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Bioadsorption of nickel and cadmium ions from a binary solution onto sugarcane bagasse lignin: kinetic and thermodynamic study

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The single and binary adsorption of Cd(II) and Ni(II) from aqueous solution on lignin of sugarcane bagasse, a secondary product of sugarcane industry, has been demonstrated in this work. Experimental parameters affecting the adsorption are studied, such as the lignin dose, *p*H, contact time and temperature. The optimal values found for these parameters, both binary and single adsorption, are the followings: lignin dose (7g / L), *p*H (6), contact time (12 hours) and temperature (40°C). Different empirical adsorption models are used for the evaluation of sorption equilibrium data. Experimental results were interpreted considering speciation curves of ions present in the solution. In single and binary system adsorption data are analyzed using the following adsorption isotherms: single, non-modified, extended and modified Langmuir; single, non-modified and modified Redlich–Peterson; single and extended Freundlich; single and multicomponent Langmuir-Freundlich; and Sheindorf–Rebuhn–Sheintuch. The experimental adsorption isotherms are better adjusted to the extended Langmuir model. This study indicates that the lignin is an adsorbent able to remove Ni (II) and Cd (II) in binary systems, having a greater affinity for cadmium.

Keywords: Binary Adsorption, Cadmium, Lignin, Nickel

Heavy metals are of noxious waste generated in engineering activities, hospitals, commerce, mining activities, among others. These generate concern because of the significant discharged in waters and soil which affect human health and the environment, even in relatively low concentrations[1]. Additionally, the distribution and accumulation of these substances in food chains often cause serious pressures to public health even in relatively low concentrations[2]. Cadmium (Cd) and nickel (Ni) are heavy metals, widely used in the different process and their negative effects caused on human health have been studied[3]. The ministry of environment and sustainable development of Colombia through resolution 631 of 2015 decrees that the maximum permissible limits of Cd and Ni ions in discharged into surface water and sewage systems, depending on the productive sector is approximately 0.1 mg/L and 0.5 mg/L[4]. There are several techniques for the removal of these metals, such as filtration, adsorption, oxidation, dilution, among others[5].

The adsorption is a separation process used for the removal of contaminants from wastewater due to simple operation, are highly efficient and low cost. The use low-cost material as the biosorbents, activated carbon, zeolites, and clays natural, are used for the adsorption of heavy metals[6]. The study of binary or multicomponent adsorption of heavy metals is due to the fact that in water discharges there is not one contaminant but two or more. Therefore, it is interesting to analyze the behavior of these metal ions on an adsorbent, in addition to knowing their affinity and the competition that may exist between them to occupy active sites of adsorption[7].

In recent years, different multicomponent system of heavy metals have been studied on various adsorbents[8], for example; Cd(II)-Cu(II) on kraft lignin[9]; Cu(II)-Pb(II)-Zn(II)-Cd (II) on native cyanobacterial species[10]; Ni(II)-Zn(II)-Cu(II) on *Sargassumilicifolium*[11]; Cd(II)-Zn(II) on activated sludge[12]; Zn(II)-Ni(II)-Cd(II) on polyamide resin[13], have been examined in a recent work. Recent studies on the sorption of the multicomponent system have revealed that adsorption capacity in the single and binary system sorption decreased in the order Cd>Ni, which demonstrates that Cadmium has greatest ionic potential and affinity in adsorption due to competition for available adsorption sites and the electronegativity of the ions[14,15].

The single adsorption of heavy metals on lignin has been studied as a potentially adsorbent of heavy

metals from water, due to its a natural amorphous crosslinked resin that containing afunctional groups such as aldehyde, phenolic, carboxyl, benzyl alcohol, hydroxyl, and methoxyl groups[15]. Lignin is the second most abundant aromatic polymer in nature, after cellulose[16,17]. Lignin main function is to consolidate the cellulosic fibers of plants.The pulp and paper industry are produced more than 40 million tons/year as a mostly non-commercialized waste product[16].The adsorption mechanisms of metal ions on lignin were reviewed in different works[15,18,19].

The purposes of the research were to study the binary adsorption of nickel and cadmium on bagasse lignin and use the following adsorption models to adjust the equilibrium data: single, extended, non-modified, and modified Langmuir; single, modified and non-modified Redlich–Peterson; single and extended Freundlich; single and multicomponent Langmuir-Freundlich; and Sheindorf–Rebuhn–Sheintuch. Method used to predict the isotherm was Non-linear regression[20]. In addition, it was investigated the behavior of the presence of cadmium ion on the removal of nickel ion on bagasse lignin and vice versa. Another objective of this work was to understand the influence of lignin functional groups and predominant species in adsorption of metal ions. Speciation diagrams calculated the predominant species.

Experimental Section

Lignin from pulping soda of sugarcane bagasse was provided by the research group in Pulp and Paper Universidad Pontificia Bolivariana. The lignin used was sieved to obtain a particular diameter between 27 and 30 µm. The metals used as the adsorbates in this study were Cadmium nitrate tetrahydrate, (chemical formula Cd(NO3)2 · 4H2O, FW = 308.47 g/mol) and Nickel (II)nitrate hexahydrate, (chemical formula Ni(NO3)2 · 6H2O, FW = 290.81 g/mol). Stock solutions of the test reagents were prepared by dissolving the desired amount of reagents in distilled water.

Chemical characterization

The chemical characterization of the adsorbent material was performed using the ASTM standards, ash (D1102-84), humidity (E871-82), Klason Lignin (D1106-96) and sodium hydroxide solubility (D1109-84). Analyses were made by triplicate.

Determination of the acid groups by potentiometric titration

Lignin 0.3g and 30 mL sodium bicarbonate 0.1 N were mixed for 30 min with constant stirring. Then, the mixture was filtered and the residual sodium bicarbonate wastitrated potentiometrically with hydrochloric acid 0.1N[18].

Determination phenolic hydroxyl

Lignin 0.2 g known moisture was dissolved in 50 mL 96% dioxane. The solution was diluted in a ratio 1:10 in dioxane/water and adjusted to *p*H 13 with sodium hydroxide 1M. A blank was made with the same dilution but with *p*H led to 1 with the hydrochloric acid addition 1.0 M[21].

Adsorption experiments

Dose curve

Lignin between 0.01 and 0.25 g was contacted with 25 mL of 20 mg / L (average concentration of nickel discharge in the plating industry)[22] of Ni (II) or Cd (II) or an equimolar mix of both metals in solution. In the equimolar mix, the concentrations of nickel and cadmium were 10.44 and 20 mg / L respectively. A *p*H value of 6, was selected according to the results published[23]. Nickel and cadmium in solution precipitate at *p*H greater than 8.0 and 9.1, respectively[22]. The solution was continuously stirred at 28°C for 8 h until the equilibrium[22], then filtered and the filtrate was analyzed by atomic absorption, the assays were performed by duplicate.

pH curve

An equimolar mixture of nickel and cadmium was continuously stirred at 28°C. The lignin dose was 7 g / L, obtained from dose curve analysis. The solutions *p*H was varied between 2 and 7. The solution was reacting during 8h[22] having *p*H control every 30 min to stabilize. Then, the solution was filtered and analyzed by atomic absorption. The assays were performed by duplicate.

Diagrams of distribution of species Ni (II) and Cd (II)

The differents speciation diagrams a given *p*H the species present in binary Ni(II) and Cd(II) system, were construct followed this steps:

1) Identification of the nature of all species present in solution.
2) Determination and evaluation of formation equilibrium constants of all species (Table 2).
3) Determination of mass balance relations and the total concentration of each component in the solution, so that there are as many independent equations as unknowns.
4) Estimation of all n unknowns from the system of the n simultaneous equations.

These speciation diagrams will facilitate the choice of *p*H for obtaining better values for the formation constants, will give the *p*H for the maximum formation of certain species and will indicate which complexes are formed to a negligible extent[24].

Kinetics curve

An equimolar mixture of nickel and cadmium (10.44mg / L and 20 mg / L respectively) was continuously stirred at 28°C. The dose of lignin was 7 g / L. The *p*H was maintained to 6.2 ± 0.11. The contact time of lignin with the solution of nickel and cadmium was varied between 0 and 12 h. Then, the solution was filtered and analyzed by atomic absorption. The assays were performed by duplicate[22].

Adsorption isotherms

Equilibrium isotherms were determined using 7 g lignin/L and metals equimolar concentration between 10-100 mg Ni (II)/L and mg Cd(II) / L. The solutions with pH 6.2 ± 0.28 were stirred continuously at 30°C and 40°C until equilibrium is achieved at 12 h and filtered to determinate the Ni (II) and Cd (II) ions concentration, according to described above. The experiments were performed by duplicate and the results were adjusted to extended, non-modified and modified Langmuir; extended Freundlich; Freundlich-Langmuir; modified and non-modified Redlich–Peterson and Sheindorf–Rebuhn–Sheintuch models[7,25].

Results and Discussion

Chemical characterization

Table 1 shows the results of lignin characterization including moisture, ash, klason lignin, soluble lignin and solubility and the results of the acid total groups and the phenolic hydroxyl. Klason lignin was corrected by subtracting the acid insoluble ash content. Soluble lignin was determined by spectrophotometry.

The data reported are similar to those found Quintana, *et al*[26], for moisture 7.08 ± 0.08, total ash 4.17 ± 0.03, Klason lignin 62.15 ± 0.22, acid soluble lignin 3.98 ± 0.20. Hoareau[27] worked with lignin cane bagasse and obtained a moisture content of 9.5%, ash 1.1%, and Klason lignin 25.3%. Other works report[9] ash percentage between 3.2 - 4.6%.

Table 1 — Chemical characterization of the lignin: Moisture, ash, Klason lignin, soluble lignin and solubility and the results of the acid total groups and the phenolic hydroxyl.

Parameters	Results
Moisture (wt)%	8.89 ± 0.003
Total ash[a] (wt)%	6.58 ± 0.8
Klason lignin[b] (wt)%	63.2 ± 0.14
Soluble lignin (wt)%	3.22 ± 0.37
Solubility (wt)%	7.01 ± 0.18
Total acids (wt)%	0.094 ± 0.02
OH phenolic (wt)%	0.51 ± 0.02

[ab]Dry basis

Sugars presence decreases the lignin solubility, making the adsorbent affinity with metal ions also decrease. But, if the medium pH increases, it favors the formation of hydrolyzed species with major ionic size that enables interaction between the functional groups and metal. So, the affinity between them is also increased[28]. Functional groups quantification gives information about the solubility of the adsorbent, degree of degradation and modification. The data were compared with those reported by Quintana, *et al*.[29], where the total acid number is 0.11 ± 0.01 and phenolic hydroxyls is 0.73± 0.044. Hoareau[27] obtained a percentage of total acids of 0.74 and phenolic hydroxyl of 1.13.

The great capacity of adsorption of the lignin is partly attributed to phenols and other functional groups on their surface. Nevertheless, it cannot be due to a single functional group, among them there is one that has a greater affinity for the metallic ion. Most binary adsorption studies show that the functional groups present major affinity for ions with major ionic radius or index covalent and produced greater competition between ions with similar characteristics. It is concluded that an increase in the active groups improves the retention of the metal ion by the lignin[30].

Metal ions batch adsorption

Dose curves

Figure 1 shows theeffect of lignin dose on the single equilibrium metal uptake. Percentage of Ni(II)

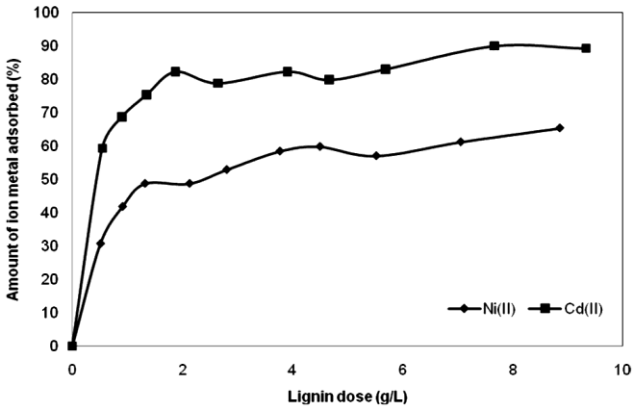

Fig. 1 — Effect of lignin dose on the single equilibrium metal uptake. Co = 20 mg/L Ni, 20mg/L Cd; solution volume= 25 mL; *p*H 6; T= 28°C and t = 8h

and Cd(II) ions adsorbed at equilibrium were calculated according to,

$$Removal\ (\%) = \frac{C_o - C_e}{C_o} x100\% \quad \ldots (1)$$

where, C_0 represents the initial concentration of adsorbate in solution, and C_e, concentration in the equilibrium of the adsorbate in solution[31].

It is observed that increasing of lignin dose, it is increased the surface area available so the removal of nickel and cadmium individuals solutions[22] also increases. Maximum removal percentages obtained were Ni (60.2%) and Cd (87.9%), at lignin dose of 7 g/L. Basso[32] reports a dose for this metals between 2-4 g/L, these doses are lower than that found in this work. Fig. 1 shows that lignin has a greater affinity for cadmium

This behavior can be caused by an electrostatic attraction between the surface of the lignin and the metal ion. This bond strength is due to the size of the ion radius, the larger size, major is retaining force. This occurs because of an electrostatic repulsion of metal ions with lower ionic radius with the binding sites of lignin, which determines the order of preference Cd(II)> Ni (II)[31]. These curves are similar to those reported by Mancera[22] and Basso[32].

Figure 2 shows the effect of lignin dose on the binary equilibrium metal uptake for an equimolar solution. From binary solution, data is concluded that the maximum removal is 80.7% for nickel and cadmium when the dose of lignin is 7 g / L. Lignin dose for the binary solution is almost the double if is compared with the single 20 ppm curves. Therefore, the adsorption efficiency is affected by the adsorbent dose increment. The dose increment produces a decrease in the amount adsorbed per unit mass due to the adsorption sites unsaturation or to the particles interaction. This state may result in a decrease of the total surface area of the adsorbent and an increase in the length diffusional[33].

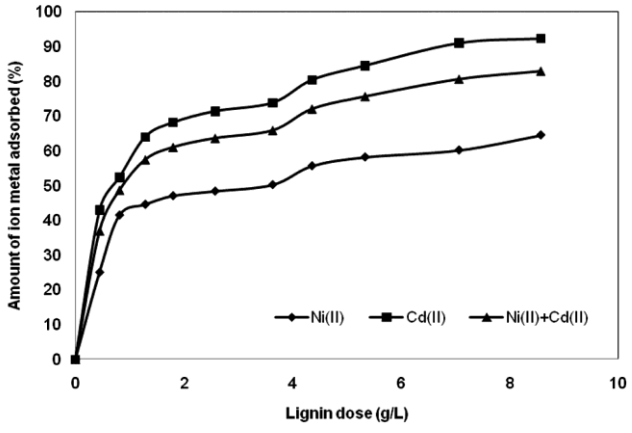

Fig. 2 — Effect of lignin dose on the binary equilibrium metal uptake for equimolar solution. Co = 10.44 mg/L Ni, 20 mg/ L Cd; solution volume= 25 mL; *p*H=6; T=28°C and t = 8h.

pH effect

Adsorption capacity depends on the solution *p*H since it affects the ion species distribution in the solution. The ion species distribution modifies the interactions between the adsorbent surface and adsorbate in solution[34]. Diagrams of ion species distribution allow to know which metal species predominates depending on the medium *p*H, also this diagram shows the concentration and composition of each species[35], Table 2

Figure 3 shows the speciation curve for ions ofNi (a) andCd (b) single at 20 ppm, and ions in an equimolar solution (c). For a good adsorption, it is important that metal species Ni^{+2} and Cd^{+2} prevailing in the solution because these ions have the smaller radius and therefore the adsorbent covered area is also smaller. Fig. 3 for individual ions shows that *p*H below 3 the predominant species are Ni^{+2} and Cd^{+2}, for *p*H between 5 and 10 have the presence of ions Cd $(NO_3)^+$ and Ni $(NO_3)^+$ but its concentration is lower than ions Ni^{+2} and Cd^{+2}. Figure 3 (c) for equimolar solution shows a similar behavior to *p*H below 3 but for *p*H between 5 and 10 the ions Cd $(NO_3)^+$ and Ni $(NO_3)^+$are predominant.

If the *p*H increases up to 10 there is a decrease in the concentrations of the species involved.

Figure 4 shows the effect of *p*H on the binary equilibrium metal uptake by lignin for an equimolar solution. It is observed at *p*H below 3 greater removals of nickel, at this *p*H predominate ions Ni^{+2} and Cd^{+2}. At *p*H above 3, a better removal of cadmium it is observed, at this *p*H predominates the

Table 2 — Chemical equilibrium in the solution for the ions Cd(II) and Ni (II) from their nitrates.

Equilibrium present in the solution of Cd (II)	Equilibrium present in the solution of Ni (II)
$H_2O \leftrightarrow H^+ + OH^-$	$H_2O \leftrightarrow H+ + OH^-$
$Cd^{+2}+H_2O \leftrightarrow Cd(OH)^- + H^+$	$Ni^{+2}+H_2O \leftrightarrow Ni(OH)^- + H^+$
$Cd^{+2}+2H_2O \leftrightarrow Cd(OH)_2+2H^+$	$Ni^{+2}+2H_2O \leftrightarrow Ni(OH)_2+2H^+$
$Cd^{+2}+3H_2O \leftrightarrow Cd(OH)_3^-+3H^+$	$Ni^{+2}+3H_2O \leftrightarrow Ni(OH)_3^-+3H^+$
$Cd^{+2}+4H_2O \leftrightarrow Cd(OH)_4^{-2}+4H^+$	$Ni^{+2}+4H_2O \leftrightarrow Ni(OH)_4^{-2}+4H^+$
$2Cd^{+2}+ H_2O \leftrightarrow Cd2(OH)^{-3}+H^+$	$2Ni^{+2}+ H_2O \leftrightarrow Ni2(OH)^{+3}+H^+$
$Cd^{+2}+NO_3- \leftrightarrow Cd(NO_3)^-$	$Ni^{+2}+NO_3- \leftrightarrow Ni(NO_3)^+$
$H^+ + NO_3- \leftrightarrow HNO_3$	$4Ni^{+2}+4H_2O \leftrightarrow Ni4(OH)_4^{+4}+4H^+$
	$Ni^{+2}+2NO_3- \leftrightarrow Ni(NO_3)_2$
	$H^+ + NO_3- \leftrightarrow HNO_3$

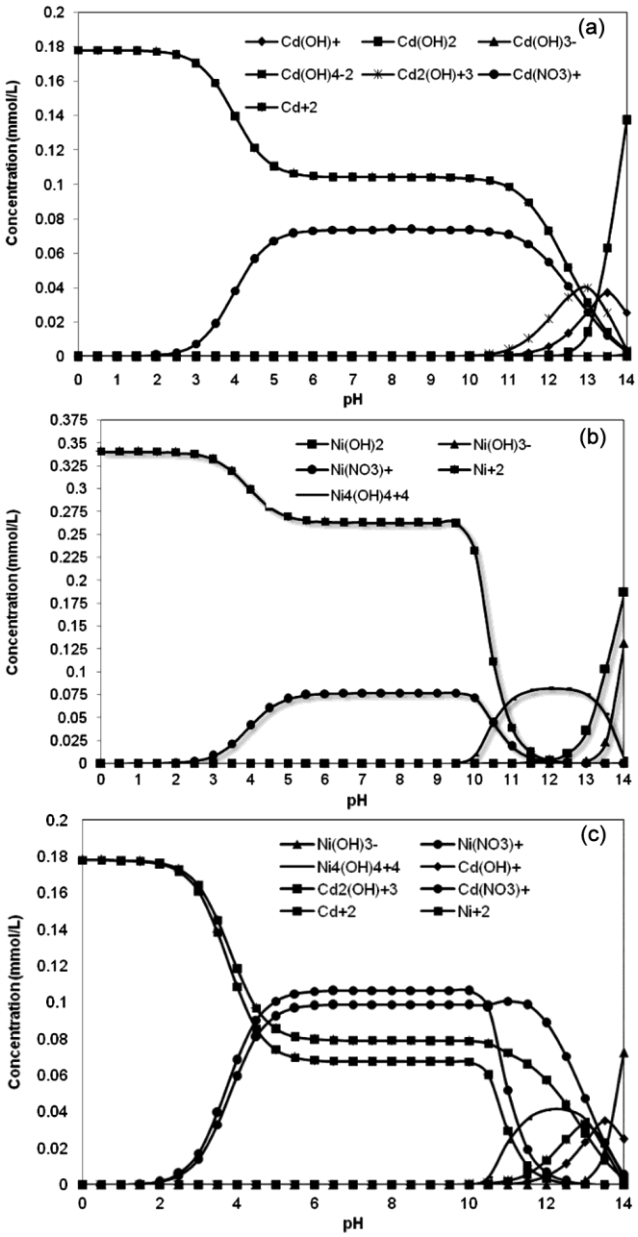

Fig. 3 — Speciation curve for ions of (a) Cd and (b) Ni single at 20 ppm, and ions in an (c) equimolar solution.

ions Cd $(NO_3)^+$ and Ni $(NO_3)^+$. This could indicate that at *p*H below 3 is most important for ions adsorption the size effect that the electronic charge effect. Maximum capacity for removal of these metals is given approximately at *p*H = 6 (87.4%). These results coincide with the zone of speciation curve where predominate the ions Ni $(NO_3)^+$ and Cd $(NO_3)^+$.

The experimental results are similar to those reported by other researchers for the adsorption of nickel and cadmium using lignin. Guo[15] obtained at *p*H above 6, removal percentage of 85% for Cu(II), Pb(II), Cd(II), Zn(II) and Ni(II). Basso[32] used *p*H 5.8 for removal of cadmium and nickel individually with various adsorbents.

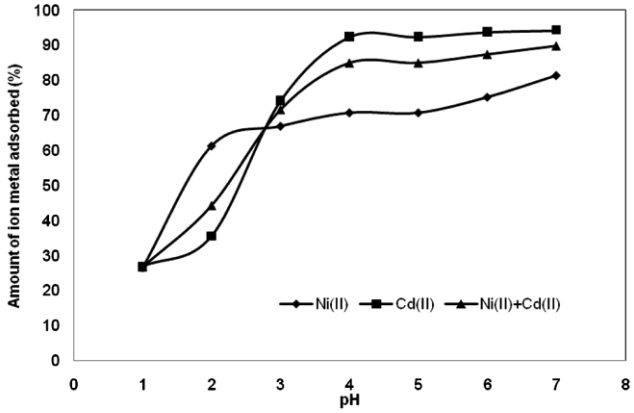

Fig. 4 — Effect of *p*H on the binary equilibrium metal uptake by lignin for equimolar solution. Co = 10.44 mg/L Ni, 20 mg/L Cd; lignin dose = 7g/L; solution volume= 25 mL; T= 28°C and t = 8h.

Kinetics curve

Kinetic experiments results produce a maximum removal (81.9% Ni, 88.04% for Cd) when the contact time is about 12 h. Adsorption processes proceed in two stages: a first stage takes place rapidly in the first few minutes of contact, and a second slower stage that can last for several hours until the equilibrium[36]. Kinetics allows determining the speed at which the metals are removed from the solution[37]. To study the kinetics, two models were selected to achieve experimental results best fit. Kinetic parameters determination was done by nonlinear regression.

Pseudo-first order model[38] is one of the most used for the adsorption of a solute from an aqueous phase and can be expressed as

$$q_t = q_e\left(1 - e^{(-k_1 t)}\right) \quad \ldots(2)$$

where q_e and q_t represent the adsorption capacities (mmol/g) of lignin at equilibrium and at a particular time t (h) respectively. Kinetic rate constant is denoted by k_1 (h^{-1}).

Pseudo-second order (PSO) equation is shown below as[39]

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad \ldots(3)$$

Kinetic rate constant in this model is denoted by k_2 (g / h mmol).Integrated form of this model is shown below:

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

where $k_2q_e^2$ =h, is the initial adsorption rate in mmol/g h. Adsorption capacity at any time was calculated by the following equation:

$$q_t = \frac{(C_i - C_f}{m} V \quad \ldots (5)$$

where C_i is the initial metal concentration in mmol/L, C_f is the metal concentration at a particular time in solution in mmol/L, V is the volume of the solution in litters (L), and m is the dry mass of lignin in gram (g).

Model parameters q_e and k_2 must be obtained by nonlinear regression, minimizing the objective function (FO), according to the following expression:

$$FO = \sum_{i=1}^{N} \left(q_{ti,exp} - q_{ti,mod}\right)^2 \quad \ldots (6)$$

where N is the number of experimental points, $q_{ti,exp}$ and $q_{ti,mod}$ are the experimental and modeled adsorption capacities respectively[22]. The best fit of experimental data was achieved with pseudo-second order model (Table 3).

The number of active surface site is directly proportional to the rate[9,37]. In Figure 5 shows the experimental data and the curves of the model chosen for the equimolar mixtures.

Mohan[9] reports q_e = 0.15 mmol/g and k_2= 0.0188 g/mol*h for Cd adsorption in kraft lignin at 10°C; Guo[15] reports for adsorption in lignin, for Ni a q_e = 0.110mmol/g and k_2= 153.3 g/mmol h, for Cd a q_e = 0.162 mmol/g and k_2= 88.50 g/mmol h. The results are not similar because the initial concentrations are very different. On the other hand, the reported values are for metals single adsorption. In this work, Cd (II) initial adsorption rate ($h = k_2q_e^2$) is double than of Ni (II). This behavior is due to that the electrostatic repulsion in the ion binding sites of lignin is higher for nickel than for cadmium.

Table 3 — Kinetic parameters for pseudo-second order adsorption model.

Metal	k_2 (g/mmol h)	q_e(mmol/g)	h(mmol/g h)	R^2
Ni (II)	4.2047	0.0635	0.0169	0.9856
Cd (II)	10.7620	0.0567	0.0346	0.9939
Total Ni (II) + Cd (II)	8.8561	0.0575	0.0293	0.9933

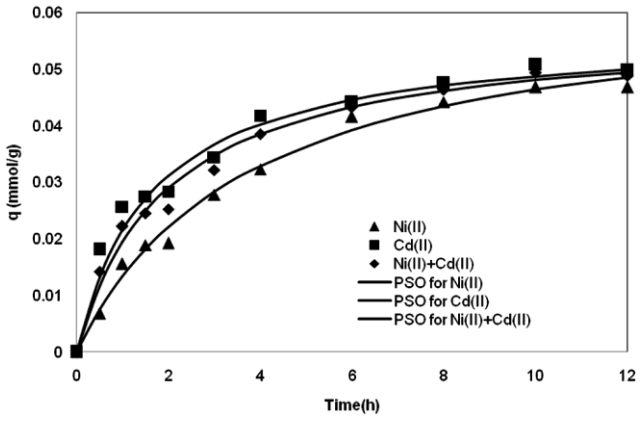

Fig. 5 — Kinetic on the binary equilibrium metal uptake in equimolar solution by lignin, experimental data and the best fit, pseudo second order model. Co = 10.44 mg/L Ni, 20 mg/L Cd; lignin dose = 7g/L; solution volume= 25 mL; T= 28°C.

Adsorption isotherms

Adsorption isotherms experimental data were adjusted using the following single and multicomponent adsorption models:

Langmuir single component isotherm (L)

$$q_i = \frac{X_{mL} K_L C_i}{1 + K_L C_i} \quad \ldots (7)$$

Freundlich single component isotherm (F)

$$q_i = X_F (C_i)^{nF} \quad \ldots (8)$$

Langmuir-Freundlich single component isotherm (L-F)

$$q_i = \frac{X_{mLF} K_{LF} (C_i)^{n_{LF}}}{1 + K_{LF} (C_i)^{n_{LF}}} \quad \ldots (9)$$

Redlich-Peterson single component isotherm (RP)

$$q_i = \frac{a_i C_i}{1 + b_i C_i^{\beta}} \quad \ldots (10)$$

Non-modified Langmuir multicomponent isotherm (NML)

$$q_i = \frac{X_{m,i} K_i C_i}{1 + \sum_{j=1}^{N} K_j C_j} \quad \ldots (11)$$

Extended Langmuir multi component isotherm (EL)

$$q_i = \frac{X_{max} K_{E,i} C_i}{1 + \sum_{j=1}^{N} K_{E,j} C_j} \quad \ldots (12)$$

Modified Langmuir multi component isotherm (ML)

$$q_i = \frac{X_{m,i} K_i \left(\frac{C_i}{\eta_i}\right)}{1 + \sum_{j=1}^{N} K_i \left(\frac{C_i}{\eta_i}\right)} \quad \ldots (13)$$

Non- modified Redlich-Peterson multicomponent isotherm (NMRP)

$$q_i = \frac{a_i C_i}{1 + \sum_{j=1}^{N} b_j C_j^{\beta j}} \quad \ldots (14)$$

Modified Redlich-Peterson multicomponent isotherm (MRP)

$$q_i = \frac{a_i \left(\frac{C_i}{\eta_i}\right)}{1 + \sum_{j=1}^{N} b_j \left(\frac{C_i}{\eta_i}\right)^{\beta i}} \quad \ldots(15)$$

Extended Freundlich multi component isotherm (EF)

$$q_1 = \frac{K_1 (C_1)^{\frac{1}{\eta_1} + x_1}}{C_1^{x_1} + y_1 C_2^{z_1}} \; q_2 = \frac{K_2 (C_2)^{\frac{1}{\eta_2} + x_2}}{C_2^{x_2} + y_2 C_1^{z_2}} \quad \ldots (16)$$

Langmuir-Freundlich multi component isotherm (LF)

$$q_i = q_{s,i} \frac{(b_{iLF} C_i)^{\frac{1}{\gamma}}}{1 + (b_{iLF} C_i)^{\frac{1}{\gamma}} + \left(b_{jLF} C_j\right)^{\frac{1}{\gamma}}} \quad \ldots (17)$$

Sheindorf-Rebuhn-Sheintuch isotherm (SRS)

$$q_i = K_i C_i \left(\sum_{j=1}^{N} a_{ij} C_j \right)^{\frac{1}{\eta_i} - 1} \quad \ldots (18)$$

where $a_{ii}=aij/\mathbf{a_{ij}}= 1$.

The parameters were estimated by nonlinear regression analysis using equation 6.

The adsorption capacity of adsorbent was calculated as follows:

$$q_e = \frac{(C_i - C_e)}{D} \quad \ldots (19)$$

where C_i and C_e are the initial and equilibrium adsorbate concentration respectively in mmol/L and D is the adsorbent dose in g/L[22].

Langmuir and Redlich-Peterson models are best fit to experimental data for single adsorption nickel and cadmium as shown in Tables 4, 5 and Figures 6, 7, 8 & 9. But the Langmuir is the best model because this requires fewer parameters. Comparing Langmuir parameters for individual ions is observed that maximum adsorption capacity and affinity are higher for nickel than cadmium, indicating that cadmium ions were no deposited on adsorbed molecules if not on the unoccupied surface in lignin.

Many of the models fit correctly to experimental data for the binary system as shown in Table 6, Figures 10 and 11. Extended Langmuir is the best model because this requires fewer parameters. Isotherm behavior in the binary system is similar to

Table 4 — Parameters from single component equilibrium isotherm adsorption models for Ni (II).

Model	Parameters	Temperature (°C)	
		30	40
L	x_{mL}(mmol/g)	0.0251	0.0383
	k_L(L/mmol)	5.3765	2.9378
	R^2	0.9610	0.9749
L-F	x_{mLF} (mmol/g)	0.0205	0.0301
	k_{LF}(L/mmol)	47.3226	10.4294
	η_{LF}	2.1407	1.6066
	R^2	0.7734	0.9132
F	η_{LF}	0.5031	0.5958
	k_F(L/g)	0.0249	0.0332
	R^2	0.8867	0.9517
RP	k_R (L/g)	0.2791	7.5179
	a_R(L/mmol)	11.5057	239.5854
	□ **β**	0.7657	0.571
	R^2	0.9738	0.9803

Table 5 — Parameters from single component equilibrium isotherm adsorption models for Cd (II).

Model	Parameters	Temperature (°C)	
		30	40
L	x_{mL}(mmol/g)	0.1046	0.1223
	k_L(L/mmol)	68.0486	7.6519
	R^2	0.9374	0.9691
L-F	x_{mLF} (mmol/g)	0.1350	0.1205
	k_{LF}(L/mmol)	14.4709	8.8079
	η_{LF}	0.8687	1.0591
	R^2	0.8820	0.9649
F	η_{LF}	0.4173	0.5623
	k_F(L/g)	0.2151	0.1727
	R^2	0.8988	0.9549
RP	k_R (L/g)	20.2783	3.8376
	a_R(L/mmol)	131.8687	25.6992
	□ β	0.7774	0.6012
	R^2	0.9904	0.9767

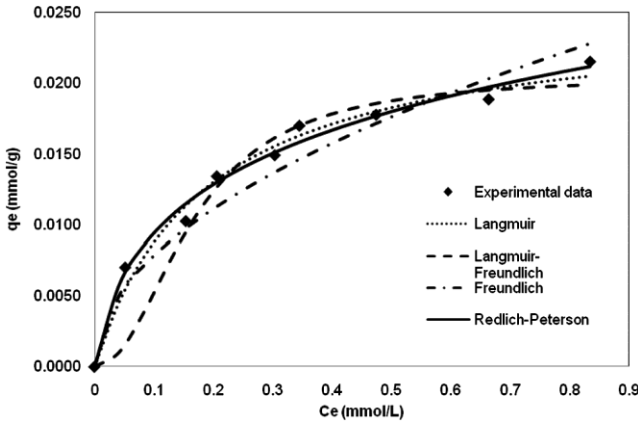

Fig. 6 — Equilibrium isotherms of Ni(II) ions on lignin, experimental data and models fit.Co=5.22-52.22 mg/L Ni; lignin dose = 7g/L; *p*H=6; T=30°C; solution volume= 25 mL and t=12h.

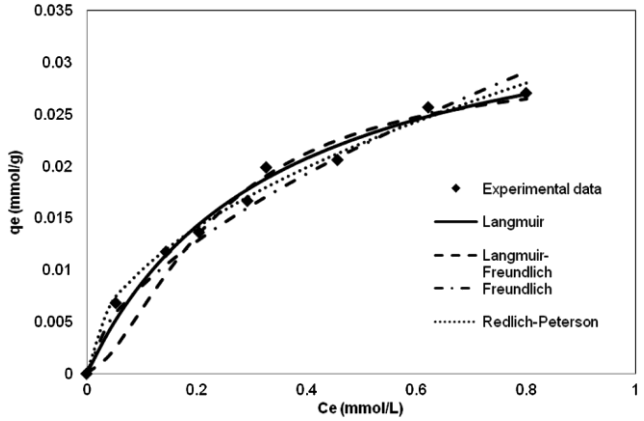

Fig. 7 — Equilibrium isotherms of Ni(II) ions on lignin, experimental data and models fit. Co=5.22-52.22 mg/L Ni; lignin dose = 7g/L; *p*H=6; T=40°C; solution volume= 25 mL and t= 12h.

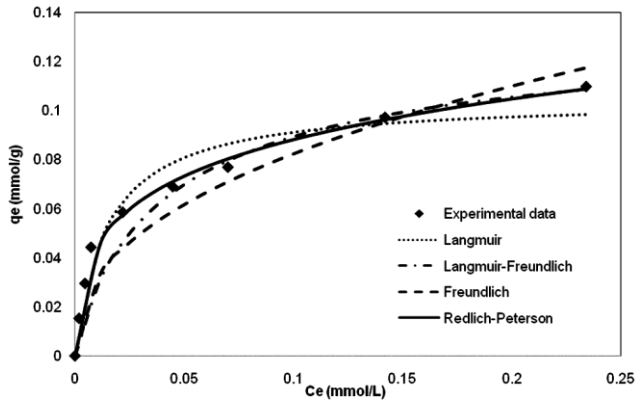

Fig. 8 — Equilibrium isotherms of Cd(II) ions on lignin, experimental data and models fit. Co=10-100 mg/L Cd; lignin dose = 7g/L; *p*H=6; T=30°C; solution volume= 25 mL and t= 12h.

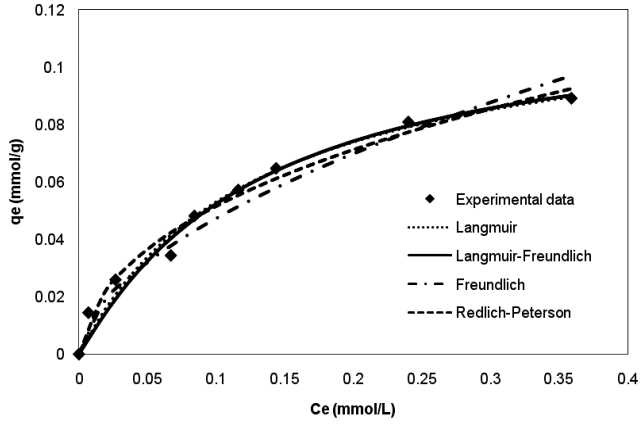

Fig. 9 — Equilibrium isotherms of Cd(II) ions on lignin, experimental data and models fit. Co=10-100 mg/L Cd; lignin dose = 7g/L; *p*H=6; T=40°C; solution volume= 25 mL and t= 12h.

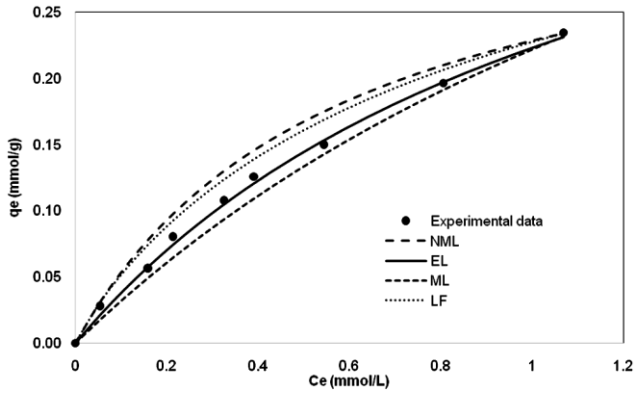

Fig. 10 — Equilibrium isotherms of equimolar binary ions on lignin, experimental data and models fit. Co=5.22-52.22 mg/L Ni, 10-100 mg/L Cd; dose sample= 7g/L; *p*H=6; T=30°C; solution volume= 25 mL and t= 12h.

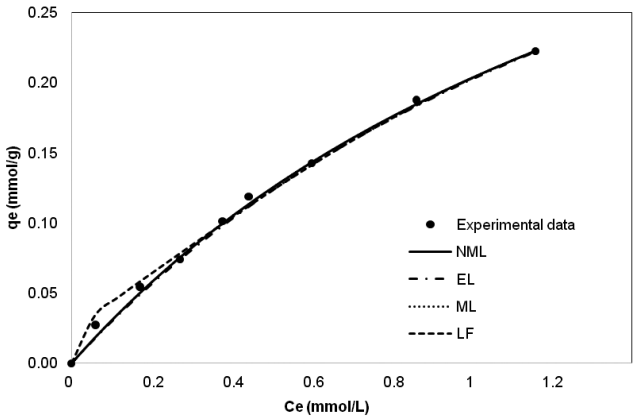

Fig. 11 — Equilibrium isotherms of equimolar binary ions on lignin, experimental data and models fit. Co=5.22-52.22 mg/L Ni, 10-100 mg/L Cd; dose sample= 7g/L; *p*H=6; T=40°C; solution volume= 25 mL and t= 12h.

single adsorption. Single component models may not define exactly the multicomponent adsorption behavior of metal ions[40].

In the extended Langmuir model, the value of X_{max} is unique for all metals and obeys the superficial uniformity hypothesis that all solutes compete for the same binding sites. It is observed that the maximum adsorption capacity (X_m) increases with temperature. This behavior suggests an endothermal process, it happens sometimes in adsorption processes in the liquid phase. This result agrees with the obtained by Mohan and Doyorum[41,42,43]. K_E parameter is related to the affinity adsorbate-adsorbent, this parameter is directlyproportional to temperature for nickel and inversely proportional to temperature for cadmium, in

contrast for single adsorption for both ions K_L parameter is inversely proportional to temperature. The affinity of the lignin by metal ions shows a higher affinity for the nickel that cadmium, the values obtained are approximately 0.8785 L / mmol and 0.6936 L / mmol respectively.

Regressions obtained with Langmuir models are better than the other models. This behavior can be explained as follows: Langmuir isotherm is applied assuming a monolayer surface, due to adsorbed molecule occupies one adsorption site and between them can be described formed ionic or covalent bonds[21]. Extended Langmuir isotherm assuming that the surface sites are uniform and that the molecules of Ni(II) and Cd(II) ions compete for the same active sites in the adsorbent[44]. Modified Langmuir assuming that the interactions between individual metal ions, and individual metal ion and the mixture are not described by their constants[44]. Extended Freundlich and Langmuir-Freundlich multicomponent models did not have a good fit, these supposed that the adsorption occurs in a heterogeneous surface and the affinity of the metal ions for the adsorbent occurs in different active sites[44,45].

In studies of adsorption in systems with mixtures metals that functional groups have a higher affinity for some ions that other ions, it is believed that the primary mechanism involved in the process of adsorption are ion exchange and the complexation, which relates to certain ionic characteristics of metal as the ionic radius, electronegativity, and the exchange between H^+ present in carbonyl groups and phenolic surface of the lignin, this exchange produces a decrease in the pH of the solution, which causes previously adsorbed metal is desorbed (this process was not observed in this work). In general, the adsorbents typically have a higher affinity for ions having a major ionic radius or covalent index andis presented greater competition between ions of similar characteristics[46,47], the sequence followed is Au (III)> Pb (II)> Hg (II)> Zn (II)> La (III)> Fe (III)> Pt (IV)> Cd (II)> Co (II)> Cu (II)> Pd (II)> Cr (III)> Ni (II)> Cr (VI)> V (II)[18].

Conclusion

The lignin from sugar cane bagasse is an efficient adsorbent for nickel and cadmium ions removal for single and binary systems. For binary adsorption case, the necessary dose of adsorbent to reach the maximum metal removal is higher than single adsorption case. For *p*H between 5 and 10 have a predominance of ions Cd $(NO_3)^+$ and Ni $(NO_3)^+$ and this *p*H region correspond to maximum removal of ions. The kinetic study reveals two processes, one fast in the first 6 hours of contact and a slow where the rate of adsorption increases until equilibrium is reached within 12 h for nickel and cadmium. The order of the reaction which describes the removal of metals using lignin corresponds to the pseudo-second order model. Modified and extended Langmuir models show the best fit to the experimental data in comparison with the models for the multicomponent system. For individual metals, the best models are the Langmuir and Redlich-Peterson. Adsorption isotherms indicate the presence of competitive effects of the ions on active sites. Lignin adsorb both species although has more affinity for cadmium. Increasing the temperature from 30°C to 40°C represents an increase of adsorption capacity of Ni and Cd ions in the binary system.

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