



Removal of Zn^{2+} from aqueous single metal solutions and electroplating wastewater with wood sawdust and sugarcane bagasse modified with EDTA dianhydride (EDTAD)

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ABSTRACT

This work describes the preparation of a new chelating material derived from wood sawdust, *Manilkara* sp., and not only the use of a new support, but also a chemically modified sugarcane bagasse synthesized in our previous work to remove Zn^{2+} from aqueous solutions and electroplating wastewater. The first part describes the chemical modification of wood sawdust and sugarcane bagasse using ethylenediaminetetraacetic dianhydride (EDTAD) as modifying agent in order to introduce carboxylic acid and amine functional groups into these materials. The obtained materials such as the modified sugarcane bagasse, EB, and modified wood sawdust, ES were then characterized by infrared spectroscopy (IR) and CHN. The second part evaluates the adsorption capacity of Zn^{2+} by EB and ES from aqueous single metal solutions and real electroplating wastewater, which concentration was determined through direct titration with EDTA and inductively coupled plasma (ICP-OES). Adsorption isotherms were developed using Langmuir model. Zn^{2+} adsorption capacities were found to be 80 mg/g for ES and 105 mg/g for EB whereas for the industrial wastewater these values were found to be 47 mg/g for ES and 45 mg/g for EB. Zn^{2+} adsorption in the wastewater was found to be lower than in Zn^{2+} spiked solution due to the competition between other cations and/or interference of other ions, mainly Ca^{2+} and Cl^- that were present in the wastewater.

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1. Introduction

Due to the discharge of large amounts of metal-contaminated wastewater, the electroplating industry is one of the most hazardous among the chemical-intensive industries. Inorganic effluent from these industries contains toxic metals such as Cd, Cr, Cu, Hg, Ni, Pb, and Zn, which tend to accumulate in the food chain and they are usually associated with toxicity [1,2].

Zinc is one of the most important metals widely used in electroplating industries and it is an essential element for enzyme activators in humans and its deficiency results in severe health consequences, but it is toxic at levels upper of 100 mg/day [3]. Zinc toxicity has been found in both acute and chronic forms. Toxicity from chronic ingestion of zinc usually occurs as copper deficiency. Intake of zinc ranging from 100 to 150 mg/day interferes with copper metabolism and cause low copper status, reduced iron function, red blood cell microcytosis, neutropenia, reduced immune function, and reduced levels of high-density lipoproteins. Ingest-

ing 200–800 mg/day of zinc can cause abdominal pain, nausea, vomiting, and diarrhea. There are other reported effects including lethargy, anaemia, and dizziness. The Brazilian Federal Legislation [4] established in 2005 that the maximum discharge limit for zinc is 5 mg/L.

There are some important points that should be considered in order to choose the method to recycle the metals in the plating process such as (1) the concentrated solution from the process will be directly treated or diluted, (2) the type of treatment for by-product sludge, and (3) the water recycling.

Treatment processes employed for zinc removal from wastewater normally involve high pH precipitation, but it produces voluminous sludge that must be treated and disposed off normally at higher cost [5]. The adsorption is by far the most versatile and widely used for the removal of different pollutants [6] from water and wastewater. Pereira et al. [7] have studied zinc removal from electroplating wastewater in batch and continuous mode using sugarcane bagasse (MB2) and wood sawdust, *Manilkara* sp., (MS2) modified with succinic anhydride. Removal efficiency in batch mode was higher than 95% when adsorbent concentration was 1.0 g/L and in continuous mode was 65.7% and 57.8% for MB2 and MS2, respectively.

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Lignocellulosic materials are one of the most common adsorbents since they are raw materials available in large quantities that can be by-products of industrial processes [8,9]. Among these materials, sugarcane bagasse [6,7,10–17] and wood sawdust [7,18–20], are attractive options and their use as sorbents may be a benefit to the environment reducing agricultural wastes since they might be converted into cheap adsorbents replacing the traditional synthetic resins [21]. The use of various adsorbents for this purpose has recently been reported by some researchers to remove zinc from aqueous solutions or from wastewater [22–25].

Succinic, maleic, and phthalic are examples of cyclic anhydrides that have been used for surface modification of cellulosic fibers [16,26,27], lignins [28], and/or hemicelluloses [29]. This kind of surface modification introduces carboxylic acid functional groups (–COOH) by esterification reaction, resulting then in an increase of the adsorption capacity of these lignocellulosic materials.

EDTAD is a biodegradable and active agent containing two anhydride groups *per* molecule that can be used to introduce chelating abilities to the lignocellulosic materials through esterification reaction. This reaction allows introducing carboxylic and amine functional groups that present high ability to form stable complexes with heavy metal ions. Carboxylic and amine functional groups are often used as chelating agents with the aim of separating or concentrating metal ions from aqueous solutions [30].

Surface modification with EDTA dianhydride (EDTAD) has recently been reported in the literature [17,30,31]. Introduction of EDTAD on solid support has also been reported by Inoue et al. [31] who aimed to modify chitosan and polyallylamine with EDTAD. These authors have used the new obtained materials to separate metal ions based on the difference in adsorption affinity. Recently Yu et al. [30] modified the biomass of yeast with EDTAD to use it to optimize the adsorption selectivity of some metal ions. In our previous work [17], cellulose and sugarcane bagasse were chemically modified with EDTAD to obtain new lignocellulosic modified materials EC from cellulose and EB from sugarcane bagasse. These materials were used to adsorb Cu(II), Cd(II), and Pb(II) from aqueous single metal solutions.

This present study describes the preparation of a new material from wood sawdust, *Manilkara* sp., and from sugarcane bagasse using ethylenediaminetetraacetic dianhydride (EDTAD) as modifying agent. Experimental procedure used to modify sawdust and sugarcane bagasse was described by Karnitz Júnior et al. [17]. The aim of present study was to evaluate if these modified materials might work as effective sorbents in order to remove zinc(II) from a spiked solution and an electroplating wastewater even with the presence of other ions and competition for sorptive sites. Adsorption studies were developed at different contact times, pHs, and initial cation concentrations. The adsorption isotherms were fitted by Langmuir model [15,16].

2. Materials and methods

2.1. Materials

Sugarcane bagasse was collected at Ouro Preto, Minas Gerais, Brazil. Wood sawdust, *Manilkara* sp., was collected from a sawmill at Belo Horizonte, Minas Gerais, Brazil. EDTA (disodium salt) and acetic anhydride were purchased from SYNTH (Brazil) and used without purification. Pyridine was purchased from VETEC and was refluxed overnight with NaOH and distilled. *N,N*-Dimethylformamide (DMF) was purchased from Tedia and was distilled under reduced pressure before use. ZnSO₄ was purchased from SYNTH (Brazil). Stock Zn²⁺ solution (1000 mg/L) was prepared with ZnSO₄ and distilled water, and all the other Zn²⁺ solutions used in this study were prepared from the stock solution. Grade quantita-

tive filter paper (Cat. No. 1441–150) for instrumental analysis was purchased from Whatman Company.

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

2.2. Adsorbents

2.2.1. Adsorbents pre-treatment

Sugarcane bagasse and wood sawdust were dried at 100 °C in an oven for approximately 24 h and then the material size was reduced to powder by milling with tungsten ring. The resulting material was sieved with a 4-sieve system (20, 32, and 65 mesh), and the fraction from 32 to 65 mesh 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 again in a soxhlet system with *n*-hexane/ethanol (1:1) for 4 h [32].

2.2.2. Adsorbents chemical modification

EDTAD was synthesized according to methodology described by Karnitz Júnior et al. [17]. Sugarcane bagasse (B) or wood sawdust (S) (5 g) was reacted with EDTAD (15.0 g) in anhydrous DMF (210 mL) for 24 h at 75 °C in order to obtain modified sugarcane bagasse (EB) or modified wood sawdust (ES). The modified materials were separated by filtration in sintered glass funnel, washed with DMF, deionized water, saturated sodium bicarbonate solution, deionized water, ethanol 95%, acetone, and then dried in an oven at 80 °C for 1 h. Dried materials were left to cool in a desiccator and the mass percent gains were measured [17].

2.3. Adsorbents characterization

2.3.1. FTIR analysis

The samples were prepared by mixing 1 mg of each material with 100 mg of spectroscopy grade KBr. The FTIR spectra were recorded using Nicolet Impact 410 equipment with detector at 4 cm^{−1} resolution from 500 to 4000 cm^{−1} and 32 scans per sample.

2.3.2. Elemental analysis

The elemental analyses were accomplished using 201 Perkin Elmer Series II CHNS/O Model 2400 analyzer.

2.3.3. Mass percent gain (mpg)

The mass percent gain (mpg) of EB and ES is calculated according to Eq. (1).

$$\%mpg = \frac{M_f - M_i}{M_i} 100 \quad (1)$$

where M_f is the mass of modified material and M_i is the mass of unmodified material.

2.4. Wastewater

2.4.1. Wastewater characterization

An electroplating wastewater is a complex effluent that contains a wide range of metal ions as can be seen from Table 1. Therefore, in order to avoid the interferences in the titration method that are caused by other metal ions the inductively coupled plasma (ICP-OES, Spectro, Ciroc CDD) was used in the characterization of the electroplating wastewater and in the following experiments to determine Zn²⁺ concentration. Chloride ion was determined by Mohr method and its concentration was found to be 7214 mg/L, whilst the anionic surfactants were determined by

Table 1
Wastewater characterization in function of the concentration and percentage of removal for some cations before and after treatment with EB and ES.

Wastewater	Concentration (mg/L)						Removal (%)					
	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 EB	57.40	0.07	22.26	1.41	19.74	4.25	30.0	75.4	0.4	0.2	7.6	90.2
Treatment with ES	45.33	0.08	22.54	1.41	21.19	3.12	44.7	71.2	1.7	0.4	0.8	92.8

the EBAS method according to the Standard Methods [33] and their concentration were found to be 11.9 mg/L.

2.5. Batch sorption studies with (I) spiked solution and (II) real wastewater

2.5.1. Sorption study of spike solution as function of contact time

Experiments with each material were performed to determine the adsorption equilibrium time. The time intervals used were from 10 to 60 min. Amounts of 50.0 mg of EB or ES were placed into a 250-mL Erlenmeyer with 50.0 mL of Zn²⁺ solution of known concentration (200 mg/L) under constant stirring (100 rpm). An adsorbent dose of 50.0 mg was chosen in order to keep the concentration of the adsorbent in the suspension at 1 g/L. The experiments were done at pHs 3.9 for EB and 5.3 for ES. Insignificant pH variations about 0.1 units were noticed during each experiment. The suspensions were separated by single filtration using Whatman quantitative filter paper no. 41 for instrumental analysis and the concentration of Zn²⁺ was determined by direct titration with EDTA (3 mmol/L) at pH 10 using Erichrome Black T as indicator.

2.5.2. Sorption study of spike solution as function of initial pH

Experiments with each material were performed to determine the effect of pH on Zn²⁺ adsorption. Amounts of 50.0 mg for EB and ES were placed into a 250-mL Erlenmeyer with 50.0 mL of metal ion solution of known concentration (200 mg/L) under constant stirring (100 rpm). The pH was adjusted with drops of an aqueous HCl or NaOH solutions (0.01–1.0 mol/L). The pH range studied for EB and ES was from 2.5 to 6.5. The reaction times used were those obtained from study of Zn²⁺ adsorption as function of contact time that was 50 min. for both materials. There were significant pH variations about 0.1–0.5 units during the experiments, but they were being corrected by addition of drops of an aqueous NaOH or HCl solution (0.01–0.1 mol/L). The suspensions were separated by single filtration using Whatman quantitative filter paper no. 41 for instrumental analysis and the metal ion concentration was determined by titration as described in Section 2.5.1.

2.5.3. Sorption study of spike solution as function of initial concentration

Experiments were performed for each material to determine the adsorption isotherms. In each experiment, amounts of 50.0 mg for EB and ES were placed into a 250-mL Erlenmeyer with 50.0 mL of Zn²⁺ solution of known concentrations from 180 to 300 mg/L under constant stirring (100 rpm). Each experiment was performed using an adsorption equilibrium time of 50 min and a pH range of 6.2–6.3, both obtained from Sections 2.5.1 and 2.5.2. There were significant pH variations about 0.1–0.5 units during the experiments, but they were being corrected by addition of drops of an aqueous NaOH or HCl solution (0.01–0.1 mol/L). The suspensions were separated by single filtration using Whatman quantitative filter paper no. 41 for instrumental analysis and the metal ion concentration was determined by titration as described in Section 2.5.1.

2.5.4. Sorption study of real wastewater as function of contact time

Experiments with each material were performed to determine the adsorption equilibrium time. The time intervals used were from 10 to 60 min. Amounts of 50.0 mg of EB or ES were placed into a 250-mL Erlenmeyer with 50.0 mL of wastewater under constant stirring (100 rpm). An adsorbent dose of 50.0 mg was chosen in order to keep the concentration of the adsorbent in the suspension at 1 g/L. The initial wastewater pH (pH 12) was adjusted with concentrated HNO₃ solution before adding the modified materials. The adsorption experiments were done at pH 6.0. No pH corrections were done along the experiments. The suspensions were separated by single filtration using Whatman quantitative filter paper no. 41 for instrumental analysis and the concentration of Zn²⁺ was determined by inductively coupled plasma (ICP-OES, Spectro, Ciroc CDD).

2.5.5. Sorption study of real wastewater as function of initial pH

Experiments with each material were performed to determine the effect of pH on Zn²⁺ adsorption. Amounts of 50.0 mg for EB and ES were placed into a 250-mL Erlenmeyer with 50.0 mL of wastewater under constant stirring (100 rpm). The pH was adjusted with an aqueous HCl or NaOH solution (0.01–1.0 mol/L). The pH range studied for EB and ES was from 2.5 to 6.5. The reaction times used were those obtained from adsorption study of Zn²⁺ as function of contact time that was 50 min for both materials. There were significant pH variations about 0.1–0.5 units during the experiments, but they were being corrected by addition of drops of an aqueous NaOH or HCl solution (0.01–0.1 mol/L). The suspensions were separated by single filtration using Whatman quantitative filter paper no. 41 for instrumental analysis and the concentration of Zn²⁺ was determined by ICP-OES.

2.5.6. Sorption study of real wastewater as function of initial concentration

Experiments were performed for each material to determine the adsorption isotherms. In each experiment, amounts from 0.4 to 1.2 g/L of EB and ES were placed into a 250-mL Erlenmeyer with 50.0 mL of wastewater under constant stirring (100 rpm). Each experiment was performed using a contact time of 50 min and a pH of 6.3, both obtained from Sections 2.5.4 and 2.5.5. There were significant pH variations about 0.1–0.5 units during the experiments, but they were being corrected by addition of drops of an aqueous NaOH or HCl solution (0.01–0.1 mol/L). The suspensions were separated by single filtration using Whatman quantitative filter paper no. 41 for instrumental analysis and the concentration of Zn²⁺ was determined by ICP-OES.

3. Results and discussion

3.1. Adsorbents synthesis and characterization

The synthesis route used to prepare EB and ES and the possible mechanism involved in Zn²⁺ removal are shown in Fig. 1. Sugarcane bagasse or wood sawdust was reacted with EDTAD for 24 h in anhydrous DMF at 75 °C in order to obtain EB and ES, respectively. Reaction between hydroxyl groups of lignocellulosic

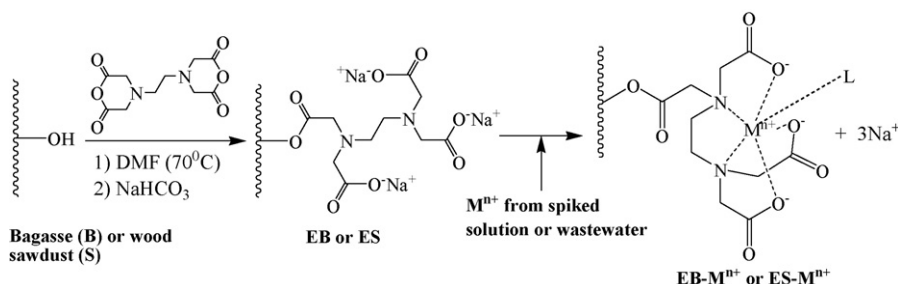


Fig. 1. Synthesis scheme of the modified materials EB and ES and adsorption mechanism of a metal ion onto EB or ES (M^{n+} : metal ion; L: a ligand).

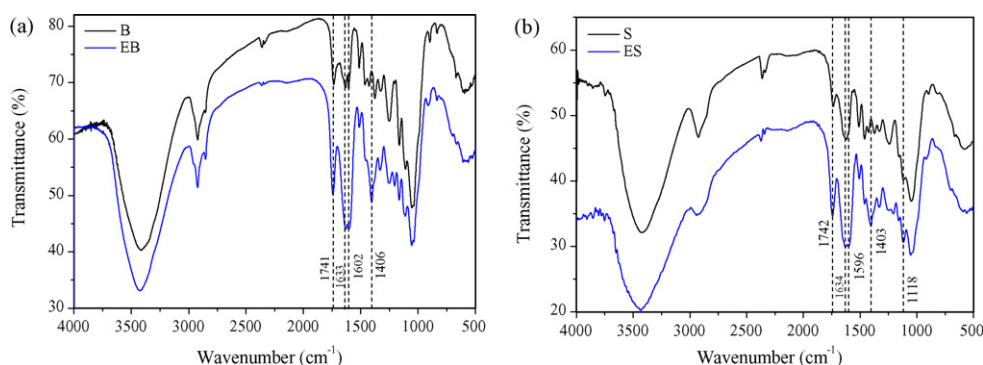


Fig. 2. FTIR spectrum of B and EB (a) and S and ES (b).

materials and anhydride functions of EDTAD allowed the introduction of carboxylic and amine functional groups to the materials through formation of ester linkage. The mass percent gains (mpg) were calculated according to Eq. (1). Both materials were obtained with mass percent gain of 40%.

The characterization of esterified materials was accomplished by FTIR spectroscopy. Fig. 2 shows the FTIR spectra for EB and ES and unmodified starting materials (B: sugarcane bagasse; S: wood sawdust).

As depicted in Fig. 2, the two major changes noticed in FTIR spectra for EB and ES when compared to the unmodified starting materials are (1) the arising of a strong band at 1742 cm⁻¹ for ES and of a strong band at 1741 cm⁻¹ for EB, corresponding to asymmetric and symmetric stretching of ester C–O; (2) the arising of strong bands at 1634, 1596 and 1403 cm⁻¹ for ES and of strong bands at 1633, 1602 and 1406 cm⁻¹ for EB, corresponding to asymmetric and symmetric stretching due to presence of the carboxylate ion, respectively. The ester and carboxylate IR bands indicate that the EDTAD was introduced via formation of the ester bond with consequent releasing of a carboxylic functional group.

The materials B, EB, S, and ES were characterized by elemental analysis in order to analyze nitrogen amount before and after esterification with EDTAD. Table 2 presents the obtained results.

In comparison with B and S, EB and ES showed the appearance of a higher content of nitrogen after the esterification, which could prove the introduction of the EDTAD. Nitrogen content obtained by elemental analysis was used to estimate the quantity of EDTAD that

was added to the B and S after modification. Thus, it was possible to determine the concentration of EDTA moiety into modified materials (C_{EDTA} (mmol/g)). The results are shown in Table 2. EB and ES showed very close values of nitrogen content and concentration of EDTA introduced.

3.2. Batch sorption studies of spike solution

The studies of the adsorption properties of EB and ES were accomplished for each material in aqueous Zn²⁺ solution. Adsorption study as function of contact time was first carried out. The obtained results are shown in Fig. 3. The adsorption equilibrium time was attained in 50 min for both materials, EB and ES. An adsorption equilibrium time of 50 min was chosen for pH and concentration-dependent experiments for both materials.

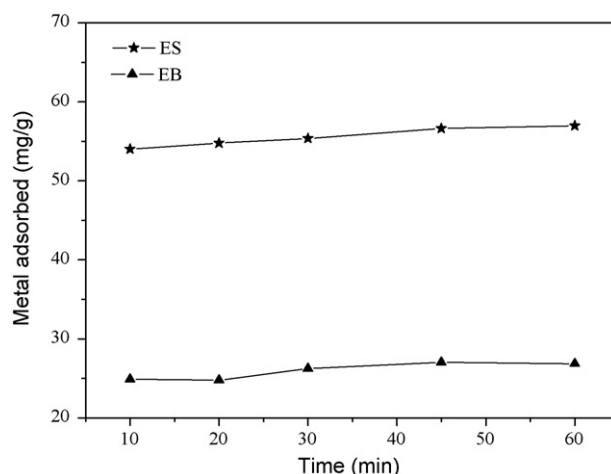


Fig. 3. Adsorption of Zn²⁺ on EB and SB as a function of time.

Table 2
Elemental analysis of the unmodified and esterified materials with EDTA dianhydride and concentrations of EDTA introduced.

Material	C (%)	H (%)	N (%)	C_{EDTA} introduced (mmol/g)
B	43.98	6.02	0.13	–
EB	39.93	4.55	2.32	0.786
S	48.78	7.02	0.30	–
ES	43.97	6.62	2.56	0.807

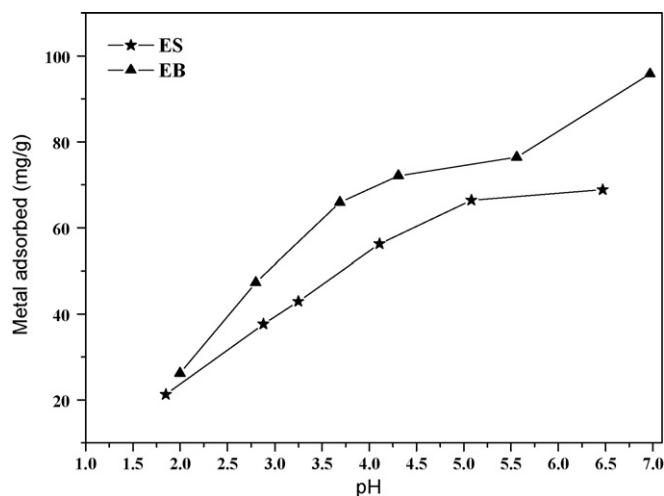


Fig. 4. Adsorption of Zn^{2+} on EB and ES as a function of pH.

The removal of metal ions from aqueous solutions by adsorption is dependent on the pH of the solution since it affects adsorbent surface charge, degree of ionization of the functional groups, and metal ion speciation. Adsorption of Zn^{2+} by EB and ES as function of pH is shown in Fig. 4. The adsorption of Zn^{2+} increases when the pH was increased and reached a maximum at approximately pHs 7.0 and 6.5 for the EB and ES, respectively.

It can be noticed that even at low pH values the adsorption phenomena occurred. This could be attributed to capability of iminodiacetate group to form stable complexes. During the chelation process, zinc ions form a coordinate bond with the electron pair of negatively charged oxygen and unshared electron pair of nitrogen in iminodiacetate which have nitrogen atoms linked to a short chain carboxylic groups. Due to this short chain, inductive effects must have a contribution to decrease the pK_a of both carboxylic groups making possible chelating metal ions at low pHs. The effect of the substituent in the ethylene bridge of EDTA, steric and electrostatic repulsion between acetate groups was widely discussed by Hancock and Martell [34]. Inductive effects and steric hindrance appears to have a great contribution in the complex stability. Similar results were observed in our previous work [17] for the adsorption of Cu^{2+} , Cd^{2+} , and Pb^{2+} in aqueous solutions onto EB. Adsorption at acidic pH condition is a relevant result in relation to the majority of the materials tested in the literature [30].

For a pH range above 7.0 there is the possibility of zinc ions precipitate as hydroxide on the surface of the adsorbent. This explains the greater adsorbed amount on the last point in the adsorption curve as function of pH for EB (Fig. 4), which probably occurred in addition to adsorption mechanism.

A pH range from 6.2 to 6.3 and a contact time of 50 min were chosen to perform the studies in function of initial metal ion concentration and build adsorption isotherms. Adsorption isotherms for EB and ES are shown in Fig. 5. The widely used Langmuir isotherm [35] has found successful application in many real adsorp-

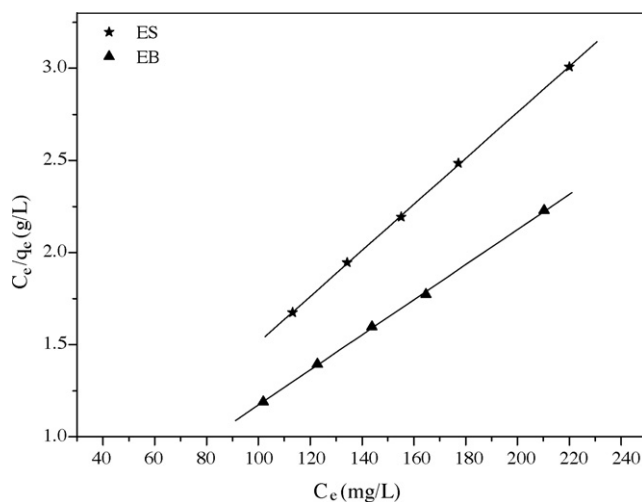


Fig. 5. Langmuir isotherm for adsorption of Zn^{2+} onto EB and ES.

tion processes and it can be expressed as:

$$\frac{C_e}{q_e} = \frac{1}{Q_{\max}b} + \frac{C_e}{Q_{\max}} \quad (2)$$

which can be rearranged to obtain a linear form where q_e (mg/g) is the equilibrium adsorption capacity; Q_{\max} (mg/g) is the maximum amount of metal ion per unit weight of the material needed to form a complete monolayer coverage on the surface bound at high equilibrium metal ion concentration C_e (mg/L); and b (L/mg) is the Langmuir constant related to the binding sites affinity. 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 ion and material [36]. A linearized plot of C_e/q_e versus C_e is obtained from the model as shown in Fig. 5. Q_{\max} and b are computed from the slopes and interceptions of different straight lines. Table 3 shows the calculated results. The high correlation coefficients (Table 3) indicated that the Langmuir model can explain Zn^{2+} 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 noticed from Table 3 that EB showed a greater Zn^{2+} adsorption capacity than ES although EB and ES showed very close values of nitrogen content and concentrations of EDTA introduced. In spite of this, the parameter b indicates that the bond energy of the metal ion complexation with the adsorbent was similar for both materials. This parameter can be used to calculate Gibbs free energy (ΔG°), according to Eq. (3).

$$\Delta G^\circ = -RT \ln b \quad (3)$$

where R is the gas constant (8.3144 J/kmol) and T is the absolute temperature (K). For EB, ΔG° was found to be -19.68 kJ/mol and for ES -19.92 kJ/mol. Negative values of ΔG° obtained for both materials indicated that the process of Zn^{2+} adsorption onto EB and ES

Table 3
Langmuir parameters for Zn^{2+} adsorption onto EB and ES with spiked solution and electroplating wastewater, concentration of EDTA and amount of metal ion adsorbed per EDTA added.

Material	Zn^{2+} source	Q_{\max} (mg/g)	b (L/mg)	R^2	Q_{\max} (mmol/g)	C_{EDTA} introduced (mmol/g)	ΔG° (kJ/mol)	Amount of Zn^{2+} per EDTA added
EB	Spiked	105.26	0.043	0.9995	1.610	0.786	-19.68	2.05
	Wastewater	45.45	0.550	0.9995	0.695		-25.82	
ES	Spiked	80.00	0.047	0.9998	1.223	0.807	-19.92	1.51
	Wastewater	47.39	0.491	0.9998	0.725		-25.71	

is spontaneous and confirmed that there was an affinity between the metal ion and the materials.

EDTA pK_a values are equal to 0, 1.5, 2.0, 2.69, 6.13, and 10.37 [17]. The materials were treated with saturated sodium bicarbonate solution before the sorption experiments in order to release carboxylate and amine functional groups. However, in the pH range from 6.2 to 6.3, the majority of the functional groups are probably protonated. We observed that when the initial concentration of Zn^{2+} increased, the equilibrium pH decreased. This decreasing of pH is consistent with the principles of ion-exchange mechanism since more Zn^{2+} are adsorbed onto EB and ES by interaction with carboxylic and amine functional groups more hydrogen ions are released to the solution, thereby decreasing the pH. Therefore, it is possible that ion-exchange mechanism is the most prevalent mechanism of sorption in spiked solution.

The adsorption results of EB for Zn^{2+} were compared for the same pH range with those results that have been reported in our previous work by Karnitz Júnior et al. [17] for the adsorption of Cu^{2+} . The Q_{max} of EB for Cu^{2+} at pH 5.3 was found to be 1.050 mmol/g. This result showed that EB had shown higher affinity for Zn^{2+} than Cu^{2+} . In another work [7], we have described the use of other modified materials, MB2 (sugarcane bagasse modified with succinic anhydride) and MS2 (wood sawdust modified with succinic anhydride), for the adsorption of Zn^{2+} from aqueous solutions. The Q_{max} of MB2 and MS2 for Zn^{2+} were found to be 125.0 and 144.9 mg/g, respectively. These materials showed higher adsorption capacities than EB and ES at pH between 6.2 and 6.3, but their adsorption capacities at pH below 3 were very lower than EB and ES.

3.3. Batch sorption studies of electroplating wastewater

The adsorption studies were accomplished for real electroplating wastewater and each material. The study was performed in batch to evaluate the efficiency of Zn^{2+} removal as function of con-

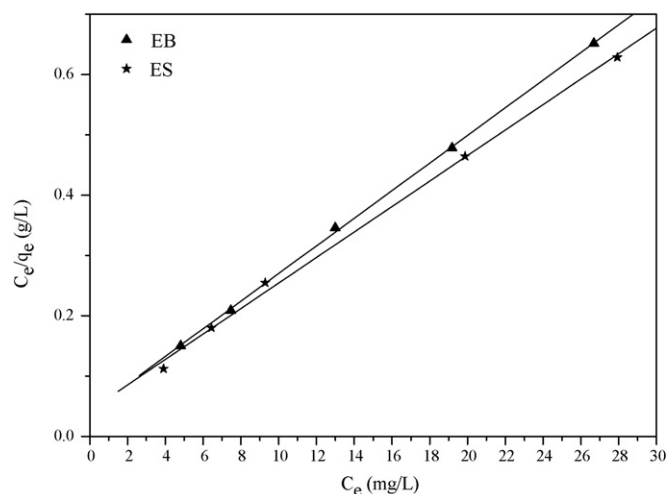


Fig. 7. Langmuir isotherm for Zn^{2+} adsorption in the electroplating wastewater.

tact time, pH, and concentration of the adsorbent (Fig. 6). After 50 min, the adsorption equilibrium time was achieved for both materials, EB and ES. For a pH between 6 and 7, there was removal efficiency greater than 80%. As it was noticed for the adsorption in spiked solution that even at low pH values the adsorption of Zn^{2+} occurred. At pH 2, the removal efficiency was around 20%. This is a relevant result to treat another acidic effluent containing Zn^{2+} since electroplating wastewater containing Zn^{2+} had an initial wastewater pH equal to 12 in relation to the majority of the materials tested in the literature [30]. For an adsorbent concentration (C_{ad}) of 1.2 g/L in the wastewater, it was possible to obtain an adsorption efficiency of 92% for ES and of 89% for EB. These results showed that even with the presence of other metallic ions these materials exhibited a very good efficiency for Zn^{2+} removal.

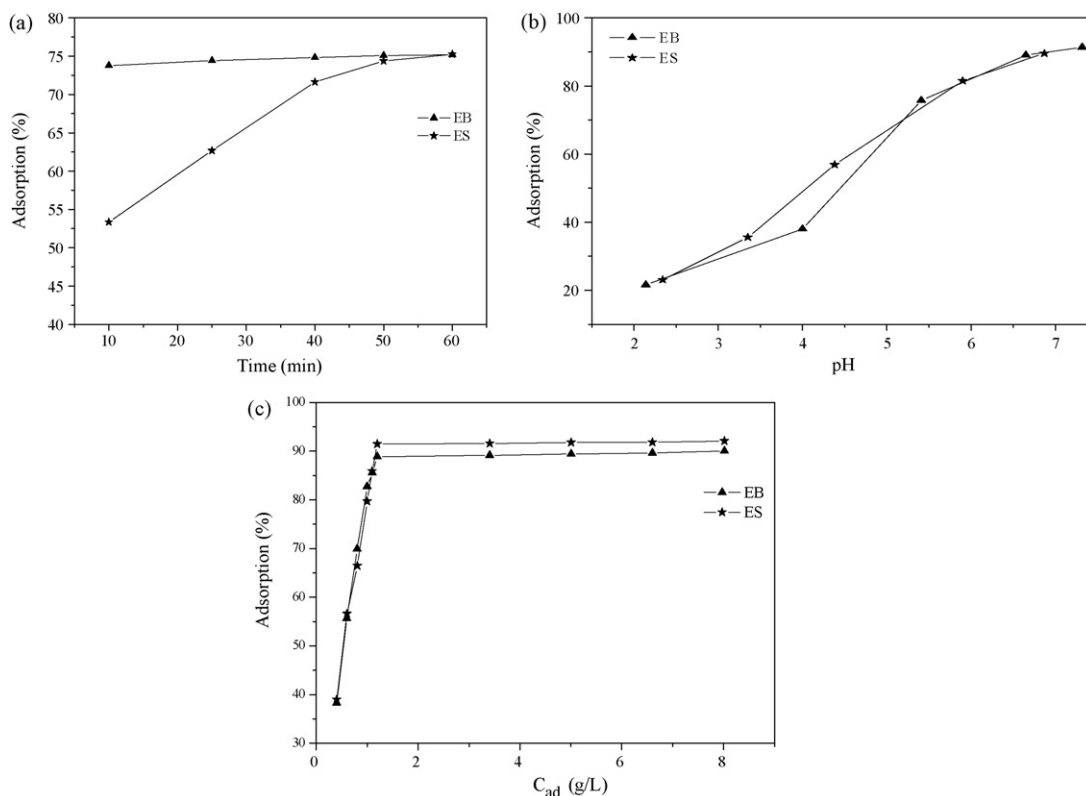


Fig. 6. Adsorption of Zn^{2+} on EB and ES as a function of time (a), pH (b) and concentration of adsorbent (c) with real electroplating wastewater.

The sorption study as function of initial concentration was carried out keeping the pH between 6.3 and 6.5 and a contact time of 50 min. Adsorption isotherms (Fig. 7) were studied by Langmuir model and the Langmuir parameters are shown in Table 3. The high correlation coefficients (Table 3) obtained from the Langmuir model indicated that this model can explain Zn^{2+} adsorption in real wastewater by the modified materials very well.

It can be noticed from Table 3 that the Zn^{2+} adsorption capacity was approximately equal for both materials, ES and EB, which disagreed with the obtained results that are shown in Table 3. The difference that was found between the sorbed amount of Zn^{2+} for these materials in the electroplating wastewater and in Zn^{2+} spiked solution (Table 3) was probably due to the different composition of the solutions. In the electroplating wastewater occurred the effect of ionic interaction. It was possible that this effect affected the adsorption capacity of the materials with the same magnitude making the sites available for zinc adsorption approximately equal.

It can be noticed that the Q_{max} values for adsorption of Zn^{2+} in real wastewater showed in Table 3 are nearly half of the obtained values for adsorption of Zn^{2+} in spiked solution. These results confirmed that other metallic species in the electroplating wastewater competed for the binding sites of the modified materials EB and ES, thereby decreasing the amount of Zn^{2+} sorbed.

The parameter b was higher for EB, which means that the zinc ions had more affinity for EB than ES. The Gibbs free energy (ΔG°) was calculated and it was found to be -25.82 kJ/mol for EB and -25.71 kJ/mol for ES. These results showed that the process of Zn^{2+} adsorption in the wastewater was spontaneous confirming that there was a high affinity between Zn^{2+} ions and ligand sites of EB and ES. The fact that higher b values were obtained with a complex effluent when compared to spiked 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.

The adsorption results of EB for Zn^{2+} in the electroplating wastewater were compared with those that have been reported in our previous work by Pereira et al. [7] for the adsorption of Zn^{2+} in the same electroplating wastewater using another modified materials MB2 and MS2. The Q_{max} of MB2 and MS2 for Zn^{2+} were found to be 54.64 and 60.98 mg/g, respectively. These materials showed higher adsorption capacities than EB and ES.

3.4. Interference of other ions

Adsorption in multi-component systems is complicated due to the fact that many solute–surface interactions are involved. The effect of ionic interaction [24] in the adsorption process may be represented by the ratio of the adsorption capacity for one metal ion in the presence of other ions, Q_{mix} ; to the adsorption capacity for the same metal ion when it is present alone in the solution, Q_0 ; Then, if:

- I. $Q_{mix}/Q_0 > 1$ the adsorption is promoted by the presence of other ions.
- II. $Q_{mix}/Q_0 = 1$ there is no observable net interaction.
- III. $Q_{mix}/Q_0 < 1$ the adsorption is suppressed by the presence of other ions.

The values of Q_{mix} and Q_0 were found to be 45.45 and 105.26 mg/g for EB and 47.39 and 80.00 mg/L for ES. The value of Q_{mix}/Q_0 was found to be 0.43 and 0.59 for EB and ES, respectively. The results of Q_{max} obtained from adsorption isotherm of Zn^{2+} in single aqueous solution are considered here as Q_0 due to the absence of other ions, whilst the results of Q_{max} obtained from adsorption isotherm of Zn^{2+} in wastewater are considered as Q_{mix} due to the presence of several different ions. The calculated values

of Q_{mix}/Q_0 for both materials were lower than 1 as mentioned earlier. These results confirmed that Zn^{2+} adsorption was suppressed by other ions in the electroplating wastewater, thereby reducing its adsorption capacity.

The effect of other cations on Zn^{2+} adsorption behavior in the wastewater was studied under the best conditions obtained, i.e., pH range from 6 to 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 is presented in Table 1.

According to the obtained results, we noticed that there was interference of other metal cations on Zn^{2+} adsorption, but in spite of the competition, the effect on Zn^{2+} adsorption was minimal. Although the concentration of Ca^{2+} (82.00 mg/L) exceeded the concentration of Zn^{2+} (43.24 mg/L) in the wastewater. It can be seen from Table 1 that the removal efficiency for Zn^{2+} was higher than 90%, whilst for Ca^{2+} the removal efficiency was only about 30–45% for both modified materials. The other cations also interfered on Zn^{2+} adsorption, but their concentration and their removal were lower than the Zn^{2+} concentration and removal in the wastewater. Therefore, it seems that adsorbent materials showed preferential adsorption for the Zn^{2+} when the electroplating wastewater was treated under the conditions used in this study. Similar results were also reported by Pereira et al. [7] when MB2 and MS2 were used as sorbents. Some anions such as Cl^- , SO_4^{2-} , and CN^- have affinity for metal ions forming insoluble or soluble complexes [37]. It is possible that chloride ions formed stable complexes with Zn^{2+} , thus suppressing Zn^{2+} and/or $Zn(OH)^+$ adsorption by the adsorbents. The presence of anionic surfactants might also have influenced the sorption of zinc ions by binding that keep them in solution. The concentration of chloride ions and surfactants in the electroplating wastewater was found to be 7214.0 and 11.9 mg/L, respectively.

In these experimental conditions it was observed that zinc ions might have been sorbed by ion-exchange and surface adsorption mechanisms. According to the obtained results from batch sorption studies with electroplating wastewater, ion-exchange seemed to be the prevalent mechanism. The stability constant ($\log K$) for Zn^{2+} in presence of chloride ions or anionic surfactants must have been high enough to form stable complex and thus changing Zn^{2+} adsorption behavior of adsorbent materials. The ionic strength of the medium was also one of the factors that affected the availability of the metal ion, and might have contributed to the lower Q_{max} values of Zn^{2+} adsorption in the electroplating wastewater. Nevertheless, the modified adsorbents (EB and ES) are still selective for the Zn^{2+} .

4. Conclusions

The chemical modification of the lignocellulosic materials sugarcane bagasse (B) and wood sawdust (S) with EDTA dianhydride was confirmed by infrared spectroscopy, elemental analysis, and mass percent gain. The Zn^{2+} adsorption studies with the obtained adsorbents EB and ES were successfully performed in spiked solution and in real wastewater from a zinc electroplating line.

Sorption studies as function of contact time showed that the adsorption equilibrium time was attained in 50 min for all materials studied. The adsorption data showed that an increase in pH improved Zn^{2+} adsorption for all systems, and that Langmuir model explained the adsorption of Zn^{2+} for all materials very well. The calculated Zn^{2+} adsorption capacities were found to be 80 mg/g for ES and 105 mg/g for EB in single metal ion solution, whilst for the industrial wastewater these values were found to be 47 mg/g for ES and 45 mg/g for EB. These results indicated that other ions present in the industrial wastewater competed with Zn^{2+} for the adsorbent binding sites.

The adsorption capacity decreased when the Zn^{2+} was adsorbed in systems where there was a competition with other cations or interference of other ions as it happened when Zn^{2+} adsorption was studied with electroplating wastewater. In this study we noticed this influence, mainly due to the presence of Ca^{2+} and Cl^- in wastewater. Then, Zn^{2+} adsorption in wastewater was lower than in single metal ion solution, although it was possible to obtain a removal of Zn^{2+} around 90%, showing that the adsorbent materials were selective for the Zn^{2+} ions.

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