bagasse waste biomass," *Ecological Engineering*, vol. 60, pp. 99-107, 2013.
- [37] E. Daneshvar, M. Kousha, M. S. Sohrabi, A. Khataee, and A. Converti, "Biosorption of three acid dyes by the brown macroalga *Stoechospermum marginatum*: isotherm, kinetic and thermodynamic studies," *Chemical Engineering Journal*, vol. 195-196, pp. 297-306, 2012.
- [38] R. Tabaraki, A. Nateghi, and S. Ahmady-Asbchin, "Biosorption of lead (II) ions on *Sargassum ilicifolium*: application of response surface methodology," *International Biodeterioration and Biodegradation*, vol. 93, pp. 145-152, 2014.
- [39] J. Crank, *The Mathematics of Diffusion*, Oxford University Press, Oxford, UK, 1975.



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