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Removal of Ca(II) and Mg(II) from aqueous single metal solutions by mercerized cellulose and mercerized sugarcane bagasse grafted with EDTA dianhydride (EDTAD)

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ABSTRACT

In a previous work, chemically modified cellulose (EMC) and sugarcane bagasse (EMMB) were prepared from mercerized cellulose (MC) and twice-mercerized sugarcane bagasse (MMB) using ethylenediaminetetraacetic dianhydride (EDTAD) as modifying agent. In this work we described in detail the modification of these materials in function of reaction time and EDTAD amount in the reaction media. The resistance of ester bond at pH 1, 2, 11, and 12 was also evaluated by FTIR. The results were used to model the hydrolysis process and a kinetic model was proposed. The modified materials (EMMB and EMC) were used to adsorb Ca^{2+} and Mg^{2+} ions from aqueous single solutions. The adsorption isotherms were developed at two pH values. These materials showed maximum adsorption capacities for Ca^{2+} and Mg^{2+} ions ranging from 15.6 to 54.1 mg/g and 13.5 to 42.6 mg/g, respectively. The modified material from sugarcane bagasse (EMMB) showed larger maximum adsorption capacities than modified material from cellulose (EMC) for both metals.

1. Introduction

The hardness in water represents the contents of divalent ions such as iron, manganese, calcium, and magnesium. However, calcium and magnesium are the most common sources of water hardness (Park, Song, Yeon, & Moon, 2007). According to Bekri-Abbes, Bayoudh, and Baklouti (2008) water slightly, moderately hard and hard contains about 17–60, 60–120, and 120–180 mg/L of Ca^{2+} or Mg^{2+}, respectively. Removal of hardness from water is a treatment or pretreatment practiced in a wide variety of installations including chemical industries, power plants, laundries, individual households, and drinking water treatment plants. Many industrial unit operations and unit processes require near-complete removal of hardness to avoid scaling in heat-transfer equipment, fouling in membranes, and high consumption of detergents and sequestering chemical in cooling and washing water. Therefore, removal of hardness from water is of relevance to produce or treat water in order to eliminate or decrease problems associate with water hardness (Christa & Thomas, 2009; Greenleaf & Sengupta, 2006; Park et al., 2007; Wiśniewski & Różańska, 2007).

Line softening and cation exchange are the most commonly used processes practiced to date for hardness removal. While line softening produces voluminous sludge to be disposed, ion-exchange processes may generate concentrated brine or mineral acid as a waste regenerant stream. Residual management will continue to be a major concern with these processes. One major shortcoming of an ion-exchange-type separation process is the use of aggressive chemicals such as acid, salt, or alkali as regenerants and consequent difficulties in disposing of these waste regenerant streams (Greenleaf & Sengupta, 2006). However, the main advantages of ion exchange over other techniques are the simplicity of operation which makes it attractive to the chemical purification field, the recovery of the cations, high selectivity, production of less sludge (Park et al., 2007; Yu, Qi, Qu, Wang, & Chu, 2009).

Since 1990's the adsorption of metal ions by low-cost renewable organic materials has gained momentum. The utilization of biomass and agricultural waste materials for removal of metal ions has been explored. Recently attention has been diverted towards the biomaterials which are byproducts or the wastes from large scale industrial operation such as sugarcane bagasse (Sud, Mahajan, & Kaur, 2008). According to the last official survey from CONAB, an agency from the Brazilian Ministry of Agriculture, the national production of sugarcane in 2008/2009 was 558 million tons (Gurgel, de Freitas, & Gil, 2008a; Karnitz, Gurgel, de Freitas, & Gil, 2009). Sugarcane bagasse has around 50% cellulose, 27% polyoses, and 23% lignin (Caraschi, Campana, & Curvelo, 1996). Cellulose and polyoses have primary and secondary hydroxyl groups, and lignin has hydroxyl phenolic groups that can be used to attach functional groups with a particularly high selectivity for Ca^{2+} and Mg^{2+} adsorption.

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In recent decades, many researchers around the world have examined the modification of low-cost materials, and there are many studies in the literature that report versatile chemical transformations of cellulose (Gellerested & Gatenholm, 1999; Gurnani, Singh, & Venkataramani, 2003). However, there have been very few works on modification of sugarcane bagasse (Gupta & Ali, 2000; Gupta & Ali, 2004; Gurgel et al., 2008a; Hassan & El-Wakil, 2003; Ibrahim, Hanafiah, & Yahya, 2006; Karnitz et al., 2007; Karnitz et al., 2009; Krishnan & Anirudhan, 2002; Nada & Hassan, 2006). In this context, ethylenediamine-*N*,*N*,*N*′,*N*′-tetraacetic acid (EDTA) is a powerful complexing agent. Formation constants (log *K*) for Ca^{2+} and Mg^{2+} complexes with EDTA are 11 and 8.64 (Dean, 1999). Anhydride of ethylenediamine-*N*,*N*,*N*′,*N*′-tetraacetic acid (EDTAD), an active agent containing two anhydride groups per molecule, can react with hydroxyl groups of cellulose, hemicelluloses or lignin molecules in order to release chelating groups on solid support as carboxylic acid and amino group. The use of EDTA dianhydride (EDTAD) to modify biomass has been reported twice in the literature (Karnitz et al., 2009; Yu, Tong, Sun, & Li, 2008).

The present paper discusses the possible use of mercerized cellulose and sugarcane bagasse chemically modified with EDTAD for hardness removal. The preparation of the modified mercerized materials used to adsorbed metal ions was first described in our previous work (Karnitz et al., 2009). In order to optimize and improve the synthesis yield, the modification of the materials was evaluated in function of reaction time and amount of EDTAD in the reaction media. The resistance of ester linkage of the modified materials, EMMB from twice-mercerized sugarcane bagasse and EMC from mercerized cellulose, was evaluated in detail on both acidic and alkaline pHs. EMMB and EMC were used to adsorb Ca^{2+} and Mg^{2+} from aqueous single solutions. Studies were developed using different contact times, pHs, and initial cations concentration. The adsorption isotherms were developed at two pH values for both cations. The obtained data were analyzed by Langmuir model (Gurgel et al., 2008a; Gurgel, Karnitz, Gil, & Gil, 2008b; Karnitz et al., 2007).

2. Experimental procedure

2.1. Materials

Grade 3MM Chr cellulose chromatography paper (Cat. No. 3030-861) was purchased from Whatman Company, Maidstone, England. EDTA (disodium salt), acetic anhydride, $CaCl_2$ and $MgSO_4{\cdot}7H_2O$ were purchased from Synth (Brazil). EDTA and acetic anhydride were used without purification. Pyridine was refluxed overnight with NaOH and distilled. *N*,*N*′-Dimethylformamide (DMF) was purchased from Tedia and it was distilled under reduced pressure before use.

2.2. Synthesis of EMMB and EMC

The study of the synthesis of EMMB was carried out in two steps as followed. These steps aimed to improve synthesis yield. Mercerization step and preparation of sugarcane bagasse and cellulose were made as described by Karnitz et al. (2009).

Step 1: Effect of modification time, 500 mg of MMB and 2.5 g (9.76 mmol) of EDTAD were added in a round-bottomed flask containing 35 mL of anhydrous DMF. A reflux condenser was attached to flask. The suspension was shaken and heated up 75 °C for 24 h. The same procedure was carried out for reaction times of 6, 12, and 48 h. The modified materials were elaborated by filtration using sintered glass funnels, washed in a row with DMF, distilled water, saturated sodium bicarbonate solution (in order to release carboxylate and amine functions), distilled water, and then with ethanol 95%. The modified materials were dried in an oven at 80 °C for 1 h and stored in a desiccator. After cooling, the mass percent gains were calculated.

Step 2: Effect of EDTAD amount, 500 mg of MMB and 0.250 g (0.976 mmol) of EDTAD were suspended in 4 mL of anhydrous DMF. The suspension was shaken and heated at 75 °C for 24 h. The same procedure was carried out for EDTAD amounts of 0.5, 0.75, 1.0, 1.5, and 2.5 g (1.95, 2.93, 3.90, 5.85, and 9.76 mmol, respectively) using 8, 12, 16, 24, and 40 mL of DMF in order to keep the anhydride/solvent ratio. After modification the materials were treated as described above. The mass percent gains were also calculated.

The modification of MC with EDTAD was carried out using the best results obtained from study of the synthesis of EMMB. Mass percent gain was also calculated.

2.3. Characterization of EMMB and EMC

2.3.1. Mass percent gain

Mass percent gains were calculated according to Eq. (1).

$$\mathrm{Mpg}(\%) = \left(\frac{m_{\mathrm{modified}} - m_{\mathrm{unmodified}}}{m_{\mathrm{unmodified}}}\right) \times 100 \quad (1)$$

where m_{modified} and $m_{\mathrm{unmodified}}$ are the masses (g) of modified and unmodified materials respectively.

2.3.2. FTIR spectroscopy and elemental analysis

Modified materials (EMMB and EMC) obtained from 24 h of reaction and 1.5 g of EDTAD amount were chosen for characterization. Samples were previously dried at 80 °C in an oven and left to cool in a desiccator. Samples of 1 mg of EMMB or EMC were mixed with 100 mg of spectroscopy grade KBr. FTIR spectra were recorded by Nicolet Impact 410 FTIR spectrometer with detector at 4 cm^{-1} resolution from 500 to 4000 cm^{-1}. The spectra were analyzed by Microcal™ Origin™ 8.0 software in order to characterize the main bands after modification.

Samples were analyzed by CHNS Perkin Elmer Series II equipment. The analyses were accomplished in duplicate for each sample.

2.3.3. Hydrolysis study of ester bond

A study of hydrolysis of ester bond in function of time at pH 1, 2, 11, and 12 was carried out. Three samples of EMMB (250 mg) were added to 250-mL Erlenmeyer flasks with 100.0 mL of aqueous HCl or NaOH standard solution. The mixtures were shaken for 1, 4, and 24 h at 25 °C. After the experiments, the mixtures were separated by single filtration, washed with deionized water, saturated sodium bicarbonate solution, deionized water, and then ethanol 95%. The materials were dried in an oven at 80 °C for 1 h and left to cool in a desiccator. The hydrolysis of the ester bond was evaluated by FTIR spectroscopy. In order to quantify the hydrolysis, experiments FTIR spectra were deconvoluted using Microcal™ Origin™ 8.0 software and the band at 1743 cm^{-1} was isolated by assuming that it has a Gaussian profile. The deconvolution procedure was carried out as follows: (1) the spectral region from 1500 to 2000 cm^{-1} was chosen and isolated; (2) A baseline was created considering this interval; (3) The band at 1743 cm^{-1} was fitted assuming Gaussian profile; (4) Finally, the integrated areas were computed and plotted in function of hydrolysis time. Integrated areas are related to the concentration of the ester bond and, therefore, a semi-quantitative study can be performed (Velasco, Rubio, Rubio, & Oteo, 1999).

2.4. Adsorption study of Ca^{2+} and Mg^{2+} onto EMMB and EMC

The studies of the adsorption properties of EMMB and EMC were first carried out varying the contact time and pH. The best results obtained from each study were used to evaluate the effect of initial cations concentration. In order to evaluate the capacity of EMMB and EMC to adsorb cations from acidic or basic pH, adsorption isotherms were developed at two pH levels.

2.4.1. Adsorption study of Ca^{2+} and Mg^{2+} onto EMMB and EMC in function of contact time

Adsorption experiments of Ca^{2+} and Mg^{2+} onto EMMB and EMC were performed to determine the adsorption equilibrium time. The time intervals used were from 10 to 50 min. Samples of 50 mg of EMMB or EMC were added into a 250-mL Erlenmeyer containing 50.0 mL of cation solution of known concentration (85 and 75 mg/L for Ca^{2+} and 90 mg/L for Mg^{2+} for EMMB and EMC, respectively). The pH of the suspensions was adjusted up to 10 by adding up drops of NaOH or HCl solution (0.1–5.0 mol/L). The Erlenmeyer flasks were kept under constant stirring. The pH of the mixtures were strictly controlled during the experiments. Variations about 0.1 units of pH were found in relation to pH values initially adjusted. These variations were corrected by adding up acid or base solution. The equilibrium concentration of cations was determined after single filtration (Whatman quantitative filter paper No. 41) by atomic absorption spectroscopy using air-acetylene flame (atomic absorption spectrophotometer model VARIAN SpectrAA 200). The cation amount adsorbed per gram of EMMB or EMC was calculated as demonstrated by Eq. (2):

$$q = \frac{(C_i - C_f) \times V}{m_{ads}} \quad (2)$$

where q (mg/g) represents the amount of adsorbed cation, C_i and C_f (mg/L) are the cation concentrations at time zero and t, V (L) is the volume of cation solution, and m_{ads} (g) is the adsorbent mass.

2.4.2. Adsorption study of Ca^{2+} and Mg^{2+} onto EMMB and EMC in function of solution pH

Adsorption experiments of Ca^{2+} and Mg^{2+} onto EMMB and EMC were carried out to determine the influence of solution pH on the adsorption process. Samples of 50 mg of EMMB or EMC were added into 250-mL Erlenmeyers containing 50.0 mL of cation solution of known concentration (75 and 100 mg/L for Ca^{2+} and 90 mg/L for Mg^{2+} for EMMB and EMC, respectively). Solubility product constants (Ksp) of calcium and magnesium divalent (6.5×10^{-6} and 7.1×10^{-12}) (Harvey, 2000) were taken into account to calculate the pH range where these cations may not occur as hydrolyzed species, which may interfere in the adsorption process. The reaction time used was 10 min for EMMB and EMC (obtained from the Section 2.4.1). The pH range used was from 1.8 to 10.3 for Ca^{2+} and from 2.6 to 8.7 for Mg^{2+}. The pH was adjusted and controlled during the experiments as described in the Section 2.4.1. At the end of the experiments, the equilibrium pH values were taken into account. The cation equilibrium concentration was determined after single filtration by atomic absorption spectroscopy as also described in the Section 2.4.1.

2.4.3. Effect of initial cation concentration and adsorption isotherms

The effect of initial cation concentration on the adsorption process was evaluated to determine adsorption isotherms. Samples of 50 mg of EMMB or EMC were added into 250-mL Erlenmeyer flasks containing 50.0 mL of cation solution of known concentration ranging from 30 to 75 mg/L for Ca^{2+} and from 10 to 60 mg/L for Mg^{2+} for EMMB and EMC, respectively. The reaction time used was 10 min (obtained from the Section 2.4.1). The experiments were performed at two pH levels, 5.5 and 10 for Ca^{2+} and 5.5 and 9.0 for Mg^{2+}. The solutions pH were adjusted and controlled as described in the Section 2.4.1. After single filtration, the equilibrium cation concentration was also determined by atomic absorption spectroscopy.

2.5. Gibbs free energy

According to Liu (2006), Gibbs free energy (ΔG°) for an adsorbent with relatively low adsorption capacity to adsorbate can be calculated as defined by Eq. (3):

$$\Delta G^{\circ} = -RT * Ln\ K \quad (3)$$

where R is the gas constant 8.3144 J/K mol, T (K) is the temperature, and K (L/mol) is the equilibrium constant.

2.6. Separation factor (R_L)

The essential characteristic of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L, which is defined by Eq. (4) (Rao, Ramesh, Rao, & Seshaiah, 2006):

$$R_L = \frac{1}{(1 + bC_0)} \quad (4)$$

where b (L/mg) is the Langmuir constant and C_0 (mg/L) is the initial concentration of Ca^{2+} or Mg^{2+}. The R_L value indicates the shape of the isotherm as follows.

According to Mckay, Blair, and Gardner (1982), R_L values may be between 0 and 1, larger than or equal 1, and or equal to zero. These values indicate that the adsorption isotherm is favorable, unfavorable, linear, and irreversible, respectively.

3. Results and discussion

3.1. Synthesis and characterization of EMMB and EMC

Fig. 1 illustrates the synthesis route used to prepare EMMB and EMC and a suggested mechanism for Ca^{2+} or Mg^{2+} adsorption onto EMMB or EMC. The synthesis of EMMB was made in two steps. In the first step the effect of modification time was evaluated. The aim of this study was to determine the minimum reaction time necessary to introduce the largest amount of EDTAD into MMB. For this, time intervals of 6, 12, 24, and 48 h were used. The mass percent gains were calculated and used to evaluate the synthesis yield. The obtained results are shown in Table 1 and Fig. 2. As can be seen from Table 1 and Fig. 2, the largest mass percent gain (45.1%) was obtained when MMB was reacted with EDTAD for 24 h. Between 24 and 48 h a mass percent loss was noticed. This small mass percent loss may have occurred due to crosslink reaction involving the second anhydride function of EDTAD and non-esterified hydroxyl groups from MMB.

In a second step the effect of EDTAD amount was evaluated. The reaction time of 24 h was adopted. This study aimed to verify the minimum amount of EDTAD necessary to obtain the largest mass percent gain. In order to perform this study, EDTAD amounts of 0.25, 0.5, 0.75, 1.0, 1.5, and 2.5 g were chosen. The EDTAD/solvent ratio was kept as can be seen from the Section 2.2. The EDTAD/solvent ratio is a very important variable and its variation may affect the synthesis yield. The mass percent gains were also calculated and used to evaluate the synthesis yield. The obtained results can be seen in Table 1 and Fig. 2. As can be seen from Table 1 and Fig. 2, the mass percent gain reached a plateau when at least 1.5 g of EDTAD are used in the modification of MMB. In this reaction conditions the mpg was found to be 44.1%. Then, this amount was considered as being the best amount of EDTAD to introduce the largest functionality to MMB.

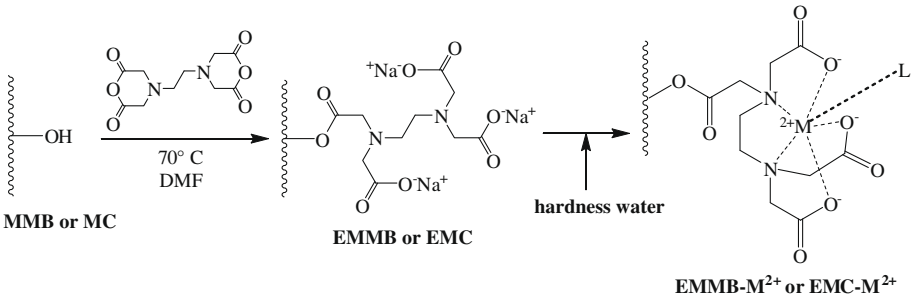

Fig. 1. Synthesis scheme of EMMB or EMC and adsorption mechanism of metal ion on EMMB or EMC (M^{2+}, Ca^{2+} or Mg^{2+}; L, ligand).

Table 1
Data from the modification of MMB and MC with EDTAD in function of time and anhydride amount.

Synthesized material	Reaction time (h)	EDTAD (g)	Mpg (%)
EMMB	6	2.5	24.2
	12		39.9
	24		45.1
	48		42.8
	24	0.25	39.0
		0.5	42.9
		0.75	44.3
		1.0	44.8
		1.5	45.1
		2.5	45.1
EMC	24	1.5	22.8

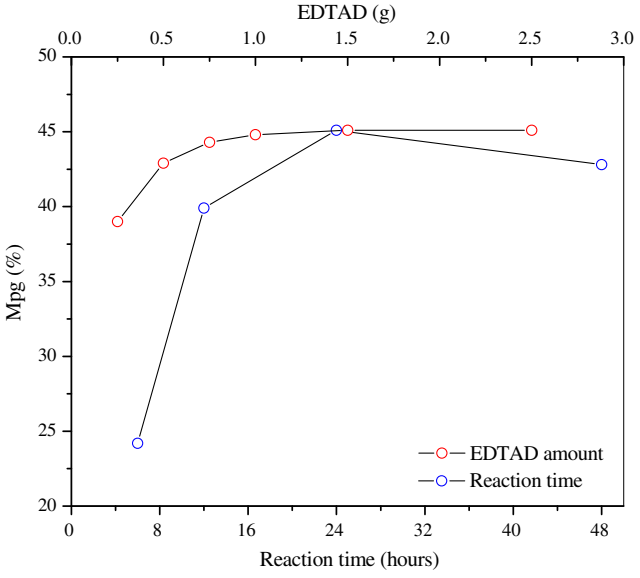

Fig. 2. Modification of MMB with EDTAD as a function of reaction time and EDTAD amount.

Elemental analysis was made for the best obtained material, EMMB, which showed nitrogen content of 3.09%. Nitrogen content was used to estimate the EDTAD amount introduced into MMB. This calculus demonstrated that 1.04 mmol of EDTAD were introduced per gram of MMB. These optimized conditions (24 h of reaction and 1.5 g of anhydride) were also used to introduce EDTAD into MC. EMC was obtained with a mass percent gain of 28.2% and nitrogen content of 1.78%. The amount of EDTAD introduced into EMC was found to be 0.636 mmol/g. The characterization of MMB and EMMB, and MC and EMC by FTIR was made and discussed in our previous work (Karnitz et al., 2009).

Therefore, these studies allowed economizing EDTAD and this way optimizing the synthesis conditions.

3.2. Hydrolysis study of ester bond

The reaction of EDTAD with hydroxyl groups from cellulose or sugarcane bagasse produces an ester bond. It is well known that the rate of hydrolysis of cellulose esters in aqueous solution is controlled by the temperature and pH (Olaru, Andriescu, & Olaru, 2001). In order to determine the resistance of the ester bonds of the modified materials with EDTAD in aqueous solution, a hydrolysis study of ester bond of EMMB in function of time was carried out at pH 1, 2, 11, and 12 at 25 °C. FTIR spectra were deconvoluted in the corresponding isolated IR band (1743 cm^{-1}) by assuming that it has a Gaussian profile. The Gaussian area of the band at 1743 cm^{-1}, which represents ester linkage, was calculated to quantify the hydrolysis. The integrated area was plotted against hydrolysis time for pH values at 1, 2, 11, and 12. Fig. 3 shows the FTIR spectra recorded for the hydrolysis experiments at pH 1, 2, 11, and 12 and Fig. 4 shows the evolution of the deconvoluted IR band (1743 cm^{-1}) with respect to hydrolysis time and pH.

3.2.1. Pseudo-first-order kinetic model

Experimental data from hydrolysis study of ester bond was evaluated using pseudo-first-order kinetic model. In order to model the hydrolysis process, the following assumptions must be introduced:

(1) Integrated Gaussian areas (A) must be proportional to the concentration of hydrolysable ester bonds [—O—C=O] in EMMB.
(2) Acid and basic hydrolysis reactions occur in heterogeneous phase.
(3) EMMB is easily dispersed in acid or basic aqueous solution, and therefore, the mass transfer limitation during hydrolysis was not considered.

$$-\frac{d[\text{—O—C=O}]}{dt} = -\frac{dA}{dt} = k * A \tag{5}$$

where k (h^{-1}) is the reaction rate constant for the irreversible pseudo-heterogeneous-first-order reaction and A (a.u.) is the integrated Gaussian area, which is proportional to concentration of ester bonds. Integration of Eq. (5) gives:

$$A_t = A_0 * e^{(-k*t)} + C \tag{6}$$

where A_t and A_0 are the integrated Gaussian areas (a.u.) at time t and zero, k is the pseudo-first-order rate constant (h^{-1}), t is the hydrolysis time (h), and C is an integration constant.

The hydrolyzed amount of ester bond for different contact times and pH values, non-linear regression parameters for pseudo-first-

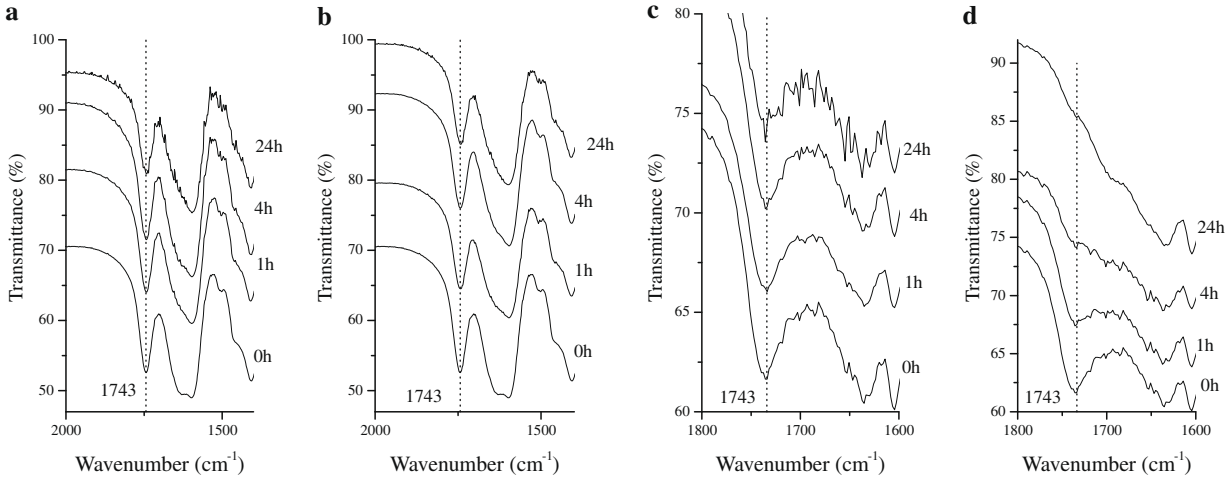

Fig. 3. FTIR spectra of EMMB hydrolyzed in different contact times at (a) pH 1, (b) pH 2, (c) pH 11, and pH 12.

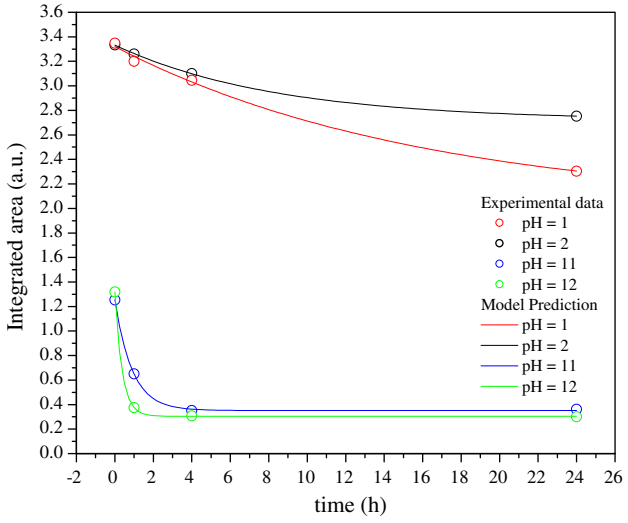

Fig. 4. Integrated areas for 1743 cm^{-1} band as a function of hydrolysis time for EMMB at different pH values.

order kinetic model as well as correlation coefficients for the adjusted model are shown in Table 2.

As can be seen from Table 2, the high correlation coefficients values indicated that the hydrolysis of ester bond of EMMB obeyed a pseudo-first-order kinetic model. In acidic pH values, EMMB showed a good resistance against hydrolysis up to 4 h. After 4 h EMMB suffered considerable degradation mainly at pH 1. In basic pH values, the hydrolysis of ester bond was found to be faster than acidic pH values and after 4 h the basic hydrolysis reached larger percentages than acid hydrolysis. These results indicated that EMMB showed a reasonable stability in acidic pH, mainly at shorter times, and began to suffer larger degradation at basic pH.

The value of the rate constant for ester hydrolysis at pH 1 was about 2 times larger than pH 2, while the rate constant for ester hydrolysis at pH 12 was about 2.5 times larger than pH 11. The alkaline hydrolysis (pH 11) was about 22 times larger than acidic hydrolysis (pH 1). These results demonstrated that EMMB was more resistant to acid than basic media.

Adsorption studies of this work and our previous work (Karnitz et al., 2009) showed that adsorption equilibrium times of metal ions onto EMMB and EMC were lower than 20 min. These results and the half-life times obtained from hydrolysis of ester bond of EMMB indicated that EMMB and EMC may be used in a large pH range ($\geqslant$2 and <11) without a significant degradation of the solid support.

3.3. Adsorption study of Ca^{2+} and Mg^{2+} ions onto EMMB and EMC

3.3.1. Effect of contact time on adsorption

Adsorption studies as function of contact time were performed in aqueous single solutions for each material and metal ions. The adsorption equilibrium time for EMMB and EMC was attained in 10 min for both metal ions (Figures not shown). Therefore, a contact time of 10 min was chosen for pH and concentration-dependent experiments.

3.3.2. Effect of pH on adsorption

In most equilibria between metal ions and ligands, the metal ions compete with protons for the binding sites on modified polymeric matrix so that, as in almost all aqueous equilibria including acid dissociations, pH will be of dominant importance. The distribution of metal cations between free and bound states will depend on pH, and much less metal ion should be bound under acidic conditions than at basic pH. Also, the extent of ionization of functional groups in EMMB or EMC is pH-dependent, i.e. the carboxylic and amine groups on solid support are protonated at low pH values.

Table 2
Hydrolyzed amount of ester bond and pseudo-first-order kinetic parameters for hydrolysis of ester bond of EMMB.

Material	pH	Hydrolyzed amount of ester bond (%)[a]			Pseudo-first-order kinetic model parameters			Correlation coefficient (R^2)	Half-life (h)
		1 h	4 h	24 h	k (h^{-1})	A_0 (a.u.)	C		
EMMB	1	4.4	9.1	31.2	0.1201	0.6138	2.7191	0.9997	5.77
	2	2.3	7.1	17.4	0.0622	2.0106	1.3094	0.9876	11.14
	11	48.2	72.0	72.0	1.1144	0.9035	0.3521	0.9988	0.622
	12	71.6	76.5	77.3	2.6683	1.0139	0.3048	0.9998	0.260

[a] Data calculated from integrated Gaussian area.

Conversely, at higher pH the deprotonated groups, i.e. negatively charged carboxylate and free electron pair on nitrogen, will be more nucleophilic than the protonated species, and therefore can form ion pairs or complexes with metal ions. Fig. 5 shows the effect of pH of the solution on the adsorption of Ca^{2+} and Mg^{2+} onto EMMC and EMC. It demonstrated that the adsorbed amounts changed with pH, and revealed that the minimum adsorption capacity for Ca^{2+} and Mg^{2+} occurred at pH close to 2 and 2.5 for EMC and 2.7 and 3 for EMMB, while the maximum adsorption capacity for Ca^{2+} and Mg^{2+} occurred at pH close to 6 and 9 for EMC and 7.5 and 10 for EMMB. A rapid increase in binding of Ca^{2+} and Mg^{2+} occurred between pH 3.5 and 6 for both materials and the adsorbed amount increased when the pH was increased further. After pH 6 and 8 the adsorption of Ca^{2+} and Mg^{2+} by EMC reached a plateau, while for EMMB the adsorption amount continued increasing up to pH 7.5 and 10. Since the p*K*s of carboxyl and amine groups in EDTA are 0, 1.5, 2.0, 2.69, 6.13, and 10.37, at pH greater than 3 the ionizing carboxyl groups of bound EDTA takes place and these groups contributed to increase the adsorbed amount. This may be the reason for the rapid increase of Ca^{2+} and Mg^{2+}-binding. Similar results were noticed and discussed by Hwang and Damodaran (1997).

EMMB and EMC were used in our previous work (Karnitz et al., 2009) to adsorb Cu^{2+}, Cd^{2+}, and Pb^{2+} from aqueous single solutions. The results for Cu^{2+}, Cd^{2+}, and Pb^{2+}adsorption by EMMB and EMC showed a significant adsorption at lower pH values, result that was not observed for the adsorption of Ca^{2+} and Mg^{2+} in this work. In this way, in order to evaluate the maximum adsorption capacity of the materials, experiments in function of the initial metal ion concentration were carried out and two adsorption isotherms for each material at two pH values for both metal ions were built.

3.3.3. Adsorption isotherms

Langmuir isotherms (Ho, Chiu, & Wang, 2005) (Eq. (7)) were used to evaluate the adsorption experiments in function of the initial metal ion concentration in aqueous single solutions. The contact time used was 10 min. The adsorption studies were accomplished at pH 5.5 and 10 for Ca^{2+} and at 5.5 and 9 for Mg^{2+}. A linearized form of Langmuir equation is demonstrated by Eq. (7).

$$\frac{c}{q} = \frac{1}{Q_{max} * b} + \frac{c}{Q_{max}} \quad (7)$$

where q (mg/g) is the concentration of adsorbed metal ions per gram of adsorbent, c (mg/L) is the concentration of metal ion in aqueous solution at equilibrium, and Q_{max} (mg/g) is related to maximum adsorption capacity when the surface is fully covered with metal ions and b (L/mg) is related to the bond energy of the adsorption reaction between metal ion and ligand (Demirbas, Pehlivan, Gode, Altun, & Arslan, 2005; Gurgel et al., 2008a; Gurgel et al., 2008b).

Linearized plots of c/q against c were obtained from the model and are shown in Fig. 6a and b. Q_{max} and b were computed from the slopes and intercepts of the straight lines. The high correlation coefficients obtained from linearized Langmuir equation indicated that this model can explain very well metal ion adsorption onto modified materials (Sodré, Lenzi, & da Costa, 2001). The results for Ca^{2+} and Mg^{2+} adsorption by EMMB and EMC are shown in Table 3.

As can be seen from Table 3, EMMB showed higher maximum adsorption capacities for Ca^{2+} and Mg^{2+} at pH more acidic or basic than EMC. This result can be explained considering that the concentration of EDTA introduced into EMMB is higher than EMC (Karnitz et al., 2009). Both materials showed a larger maximum adsorption capacity for Ca^{2+} than Mg^{2+}. Adsorbed amounts were found to be lower in acidic pH than basic pH. This behavior indicates that at lower pH values adsorption sites may be unavailable owing to its protonation. As $\Delta G°$ can indicate the spontaneity degree of the adsorption process, it is possible to conclude that the type of adsorption involved is chemical adsorption. The R_L values also indicate that all the adsorption isotherms are favorable (Table 3).

Table 3 also shows a relationship between maximum adsorption capacities of EMMB and EMC for adsorbed metal ions at two pH values and the amount of EDTA added to each material. On

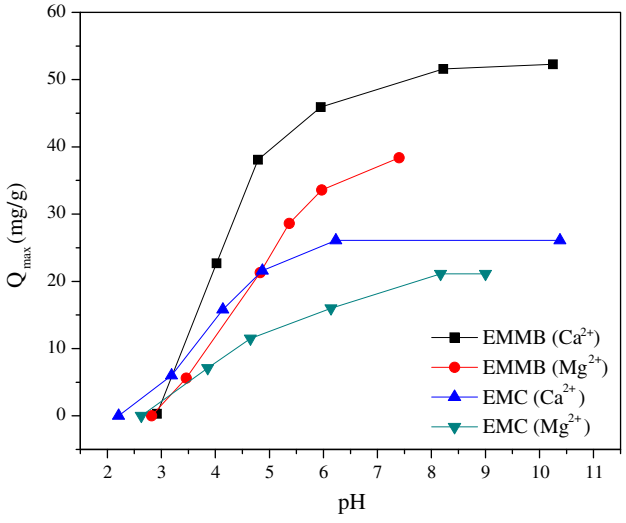

Fig. 5. Effect of pH on adsorption of Ca^{2+} and Mg^{2+} onto EMMB and EMC.

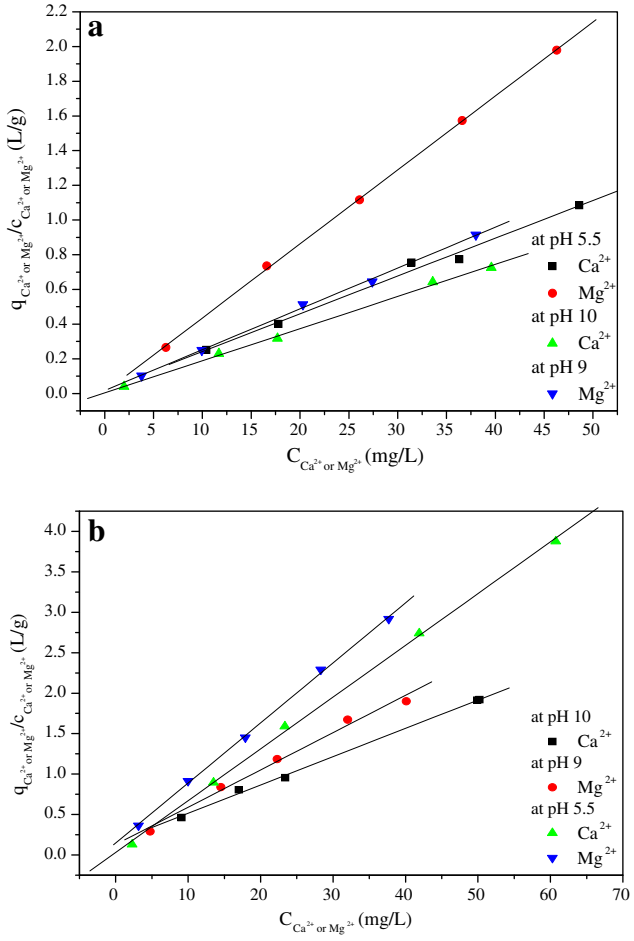

Fig. 6. Adsorption isotherms for Ca^{2+} and Mg^{2+} onto (a) EMMB and (b) EMC at different pH values.

Table 3
Langmuir parameters for adsorption of Ca^{2+} and Mg^{2+} by EMC and EMMB at two pH values, concentration of EDTA and amount of metal ion adsorbed per EDTA added.

Material	Metal ion	pH	Q_{max} (mg/g)	b (L/mg)	R^2	Q_{max} (mmol/g)	C_{EDTA} introduced (mmol/g)	$\Delta G°$ (kJ/mol)	R_L	Amount of M^{2+} per EDTA added
EMC	Ca^{2+}	5.5	15.6	2.030	0.9990	0.389	0.636	−27.5	0.016–0.007	0.61
EMMB			46.1	0.965	0.9909	1.150	1.040	−25.7	0.020–0.010	1.11
EMC	Mg^{2+}		13.5	0.500	0.9991	0.555	0.636	−22.9	0.167–0.032	0.87
EMMB			23.5	4.390	0.9997	0.967	1.040	−28.2	0.008–0.003	0.93
EMC	Ca^{2+}	10.0	28.6	0.212	0.9981	0.714	0.636	−22.0	0.136–0.060	1.12
EMMB			54.1	5.140	0.9979	1.350	1.040	−29.8	0.004–0.002	1.30
EMC	Mg^{2+}	9.0	21.7	0.359	0.9905	0.893	0.636	−22.1	0.218–0.044	1.40
EMMB			42.6	1.360	0.9986	1.750	1.040	−25.3	0.024–0.009	1.68

average one metal ion is chelated by one EDTA molecule incorporated, except for adsorption of Ca^{2+} at pH 5.5 by EMC and at 10 by EMMB and adsorption of Mg^{2+} at pH 9 by EMMB and EMC and at 5.5 by EMC. For adsorption of Cu^{2+}, Cd^{2+}, and Pb^{2+} for EMMB and EMC, on average, five metal ions were adsorbed by two EDTA molecules incorporated (Karnitz et al., 2009). These results may indicate that the complex formed by EDTA and adsorbed metal ions in our previous work (Karnitz et al., 2009) and in this work depend on the type of metal ion adsorbed and that more than one type of arrange is possible taking into account the amount of M^{2+} adsorbed per EDTA incorporated.

The adsorption results of EMMB and EMC for Ca^{2+} and Mg^{2+} were compared for the same pH zone with those that have been reported by Karnitz et al. (2009) for the adsorption of Cu^{2+}, Cd^{2+}, and Pb^{2+}. The Q_{max} of EMC for Cu^{2+}, Cd^{2+}, Pb^{2+} (at pH 5.3), Ca^{2+}, and Mg^{2+} (at pH 5.5) were found to be 1.050, 0.996, 1.120, 0.389, and 0.555 mmol/g, respectively, and the Q_{max} of EMMB for Cu^{2+}, Cd^{2+}, Pb^{2+} (at pH 5.3), Ca^{2+}, and Mg^{2+} (at pH 5.5) were found to be 1.457, 1.326, 1.607, 1.150, and 0.967 mmol/g, respectively. The results showed that EMMB and EMC have higher affinity for Cu^{2+}, Cd^{2+}, and Pb^{2+} than Ca^{2+} and Mg^{2+}. EMC showed larger maximum adsorption capacity for Pb^{2+} than other metal ions tested, while it also showed worse maximum adsorption capacity for Ca^{2+}. For EMMB, the worse and larger maximum adsorption capacities were observed for Mg^{2+} and Pb^{2+}. For more basic conditions, EMMB showed a good adsorption capacity for Mg^{2+} (Q_{max} = 1.750 mmol/g) and for Ca^{2+} (Q_{max} = 1.350 mmol/g).

4. Conclusions

This study showed that EMMB and EMC are effective adsorbents for removal of Ca^{2+} and Mg^{2+} ions from aqueous single solutions. These materials showed maximum adsorption capacities for Ca^{2+} and Mg^{2+} ions ranging from 15.6 to 54.1 mg/g and 13.5 to 42.6 mg/g, respectively. EMMB showed higher maximum adsorption capacities to adsorb Ca^{2+} and Mg^{2+} than EMC, whatever the pH range. EMMB showed a larger adsorption capacity for Mg^{2+} ions than the other metal ions studied in our previous work (Karnitz et al., 2009) and in this work. A study of hydrolysis of ester bond of EMMB in function of time was carried out at various pH values and it revealed that the hydrolysis on both acidic and alkaline pH followed pseudo-first-order kinetic model. This study also revealed that EMMB is easier hydrolyzed at basic than acidic pH values. Through this study we concluded that these materials can be used as adsorbents for hardness removal in water in a large pH range without a significant degradation of the solid support.

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