Removal of Zn^{2+} from Electroplating Wastewater Using Modified Wood Sawdust and Sugarcane Bagasse

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Abstract: This paper describes the preparation of new adsorbents derived from sugarcane bagasse and wood sawdust (*Manilkara sp.*) to remove zinc (II) ions from electroplating wastewater. The first part deals with the chemical modification of sugarcane bagasse and wood sawdust, using succinic anhydride to introduce carboxylic acid functions into the material. The obtained materials (modified sugarcane bagasse MB2 and modified wood sawdust MS2) were then characterized by infrared spectroscopy (IR) and used in adsorption experiments. The adsorption experiments evaluates Zn^{2+} removal from aqueous single metal solution and real electroplating wastewater on both batch and continuous experiments using fixed-bed columns prepared in laboratorial scale with the obtained adsorbents. Adsorption isotherms were then developed using Langmuir model and the Thomas kinetic model. The calculated Zn^{2+} adsorption capacities were found to be 145 mg/g for MS2 and 125 mg/g for MB2 in single metal aqueous solution, whereas for the industrial wastewater these values were 61 mg/g for MS2 and 55 mg/g for MB2.

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Introduction

The heavy metals are among the most harmful of the elemental pollutants and are of particular concern as their increasing level in the environment represents a serious threat to human health, living resources and ecological systems (Manahan 2000; Sankararamakrishnan et al. 2007). Therefore, the discharge of effluents containing metals into the environment is a chief concern as they are considered persistent, bioaccumulative and toxic (USEPA 1998). The high concentration of heavy metals in some industrial effluents demand wastewater technologies capable of effectively removing such pollutants so that the effluent discharge complies with the strict environmental legislation (Reynolds and Richards 1995).

Electroplating industries are one of the oldest industries that deals with surface finishing and metal deposition; and these processes produce metal-contaminated wastewater (Ajmal et al. 2001) with relatively high toxic loads. Zinc, one of the important heavy metals widely used in electroplating industries, is an essential element for enzyme activators in humans, but it is toxic at levels of 100–500 mg/day and it is a known carcinogen (Senthilkumar et al. 2006). The United States Environmental Protection Agency (USEPA) establishes the maximum discharge limits of zinc in 4.2 mg/L for any 1 day value and in 2.6 mg/L for the average of daily values for 4 consecutive monitoring days (USEPA 1998). In Brazil the maximum discharge limits is set in 5 mg/L by Federal Legislation (CONAMA 2005).

Treatment processes employed for zinc removal from wastewaters normally involve high pH precipitation, where the metal ions precipitated by the available hydroxide ions are then removed by sedimentation. The resultant sludge are then thickened and dewatered in order to be transported to landfills or incinerators. This process is expensive and often ineffective for low metal concentrations (Deliyanni et al. 2007), hence new technologies have been developed (e.g., membrane processes, ion exchange resins, adsorption) to treat metal-containing wastewaters.

Many efforts have been made recently to find cheaper and effective methods and materials for water pollution control (Ajmal et al. 2000; Bingol et al. 2004). Among these methods, adsorption is by far the most versatile and widely used for the removal of different pollutants (Gupta and Ali 2004) from water and wastewater. One of the most popular adsorbent are the lignocellulosic materials, because they are natural materials available in large quantities that can be a byproduct of industrial wastes (Ngah and Hanafiah 2008; Sciban et al. 2007). These materials, including wood sawdust (Ajmal et al. 1998; Sciban et al. 2007), sugarcane bagasse, coir pith (Suksabye et al. 2007), peanut shells (Watwoyo et al. 1999), corn cobs (Hawthorne-Costa et al. 1995), olive cake (Doyurum and Çelika 2006), and chemically modified cellulosic materials (Gurgel et al. 2008; Karnitz et al. 2007; Ngah and Hanafiah 2008; Wong et al. 2003), show great potential for water treatment.

Surface modification of such low-cost materials has become a solution to improve the adsorption capacity of cellulosic materials, and for this many methods have been developed (Ngah and

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Hanafiah 2008; Yu et al. 2008). Karnitz et al. (2007) have recently reported the use of sugarcane bagasse modified with succinic anhydride for removal of Cu (II), Cd (II) and Pb (II) from aqueous solutions, resulting in an increase of metal adsorption by new material containing carboxylic acid functional groups introduced in the fiber.

This study aimed at investigating the removal of zinc (II) from aqueous single metal solution and electroplating wastewater using sugarcane bagasse and wood sawdust chemically modified with succinic anhydride.

Materials and Methods

Materials

Sugarcane bagasse, a waste material from the sugar–alcohol industry, was collected from an alcohol factory at Ouro Preto, Brazil. Wood sawdust (*Manilkara sp.*) was collected from a saw mill at Belo Horizonte, Brazil. Succinic anhydride and pyridine were purchased from VETEC (Brazil), whereas $ZnSO_4$ was purchased from SYNTH (Brazil). Pyridine was refluxed with NaOH overnight and distilled before being used in the modification of cellulosic materials. Stock Zn^{2+} solution (1,000 mg/L) was prepared with $ZnSO_4$ and distilled water, and all the other Zn^{2+} solutions used in this study were prepared from the stock solution.

Wastewater Samples

Wastewater samples were collected from an alkali-zinc electroplating wastewater line of an electroplating industry located in Contagem, Minas Gerais, Brazil. Samples collected daily during a week in September 2007 were then mixed and used in the adsorption studies.

Material Preparation

Sugarcane bagasse and wood sawdust were dried at 100°C in an oven for approximately 24 h and then the fiber size was reduced to powder by milling with a tungsten ring. The resulting material was sieved with a four-sieve system (20, 32, and 65 mesh), and the material from the 32 to 65 mesh fraction was collected and washed with distilled water under stirring at 65°C for 1 h and then dried at 100°C. Finally, the dried material was washed anew in a Soxhlet system with *n*-hexane/ethanol (1:1) for 4 h.

Synthesis of MB1 and MS1

Sugarcane bagasse (B) or wood sawdust (S) (5 g) was reacted with succinic anhydride (15 g) under pyridine reflux (50 mL) for 24 h in order to obtain modified sugarcane bagasse (MB1) or modified wood sawdust (MS1). The modified materials (MB1 and MS1) were separated by filtration in sintered filter, washed in sequence with: solution of acetic acid in methylene chloride (1 mol/L), ethanol 95%, distilled water, chloridric acid solution (0.01 mol/L), distilled water, and finally with acetone as described by Gurgel et al. (2008). After drying the materials at 80°C in an oven for 1 h and placing them in a desiccator overnight, the mass percent gains (mpg) and degrees of succinylation of both materials were calculated, as detailed in the following.

Synthesis of MB2 and MS2

MB2 and MS2 were obtained by treatment of MB1 and MS1 with saturated sodium bicarbonate solution in a 250-mL Erlenmeyer for 30 min under constant stirring. Soon afterwards, the materials were separated by filtration in sintered filter and washed with distilled water and acetone. Finally, MB2 and SB2 were dried in an oven at 80°C and stored in a desiccator.

Materials Characterization

FTIR Analyses

The samples were prepared mixing 1 mg of material with 100 mg of spectroscopy grade KBr. The Fourier transform infrared (FTIR) spectra were recorded using Nicolet Impact 410 equipment (Chemistry Dept., University of Ouro Preto—DEQUI/UFOP) with detector at 4 cm^{-1} resolution from 500 to 4,000 cm^{-1} and 32 scans per sample.

Mass Percent Gain

The mpg of MB1 and MS1 was calculated according to

$$\text{mpg}(\%) = \frac{m_{\text{mod}} - m_{\text{unmod}}}{m_{\text{unmod}}} \times 100 \quad (1)$$

where m_{mod}=mass of modified material and m_{unmod}=mass of unmodified material.

Degree of Succinylation

The degree of succinylation of MB1 and MS1 was determined by measuring the quantity of introduced acid functions. The concentration of carboxylic functions *per* gram of material was determined by retrotitration. For this, amounts of 0.1000 g of MB1 and MS1 were treated with 100.0 mL of an aqueous NaOH solution (0.01 mmol/L) in a 250-mL Erlenmeyer for 1 h under constant stirring. Soon thereafter, the materials were separated by single filtration and three aliquots (25.0 mL) of each obtained solution were titrated with an aqueous HCl solution (0.01 mmol/L) (Karnitz et al. 2007; Gurgel et al. 2008). The concentration of carboxylic functions was calculated using

$$C_{\text{COOH}} = \left[\frac{(C_{\text{NaOH}} V_{\text{NaOH}}) - (4 C_{\text{HCl}} V_{\text{HCl}})}{m_{\text{mat}}} \right] \quad (2)$$

where C_{NaOH}=concentration of NaOH solution (mmol/L); C_{HCl}=concentration of HCl solution (mmol/L); V_{NaOH}=volume of NaOH solution (L); V_{HCl}=volume of HCl spent in the titration of excessive nonreacted base (L); and m_{mat}=material mass (g).

Zinc Adsorption Batch Experiments

Kinetic Study of Zn^{2+} Adsorption for MB2 and MS2 from Aqueous Single Metal Solution

Experiments with each material were performed to determine the adsorption equilibrium time. The interval times used were 10–60 min. An amount of 50.0 mg of MB2 or MS2 were placed in a 250-mL Erlenmeyer with 50.0 mL of Zn^{2+} solution at fixed concentration (200 mg/L) under constant stirring. The experiments were done at pHs 5.8 for MB2 and 5.9 for MS2. Insignificant pH variations ($\pm 0,1$) were noticed during each experiment. After single filtration, the concentration of Zn^{2+} ions was determined by direct titration with ethylenediaminetetraacetic acid (EDTA) (3 mmol/L) at pH 10 using Erichrome Black T as an indicator.

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pH Study of Zn^{2+} Adsorption for MB2 and MS2 from Aqueous Single Metal Solution

Experiments with each material were performed to determine the effect of pH on Zn^{2+} adsorption. An amount of 50.0 mg for MB2 and MS2 was placed in a 250-mL Erlenmeyer with 50.0 mL of metal ion solution at fixed concentrations (200 mg/L of Zn^{2+}) under constant stirring. The pH was adjusted with an aqueous HCl or NaOH solutions at 0.01–1.0 mol/L. The pH range studied for MB2 and MS2 was from 2.5 to 6.5. The reaction times used were those obtained from the kinetic study (30 min for both materials). There were significant pH variations during the experiments, but they were corrected by adding up an aqueous NaOH or HCl solution (0.01–0.1 mol/L) to the metal solution. After single filtration, the metal ions concentration was determined by titration as described earlier.

Adsorption Isotherms for MB2 and MS2 from Aqueous Single Metal Solution

Experiments were performed for each material to determine the adsorption isotherms that best represented the experimental data. In each experiment, 50.0 mg for MB2 and MS2 were placed into a 250-mL Erlenmeyer with 50.0 mL of Zn^{2+} ion solution at specific concentrations from 180 to 300 mg/L under constant stirring. Each experiment was performed using the time (30 min) and the pH (6.2–6.3) of the greatest ion adsorption obtained from kinetic and pH studies, respectively. There were significant pH variations during the experiments, but they were corrected by adding up an aqueous NaOH or HCl solution (0.01–0.1 mol/L) to the metal solution. After single filtration, the metal ions concentration was determined by titration as described earlier.

Studies with Real Electroplating Wastewater

Wastewater Characterization

The analyze of metal ions concentration was determined by inductively coupled plasma [ICP-OES, Spectro, Ciros CDD (Geology Dept., University of Ouro Preto—DEGEO/UFOP)]. Cloride ions were determined by Mohr method, whereas the surfactants were determined by the MBAS method according to the Standard Methods (AWWA 1998).

Kinetic Study of Zn^{2+} Adsorption for MB2 and MS2 from Electroplating Wastewater

Experiments with each material were performed to determine the adsorption equilibrium time. The interval times used were 10–60 min. An amount of 50.0 mg of MB2 or MS2 were placed in a 250-mL Erlenmeyer with 50.0 mL of wastewater under constant stirring. The experiments were done at pH 6.0 after adjusting the initial wastewater pH (12) with concentrated HNO_3 solution before adding the modified materials. No pH corrections were done along the experiment. After single filtration, the concentration of Zn^{2+} ion was determined by inductively coupled plasma (ICP-OES, Spectro, Ciros CDD).

pH Study of Zn^{2+} Adsorption for MB2 and MS2 from Electroplating Wastewater

Experiments with each material were performed to determine the effect of pH on Zn^{2+} ion adsorption. An amount of 50.0 mg for MB2 and MS2 was placed in a 250-mL Erlenmeyer with 50.0 mL of wastewater under constant stirring. The pH was adjusted with an aqueous HCl or NaOH solution at 0.01–1.0 mol/L. The pH range studied for MB2 and MS2 was from 2.5 to 6.5. The reaction times used were those obtained from the kinetic study (30 min for both materials). There were significant pH variations during the experiments, but they were corrected by adding up an aqueous NaOH or HCl solution (0.01–0.1 mol/L) to the metal solution. After single filtration, the metal ions concentration was determined by ICP-OES.

Adsorption Isotherms for MB2 and MS2 from Electroplating Wastewater

Experiments were performed for each material to determine the adsorption isotherms. In each experiment, varied amounts (0.4–1.2 g/L) of MB2 and MS2 were placed into a 250-mL Erlenmeyer with 50.0 mL of wastewater under constant stirring. Each experiment was performed using the time (30 min) and the pH (6.3) of the greatest ion adsorption obtained from kinetic and pH studies, respectively. There were significant pH variations during the experiments, but they were corrected by adding up an aqueous NaOH or HCl solution (0.01–0.1 mol/L) to the metal solution. After single filtration, the metal ions concentration was determined by ICP-OES.

Continuous Experiments in Adsorption Column

Continuous flow sorption experiments were conducted in a glass column of 18 mm internal diameter and 110 mm height. Experimental conditions were the same for both materials and 3.0 g of modified biomass in its dry form was placed in the column and rinsed with distilled water. The dimension of the packed columns for 3.0 g of wet material was 18×50 mm and the bed volume was estimated as 12.7 cm^3. Electroplating wastewater having an initial Zn^{2+} concentration of 70 mg/L and pH value of 6 was pumped upward through the column at 15 mL/min flow rate by a peristaltic pump (BP-600, Milan, Italy). The eluate was collected in 30 mL fractions from the exit of the column at different intervals and then filtered and analyzed for zinc (II) concentration by atomic absorption spectroscopy [Varian Spectra AA200 (Geology Dept., University of Ouro Preto—DEGEO/UFOP)]. Operation of the column was stopped when the effluent zinc (II) concentration exceeded 69.5 mg/L. The breakthrough point for the column operation was defined as the volume where the effluent concentrations of Zn^{2+} reached 5 mg/L, which is the discharge limit set by the Brazilian legislation.

Regeneration of Column Modified Biomass

The zinc-loaded modified biomass (MB2 and MS2) was regenerated in situ by washing the column with 0.1 M HCl solution pumped upward through the column at 8 mL/min flow rate. Aliquots of 10 mL were collected, filtered and analyzed for zinc (II) concentration by atomic absorption spectroscopy. Then, the column was washed with saturated sodium bicarbonate solution until reaching basic pH (approximately 10 min) and finally washed with distilled water to obtain a pH column close to 7.0.

Results and Discussion

Synthesis and Characterization of Adsorbents MB2 and MS2

The synthesis route used to prepare MB2 and MS2 is shown in Fig. 1. Sugarcane bagasse or wood sawdust were reacted with succinic anhydride for 24 h in pyridine reflux. Succinylation allowed the introduction of carboxylic functions to materials through formation of ester functions between the hydroxyl groups

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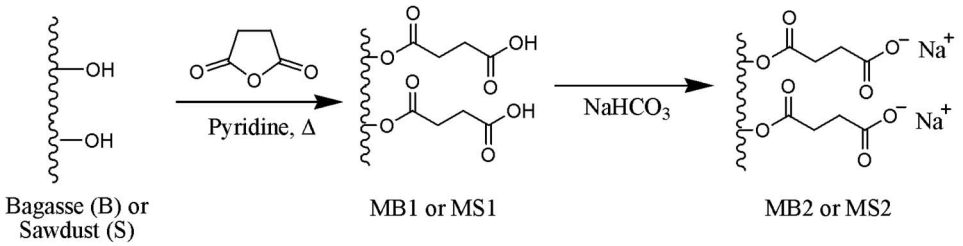

Fig. 1. Scheme for synthesis of the materials MB1, MB2, MS1, and MS2

in the bagasse and sawdust fibers and succinic anhydride. The mpg were calculated according to Eq. (1). The materials MB1 and MS1 obtained mass gains of 61 and 75%, respectively. The succinylation degrees of materials were determined by measuring the acid function introduced. The concentration of carboxylic functions *per* gram of modified materials was determined retrotitration [Eq. (2)]. The concentration of carboxylic acid functions of the materials was 6.4 mmol/g for MB1 and 7.4 mmol/g for MS1. In order to convert the carboxylic groups into carboxylate functions, which have better chelating properties, the materials MB2 and MS2 were prepared by treatment of MB1 and MS1 with a saturated sodium bicarbonate solution.

The characterization of carboxylated materials was accomplished by FTIR spectroscopy. Fig. 2 shows the FTIR spectra for MB2 and MS2 and unmodified starting material (B: sugarcane bagasse; S: wood sawdust). As depicted in Fig. 2, the two major changes noticed in FTIR spectrum for MB2 and MSB2 when compared to the starting unmodified materials are: (1) the arising of a strong band at 1,738 cm^{-1} for MS2 and of a strong band at 1,743 cm^{-1} for MB2, corresponding to asymmetric and symmetric stretching of ester C–O; (2) the arising of strong bands at 1,582 and 1,410 cm^{-1} for MS2 and of strong bands at 1,577 and 1,419 cm^{-1} for MB2, corresponding to, respectively, asymmetric and symmetric stretching due to the presence of the carboxylate ion. The ester and carboxylate IR bands indicate that succinic group was introduced via formation of the ester bond with consequent release of a carboxylic functional group.

Batch Studies of Zn^{2+} Adsorption in Aqueous Single Metal Solution on MB2 and MS2

The studies of the adsorption properties of MB2 and MS2 were accomplished for each material in aqueous Zn^{2+} ions. A kinetic study and adsorption study as a function of pH were first carried out.

The kinetic study of both materials for Zn^{2+} ions in aqueous solution is presented in Fig. 3. The equilibrium time was achieved after 20 and 30 min for MB2 and MS2, respectively. As a result, the adsorption equilibrium time of 30 min was chosen for pH and concentration-dependent experiments of both materials.

The removal of metal ions from aqueous solutions by adsorption is dependent on the solution pH since it affects adsorbent surface charge, the degree of ionization, and adsorbent speciation. Adsorption of Zn^{2+} in MB2 and SM2 as a function of pH is shown in Fig. 4. The adsorption of Zn^{2+} increased as pH increased and reached a maximum of adsorption at approximately 5.8 and 6.2 for the MB2 and MS2, respectively. For a range of pH above 7.0, there is the possibility of zinc ions precipitation on the surface of the adsorbent.

It was fixed the same range of pH (between 6.2 and 6.3) and the same contact time (30 min), to conduct the isotherm study for both materials MB2 and MS2 (Fig. 5).

Adsorption isotherms describe how adsorbates interact with adsorbents and are important in optimizing the use of the latter.

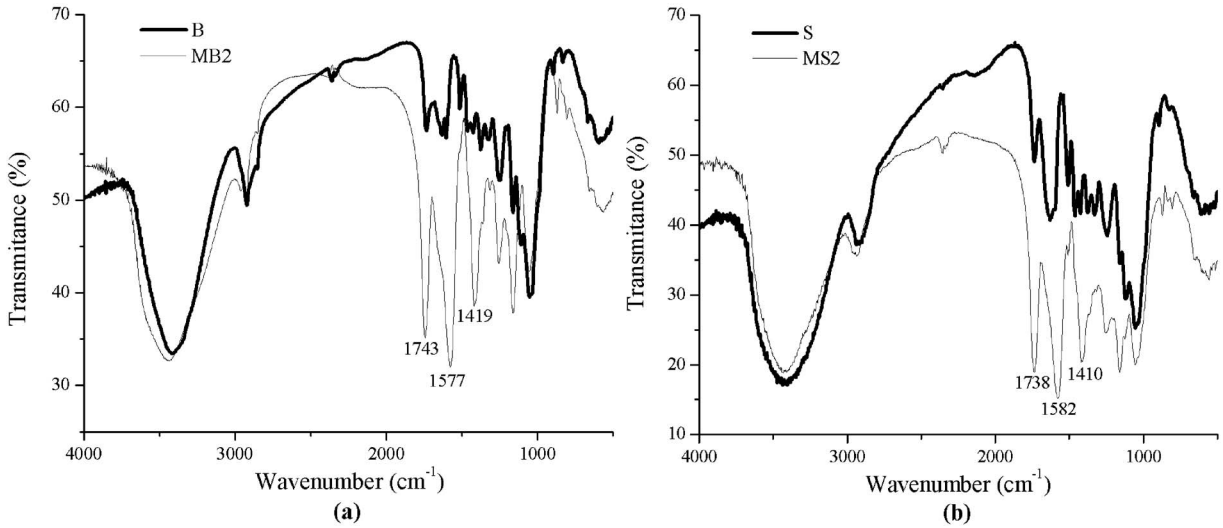

Fig. 2. FTIR spectrum of (a) B and MB2; (b) S and MS2

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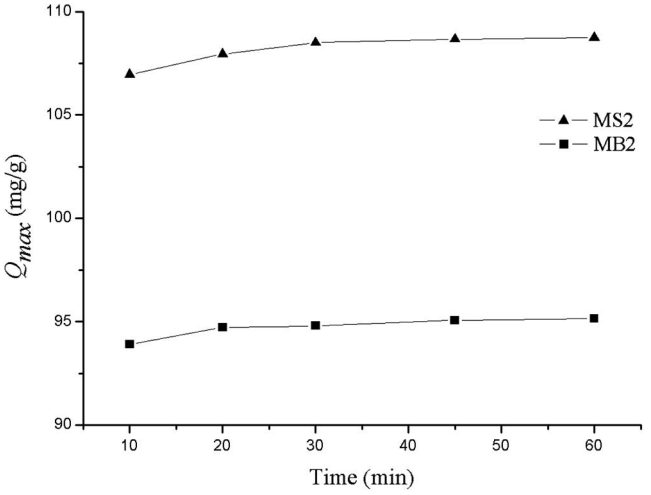

Fig. 3. Adsorption of Zn^{2+} ions on MB2 and MS2 as a function of time

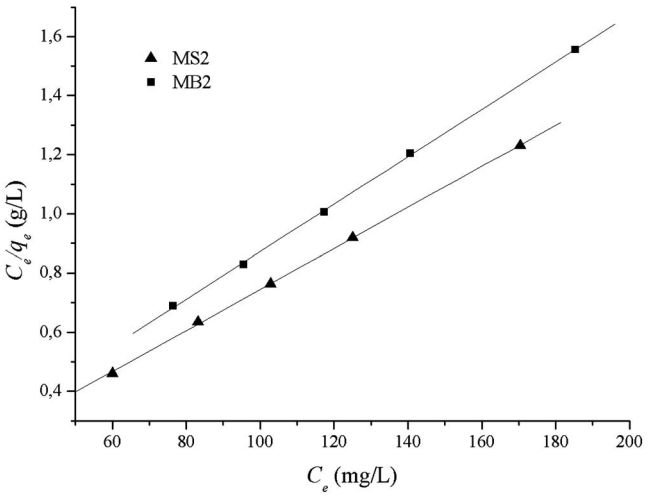

Fig. 5. Langmuir isotherm for adsorption of Zn^{2+} onto MB2 and MS2

The widely used Langmuir isotherm (Langmuir 1918) has found successful application in many real adsorption processes and is expressed as

$$q_e = \frac{Q_{\max} b C_e}{(1 + bC_e)} \tag{3}$$

which can be rearranged to obtain a linear form

$$\frac{C_e}{q_e} = \frac{C_e}{Q_{\max}} + \frac{1}{Q_{\max} b} \tag{4}$$

where q_e=equilibrium adsorption capacity (mg/g); $Q_{\max}$ =maximum amount of metal ion *per* unit weight of the material (mg/g), needed to form a complete monolayer coverage on the surface bound at high equilibrium metal ion concentration C_e (mg/L); and b=Langmuir constant related to the binding sites affinity (L/mg). $Q_{\max}$ represents the practical limiting adsorption capacity when the surface is fully covered with metal ions, assisting the comparison of adsorption performance, and b indicates the adsorption reaction bond energy between metal and material (Ho et al. 2005).

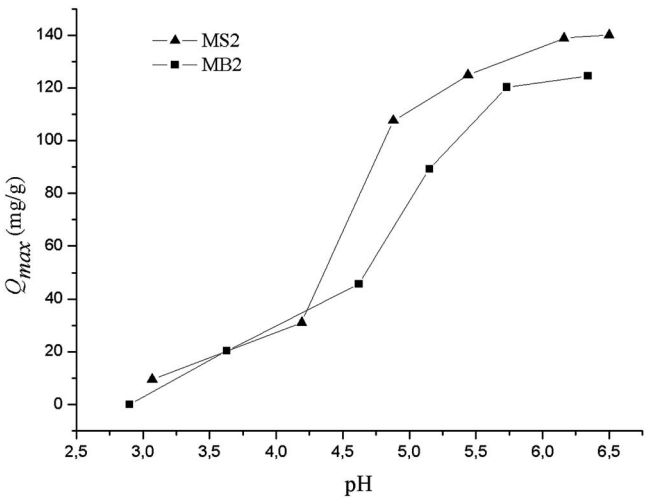

Fig. 4. Adsorption of Zn^{2+} ions on MB2 and MS2 as a function of pH

A linearized plot of C_e/q_e versus C_e is obtained from the model shown in Fig. 5. $Q_{\max}$ and b are computed from the slopes and interceptions of different straight lines. Table 1 lists the calculated results. The high correlation coefficients of linearized Langmuir equation indicate that this model can explain Zn^{2+} ion adsorption by the modified materials very well.

The Langmuir isotherm parameter $Q_{\max}$ indicates the maximum adsorption capacity of the material, in other words, the adsorption of metal ions at high concentrations. It can be observed in Table 1 that MS2 showed a greater Zn^{2+} adsorption capacity than MB2, which can be explained by the fact that MS2 has a higher carboxylic acid function concentration (7.4 mmol/g) than MB2 (6.4 mmol/g). In spite of this, the parameter b indicates that the bond energy of the metal complexation with the adsorbent material was similar for both materials. This parameter can be used to calculate the change of Gibbs free energy (ΔG°), according to

$$\Delta G^\circ = -RT \ln b \tag{5}$$

where R=gas constant (8.314 J/mol K) and T=absolute temperature (K). For MB2 ΔG° was −22.12 kJ/mol and the MS2 was −22.58 kJ/mol. Negative values of ΔG° obtained for both materials indicates that the process of Zn^{2+} adsorption is spontaneous and confirms that there is an affinity between the metal and the materials MB2 and MS2.

Batch Studies of Zn^{2+} Adsorption in the Electroplating Wastewater on MB2 and MS2

The adsorption studies were accomplished for real electroplating wastewater for each material. The study was conducted in batch to evaluate the efficiency of Zn^{2+} ions removal in function of time, pH and concentration of the adsorbent material (Fig. 6). After 40 min, the adsorption equilibrium was achieved for both

Table 1. Langmuir Parameters for Zn^{2+} Adsorption onto MB2 and MS2

Adsorbents	$Q_{\max}$ (mg/g)	b (L/mg)	R^2
MB2	125.00	0.115	0.9997
MS2	144.93	0.139	0.9997

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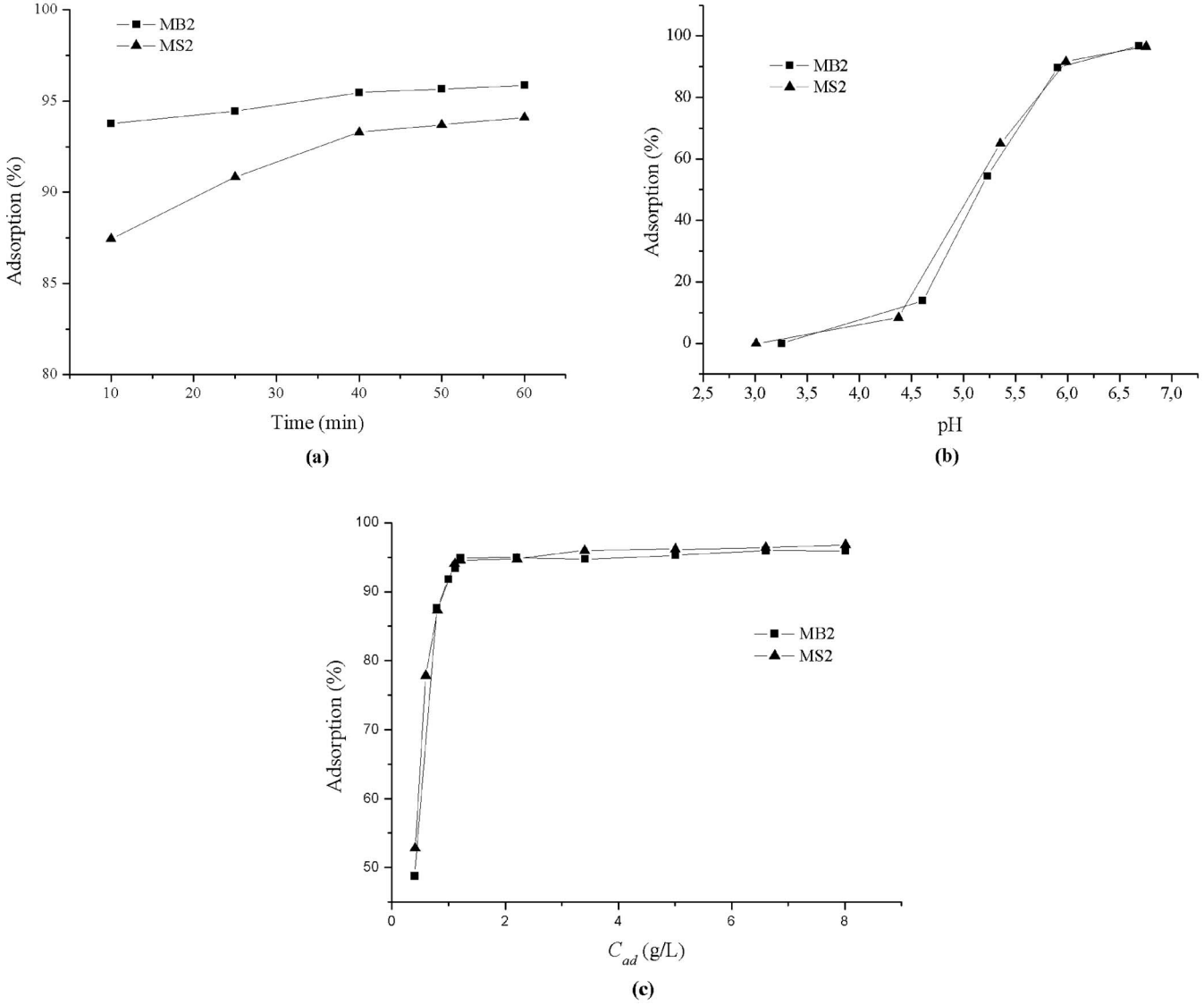

Fig. 6. Adsorption of Zn^{2+} ions on MB2 and MS2 as a function of (a) time; (b) pH; and (c) concentration of adsorbent with real electroplating wastewater

materials, MB2 and MS2. For pH between 6 and 7, there was a removal efficiency greater than 90%. From a adsorbent concentration (C_{ad}) of 1.0 g/L in the wastewater, it was possible to obtain an adsorption efficiency higher than 95%.

The isotherm study (Fig. 7) was carried out keeping the pH between 6.3 and 6.5 and a contact time of 40 min. Adsorption isotherms were studied by Langmuir model and the Langmuir parameters are shown in the Table 2. The high correlation coefficients of the linearized Langmuir equation indicate that this model can explain Zn^{2+} ion adsorption by the modified materials very well in real wastewater.

It can be observed in Table 2 that MS2 presents a greater Zn^{2+} adsorption capacity when compared to MB2, which agrees with the results presented in Table 1. The Q_{max} values presented in Table 2 are nearly half of the values presented in Table 1, which were obtained with single metal Zn^{+2} solutions. These results confirm that other metallic species in the electroplating wastewater compete for the binding sites of the modified materials MB2 and MS2, thereby decreasing the Zn^{2+} adsorption capacity.

The parameter b was higher for MB2, which means that the

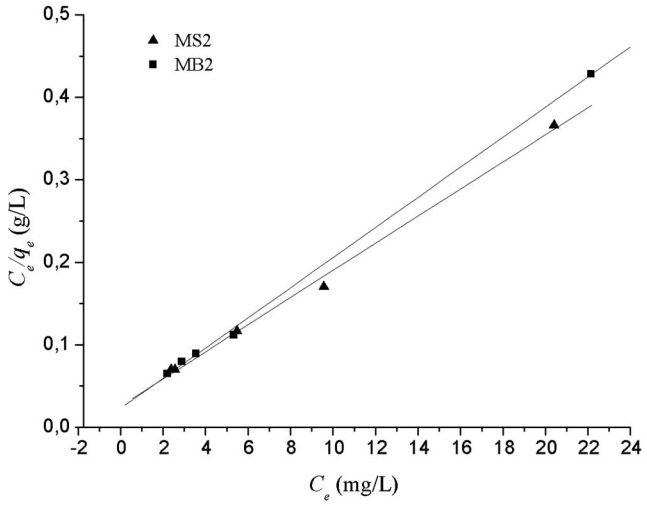

Fig. 7. Langmuir isotherm for Zn^{2+} adsorption in the electroplating wastewater

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Table 2. Langmuir Parameters for Zn^{2+} Adsorption in the Electroplating Wastewater

Material	Q_{max} (mg/g)	b (L/mg)	R^2
MB2	54.64	0.792	0.9990
MS2	60.98	0.638	0.9962

Table 5. Concentration of Ions Chloride and Surfactants in the Electroplating Wastewater

Parameter	Concentration (mg/L)
Chloride (Cl^-)	7,214.0
Anionic surfactants	11.9

zinc ions are retained with more intensity in MB2 than in MS2. The change of Gibbs free energy ($\Delta G°$) was calculated, and it was found a $\Delta G°$ of −26.89 kJ/mol for MB2 and of −26.36 kJ/mol for MS2. These results shows that the process of Zn^{2+} absorption in the wastewater is spontaneous, confirming that there is a high affinity of this metal for MB2 and MS2.

The fact that higher b values were obtained with the complex effluent when compared to single metal solution, might suggest that the other ions present in the electroplating wastewater helped to increase the strength of binding, for instance, by countering ionic repulsion near the binding sites.

Interference of Other Ions

Adsorption in multicomponent systems is complicated due to the fact that many solute–surface interactions are involved. The effect of ionic interaction (Mohan and Singh 2002) on the adsorption process may be represented by the ratio of the adsorption capacity for one metal ion in the presence of the other ions, Q_{mix}; to the adsorption capacity for the same metal when it is present alone in the solution, Q_0;

So, if

1. $Q_{mix}/Q_0 > 1$, the adsorption is promoted by the presence of other ions;
2. $Q_{mix}/Q_0 = 1$ there is no observable net interaction; or
3. $Q_{mix}/Q_0 < 1$ the adsorption is suppressed by the presence of other ions.

The effect of ionic interaction is represented for Zn^{2+} ion in Table 3. The results of Q_{max} by adsorption isotherm of ion Zn^{2+} in aqueous single metal solution are considered here as Q_0 due to the absence of other ions, whereas the results of studies of Q_{max} by adsorption isotherm of the Zn^{2+} ion in the wastewater are considered as Q_{mix} due to the presence of several other ions. The calculated values of Q_{mix}/Q_0 for both materials are lower than 1 as shown in Table 3, confirming that Zn^{2+} was suppressed by other ions in the electroplating wastewater, thereby reducing its adsorption capacity.

Table 3. Effect of Ionic Interaction for Zn^{2+} Adsorption

Adsorbent	Q_{mix} (mg/g)	Q_0 (mg/g)	Q_{mix}/Q_0
MB2	54.64	125.00	0.44
MS2	60.98	144.93	0.42

The effect of other cations on the Zn^{2+} adsorption behavior in the wastewater was studied, under the best conditions obtained, i.e., pH in the range of 6–7, contact time of 50 min and concentration of the material in the wastewater of 1.2 g/L. The concentration of the other cations before and after treatment with the adsorbent materials are presented in the Table 4.

According to Table 4, there was interference of other metal cations on Zn^{2+} adsorption, but in spite of the competition, the effect on the Zn^{2+} ions adsorption was minimal. Although the concentration of Ca^{2+} ions (82.00 mg/L) exceeded the concentration of Zn^{2+} ions (43.24 mg/L) in the wastewater, it can be seen that a removal efficiency higher than 94% of Zn^{2+} ions was obtained, while for Ca^{2+} ions the removal efficiency was only about 50% for both modified biomass. The other cations also interfered on Zn^{2+} ions adsorption, but their concentration and their removal are lower than the zinc concentration in the wastewater. Therefore, it seems that adsorbent materials show preferential adsorption for the Zn^{2+} ions when the electroplating wastewaster is treated under the conditions used in this study.

Some anions, such as Cl^-, SO_4^{2-} and CN^-, have affinity with the metal, forming insoluble or soluble complexes (Sankararamakrishnan et al. 2007). It is possible that chloride ions form stable complexes with Zn^{2+}. Thus suppressing the Zn^{2+} and/or $Zn(OH)^+$ adsorption by the adsorbents. The presence of anionic surfactants can also influence by binding with Zn^{2+} and keeping it in solution. Table 5 shows the concentration of these anions present in the wastewater.

The constant stability ($\log K$) of Zn^{2+} with chloride ions or with the anionic surfactants must be high enough to form complex stable and thus change the Zn^{2+} adsorption behavior of adsorbent materials. The ionic strength of the medium is also one of the factors that affect the availability of the metal, and might have contributed to lower Q_{max} values of Zn^{2+} adsorption in the electroplating effluent. Nevertheless, the modified absorbents (MB2 and MS2) still have an excellent adsorptivity with the wastewater, which had Zn^{2+} in a concentration range of 10–70 mg/L.

Breakthrough Curves for Zn^{2+} Adsorption in MB2 and MS2

The Thomas kinetic model (Juang et al. 2006) was chosen to evaluate the Zn^{2+} adsorption capacity (Q_{max}) by the modified ma-

Table 4. Wastewater Characterization in Function of the Concentration and Percentage of Absorption for Some Cations before and after Treatment with MB2 and MS2

	Concentration (mg/L)						Adsorption (%)					
Wastewater	Ca	Cu	K	Mg	Si	Zn	Ca	Cu	K	Mg	Si	Zn
Without treatment	82.00	0.28	22.17	1.40	21.36	43.24	—	—	—	—	—	—
Treatment with MB2	42.73	0.04	20.77	1.46	19.63	2.20	47.9	84.2	6.3	3.8	8.1	94.9
Treatment with MS2	39.63	0.05	20.96	1.30	20.15	2.37	51.7	81.8	5.5	7.1	5.7	94.5

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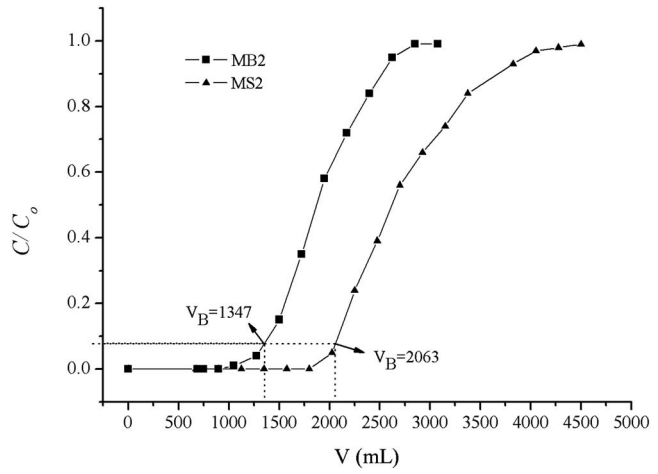

Fig. 8. Breakthrough curve for Zn^{2+} adsorption on MB2 and MS2

terials (MB2 and MS2) used in the column experiments. The linear form of Thomas (Malkoc and Nuhoglu 2006) model is expressed as

$$\ln\left(\frac{C_0}{C}-1\right)=\frac{K_{TH}Q_{max}M}{Q}-\frac{K_{TH}C_0V}{Q} \quad (6)$$

where K_{TH}=Thomas model rate constant (mL/min.mg); Q_{max} =maximum solid-phase concentration of the solute (mg/g); V=volume of metal solution passed through the column (mL); M=adsorbent mass (g); C=metal concentration effluent the column (mg/L); C_0=metal concentration affluent the column (mg/L); and Q=wastewater flow rate through the column (mL/min).

The total amount (m_{ad}) of metal ions adsorbed by the column is calculated from the following equation:

$$m_{ad}=Q_{max}M \quad (7)$$

The total amount (m_{total}) of metal ions that passed through the column can be calculated from the following equation:

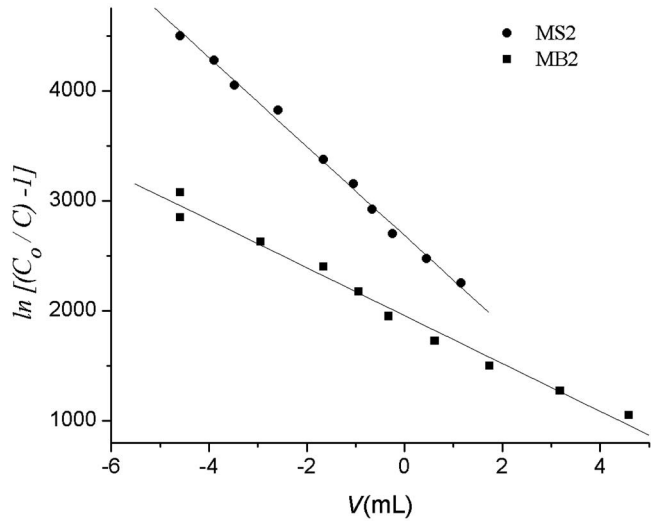

Fig. 9. Curve $\ln[C_0/C-1]$ versus V (mL) of Thomas model for adsorption of Zn^{2+} ions in the electroplating wastewater by MB2 and MS2

Table 6. Results of the Values of K_{TH} (mL/min g) and Q_{max} (mg/g) by Thomas Model for Adsorption of Zn^{2+} Ions in the Electroplating Wastewater for MB2 and MS2

	Thomas model parameters		
Adsorbents	K_{TH} (mL/min mg)	Q_{max} (mg/g)	R^2
MB2	0.96	46	0.9848
MS2	0.54	60	0.9953

$$m_{total}=\frac{C_0Qt_e}{1{,}000} \quad (8)$$

where t_e=exhaustion time (min).

The breakthrough volume (V_B) was defined as the cumulative volume of effluent that passed through the column when the Zn^{2+} effluent concentration (C) was 5.0 mg/L, which is the Brazilian discharge limit. This concentration represents 7.1% of the affluent Zn^{2+} concentration (70.0 mg/L). From the breakthrough curve (Fig. 8) it can be observed that the (V_B) for MS2 (2,063 mL) was higher than that for MB2 (1,347 mL) when the same amount of material (3.0 g) was used in the columns.

Fig. 9 shows the linearized logarithmic function of Thomas model, which enabled the determination of Thomas model rate constant K_{TH} (mL/min.g) and the Q_{max} (mg/g) as presented in the Table 6. The high correlation coefficients of linearized logarithmic function indicate that this model can properly describe Zn^{2+} adsorption by the modified materials in the column tests with the electroplating wastewater. The parameters Q_{max} obtained are very similar than those calculated for the batch studies (Table 2).

Q_{max} of MB2 and MS2 obtained through of Thomas model (Table 6) multiplied by the amount of adsorbent material in the column [Eq. (5)] gives the total amount (m_{ad}) of metal ions adsorbed by the column. These results are shown in Table 7.

After the continuous feeding adsorption tests with the electroplating wastewater the column was regenerated as described in the Materials and Methods section. After regeneration, the column was fed again with a single metal solution of Zn^{2+} and the adsorption studies carried out. After bed exhaustion, the elutant was fed into the column and regeneration studies were conducted. These cycles of adsorption followed by desorption were repeated three times to evaluate the biomass sorption capacity. The metal mass desorbed (m_d) could then be calculated by integrating the curve resulting from the plot of Zn^{2+} concentration versus elutant volume that passed through the column. The results of the first cycle are representative of all regeneration tests studied, therefore only the results of the first desorption test are shown in Fig. 10 and Table 8.

Table 8 shows that very high Zn^{2+} recovery efficiencies were obtained for both materials when using HCl 0.1 M as elutant. These results show the potential applicability of the modified materials in the removal and recovery of Zn^{2+} from electroplating

Table 7. Total Quantity of Ion Zn^{2+} Adsorbed Column for Materials Adsorbents

Adsorbents	m_{ad} (mg)	m_{total} (mg)	Total metal removal (%)
MB2	138	210	65.7
MS2	182	315	57.8

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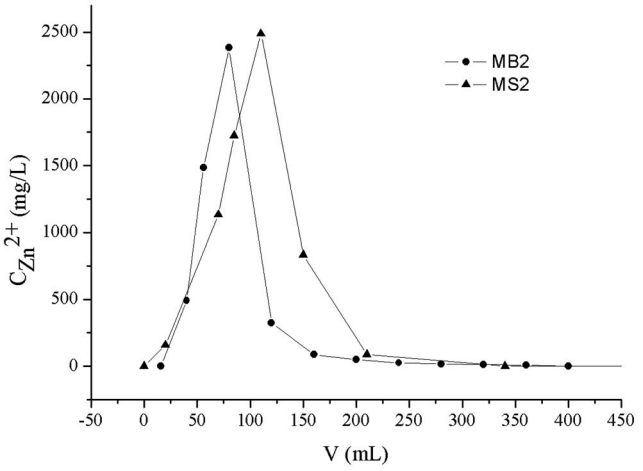

Fig. 10. Desorption curve for both materials (MB2 and MS2) when using HCl 0.1 M as elutant

wastewater. The concentrated Zn^{2+} solution could then be reused in the electroplating baths minimizing environmental impacts and industrial costs.

Conclusion

The chemical modification of the lignocellulosic materials sugarcane bagasse (B) and wood sawdust (S) with succinic anhydride was confirmed by infrared spectroscopy. The Zn^{2+} adsorption studies of the obtained adsorbents, MB2 and MS2, were successfully conducted first in batch mode with either aqueous single metal solution containing only Zn^{2+} ions or wastewater from a zinc electroplating line, and then in continuous mode using adsorbent packed columns.

The kinetic studies showed that the equilibrium time was lower than 30 min for all materials investigated when a single metal aqueous solution was used, and around 40 min for the adsorption studies carried out with the electroplating wastewater. The adsorption data showed that the increase in pH improved Zn^{2+} adsorption for all systems, and that Langmuir model best explained the adsorption of Zn^{2+} for all materials and conditions studied. The calculated Zn^{2+} adsorption capacities were found to be 145 mg/g for MS2 and 125 mg/g for MB2 in single metal aqueous solution, whereas for the industrial wastewater these values were 61 mg/g for MS2 and 55 mg/g for MB2. These results indicate that other ions present in the industrial wastewater compete with Zn^{2+} for the adsorbent binding sites. In both cases, MS2 seemed to have a higher Zn^{2+} adsorption capacity when compared to MB2, which can be explained by the fact that MS2 has a higher carboxylic acid function concentration (7.4 mmol/g) than MB2 (6.4 mmol/g).

The adsorption capacity decreases when the Zn^{2+} ions are adsorbed in situations where there is competition between other cations or interference with other ions as it happened when adsorption was studied with electroplating wastewater. In this study was observed the influence, mainly of Ca^{2+} and Cl^{-} present in wastewater. So the Zn^{2+} adsorption in the wastewater is lower that in aqueous single solution but it was possible to have a removal above 94% of Zn^{2+} ions, showing that the adsorbent materials are selective for the Zn^{2+} cation.

The column studies with continuous feeding of industrial wastewater resulted in maximum adsorption capacities Q_{max} of 46 and 60 mg/g, for MB2 and MS2, respectively, according with the Thomas model, hence the breakthough volume for MS2 (2,063 mL) was higher when compared to MB2 (1,347 mL), for the same amount of material used (3.00 g). Finally, the regeneration process of the column showed to be efficient for both adsorbents MS2 and MB2, proving the potential of these materials for removing and recovering Zn^{2+} ions from electroplating wastewater.

Table 8. Efficiency of Recovery in the Column for Materials Adsorbents

Adsorbent	m_d (mg)	Efficiency of recovery (%)
MB2	137	99
MS2	208	114

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