



Heavy metals retention capacity of a non-conventional sorbent developed from a mixture of industrial and agricultural wastes

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ARTICLE INFO

Article history:

Received 9 April 2008

Received in revised form 7 January 2009

Accepted 7 January 2009

Available online 16 January 2009

Keywords:

Zinc

Copper

Wastewater treatment

Brine sediments

Sawdust

ABSTRACT

Zinc and copper removal from aqueous solutions using brine sediments (industrial residue), sawdust (agricultural residue) and the mixture of both materials has been researched through batch and column tests. Brine sediments were found to be mainly constituted by halite and calcite, while its main cations exchangeable were sodium, calcium, magnesium and potassium. In sawdust the main exchangeable cations detected were calcium, magnesium, sodium and potassium.

FT-IR spectra of sawdust and brine sediment–sawdust mixture showed that brine sediments produced important changes in carboxylic, alcoholic and phenolic groups present in the sawdust.

The maximum zinc adsorption capacity was found to be 4.85, 2.58 and 5.59 mg/g using an adsorbent/solution ratio of 1/40, for brine sediments, sawdust and the mixture, respectively. For copper, the maximum adsorption capacity was found to be 4.69, 2.31 and 4.33 mg/g, using adsorbent/solution ratios of 1/40, for brine sediments, sawdust and the mixture, respectively. Maximum copper adsorption capacity of the mixture, on the contrary to zinc adsorption, was lightly inferior to maximum adsorption capacity obtained in brine sediments.

Adsorption isotherms data adjusted better to the Langmuir model. Additionally, columns reached the saturation point at 690 min for zinc and 360 min for copper. The main mechanism involved in the removal of both metals may be the ionic exchange between sodium and calcium ions present in brine sediments and H⁺ present in functional groups of sawdust. The use of brine sediments, sawdust and their mixture, presents an interesting option both, for wastewater decontamination (as a possible non-conventional sorbent for the removal of heavy metals) and as a waste recycling option.

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1. Introduction

Heavy metals are not biodegradable and tend to accumulate in organisms causing various diseases and disorders [1], being labeled as an emergent class of human carcinogenic compounds [2]. High concentration of some of these metals in the environment or in certain processes may cause a series of problems ranging from soil degradation and fertility loss [3], to negatively affect wastewater treatment processes [4]. Chromium, copper, lead, mercury, manganese, cadmium, nickel, zinc and iron are considered as toxic to human health and the environment [5]. Copper is widely used nowadays, and it is considered as an essential element for human life. However, like any other heavy metals, it may be potentially toxic under certain concentrations [6]. Among various diseases associated to the presence of copper in the human body, a case of neurotoxicity called “Wilson disease”, kidney failure [7] and lung cancer [8] are some of the most important. The main sources of cop-

per responsible for water pollution are industries such as mining, printing, metallurgy, paper and pulp, oil refineries and agricultural sources such as fertilizers, fungicides and animal wastes [9–11]. Zinc, like copper is known to be an essential nutrient but it may have adverse effects if its availability, mainly in the soil, exceeds certain threshold values. This element is widely used in the manufacturing of white zinc, various alloys with metals, the precipitation of gold and silver through the cyanide method and in the shape of zinc salts in the wood preservative industry, photographic paper, fertilizers, pigments and the production of steel and batteries. Toxicity due to the ingestion of zinc is uncommon, but it may generate various intestinal problems [12].

There are a series of processes currently used for the removal of heavy metals from wastewaters: chemical precipitation [13], membrane filtration [14], electrolytic reduction [15], solvent extraction [16], ionic exchange [17] and adsorption [18]. Some of these processes may be not suitable at industrial scale, due to a series of drawbacks such as: low efficiency, applicability to a wide range of pollutants, generation of residues [19], difficulty to locate optimal operating conditions when different heavy metals are present in a solution [20] and to the need of pre-treatments [21].

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The use of agricultural wastes as adsorbents may be important in next years, as they represent an unused resource with serious disposal problems. Sawdust is one of these wastes, which is considered a promising material for the removal of pollutants from wastewater, such as pigments, oils, salts and heavy metals [22]. One of its main advantages is its low cost since it requires minimal processing and it is an abundant residue from the forest industry [23]. Several researches have pointed out that the main mechanisms involved in the adsorption of heavy metals on sawdust are the ionic exchange and hydrogen bonds [18]. These suppositions are fundamentally based on the main constituents of sawdust being polymeric materials such as lignin, tannins and other phenolic compounds the main constituents which may efficiently capture heavy metals. Lignin, tannins and other phenolic compounds are active ionic exchangers, being phenolic groups mainly responsible for such processes [24]. In order to increase both pollutants adsorption capacity and efficiency of sawdust, pre-treatments such as the addition of chemical compounds or the mixture with other materials may be needed [23]. The main factors that can influence in the heavy metals adsorption process on sawdust are adsorbent dosage and size, contact time, stirring speed, as well as pH and ionic force of the aqueous solution. Generally, the adsorption efficiency increases with adsorbent dosage, contact time and stirring speed. However, this may differ for different materials. pH effect of the aqueous solution is considered as one of the controlling factors in adsorption processes, fundamentally due to possible competition at low-pH values, between H_3O^+ ions and metals for the active sites of the sorbent and the positive or negative charge that sawdust may present under a determined pH value [23].

Like agricultural wastes, industrial wastes are not always revalorized and are simply disposed of, according to current norms in the different countries. In many cases, the mineral, inert and non-toxic character of the generated wastes makes the disposal in certain places a simple and economical alternative. However, when waste production is high, disposal costs increase, generating recycling and reuse options. An example of this is the sodium perborate manufacturing industry, where the generated mineral waste has been studied as compost additive, acid soil conditioner, ionic exchanger and as a raw material in the cement industry [25].

The main non-toxic solid waste generated in the chlor-alkali industry is brine sediments, being its main constituent's mineral salts. Currently, in a Chilean chlor-alkali production facility, brine sediments are filtered, obtaining a final solid waste of low humidity (30–40%), which is sent to an industrial landfill as non-hazardous waste.

The main goal of this work was to investigate the properties of brine sediments as a possible material to be used with sawdust for heavy metals removal from wastewater.

2. Materials and methods

2.1. Chemicals

All compounds used in the different tests are of an analytical grade and were supplied by Merck. A base solution of 1000 mg/L Zn^{2+} (from $ZnCl_2$) and Cu^{2+} (from $CuCl_2$) was used in the different tests. A constant ionic force (KCl 0.1 M) was employed and deionized water was used in all distilled water tests.

2.2. Adsorbents and characterization

Brine sediments were obtained from a chlor-alkali production facility. Prior to its use, the waste was dried at 70 °C and milled.

Douglas-fir (*Pseudotsuga menziesii*) sawdust was used in this test. It was obtained from a sawmill of Southern Chile. Sawdust was washed several times, dried at 70 °C and sieved. Sawdust particles less than 1.40 mm were used.

The mixture composed of brine sediments and sawdust was prepared at a 1/1 mass ratio, and used in 1/10, 1/20 and 1/40 adsorbent/solution ratios.

The mineralogical and chemical composition of brine sediments was determined through X-ray diffraction (XRD) techniques and X-ray fluorescence (XRF), respectively.

To identify possible modifications of active sites in sawdust when adding brine sediments and during heavy metals adsorption, this material was analyzed through Fourier transform infrared spectroscopy (FT-IR). Samples were pulverized with oven-dried KBr (1:250) and pressed into pellets. FT-IR spectra were collected on a Thensor™ 37 Bruker using 32 scans between 4000 and 400 cm^{-1} .

The determination of the effective cation exchange capacity (CEC_{eff}) and the exchange cations in sawdust and brine sediments was performed through the compulsive exchange method. This method consists basically of the saturation of the sample with a $BaCl_2$ solution in order for the barium (Ba) to occupy the free exchangeable cation sites available in the adsorbent [26]. Once the sample is completely saturated (and through a $MgSO_4$ solution), total barium, available in the liquid phase as well as adsorbed in the sorbent, is precipitated in the form of barium sulfate; while magnesium occupies the free exchangeable cation sites. After measuring the magnesium concentration in the supernatant using flame atomic absorption spectroscopy (UNICAM 969 AA spectrometer, SOLAR), the effective exchange capacity of the sample was determined through Eq. (1):

$$CEC_{eff} = \frac{V_{MgSO_4} \cdot (C_b - C_2)}{m_s} \quad (1)$$

where V_{MgSO_4} is the added volume of the $MgSO_4$ solution (mL), C_b is the magnesium concentration in the blank solution (mmol/L), m_s is the dry sample mass (g) and C_2 is the corrected magnesium concentration of the sample (mmol/L), calculated as shown in Eq. (2):

$$C_2 = \frac{C_1 \cdot (V_{MgSO_4} + m_2 - m_1)}{m_{MgSO_4}} \quad (2)$$

where C_1 is the magnesium concentration in the sample (mmol/L), m_1 is the mass of the centrifuge tube with the dry sample (g), m_2 is the mass of the centrifuge tube with the sample after adding the $BaCl_2$ solution (g) and m_{MgSO_4} is the mass of the $MgSO_4$ solution (g).

The content of exchangeable cations in sawdust and brine sediments was determined by flame atomic absorption spectroscopy (AAS). The final results of exchangeable cations were obtained through Eq. (3):

$$X_c = \frac{(C_x - C_b) \cdot V \cdot 100}{MW \cdot m_s} \quad (3)$$

where X_c is the measure of exchangeable cations (cmol+/kg), C_x is the cations concentration (g/L), C_b is the blank concentration (g/L), MW is the molecular weight of the cation (g/mol), m_s is the adsorbent mass (kg) and V is the solution volume (L).

2.3. Batch tests

2.3.1. Adsorption kinetics

Zinc and copper adsorption kinetics was conducted in 100 mL plastic bottles previously washed with nitric acid (1:1, 50% HNO₃ and 50% distilled water). A total volume of 20 mL solution containing metals ($C_0 = 75$ mg/L), KCl 0.1 M and deionized water were mixed with the adsorbent. 1/10, 1/20 and 1/40 adsorbent/solution ratios were used for both sawdust and brine sediments, as well as for the mixture of both materials. pH was maintained at 7.0 for zinc and 6.0 for copper using HNO₃ or NaOH. Samples were first stirred for 1 min, 2 min, 3 min, 4 min, 15 min, 30 min, 45 min, 1 h, 2 h, 6 h, 8 h, 36 h, 48 h and 72 h at a rate of 100 rpm at 25 °C, and then filtered at vacuum through a membrane filter of 0.45 μm, finally quantifying the remaining metal concentration in the supernatant by flame AAS.

2.3.2. Adsorption isotherms

Zinc and copper adsorption isotherms were determined under the same experimental conditions as for adsorption kinetics. Solutions with metals were prepared at concentrations of 0, 25, 50, 75 and 100 mg/L. Having already obtained the experimental data, these were adjusted through Langmuir and Freundlich models. Eq. (4) presents the Langmuir model, while the linear form of the Langmuir equation can be written as describes in Eq. (5):

$$\frac{x}{m} = \frac{V_m \cdot K \cdot C_e}{1 + K \cdot C_e} \quad (4)$$

$$\frac{C_e}{x/m} = \frac{1}{K \cdot V_m} + \frac{C_e}{V_m} \quad (5)$$

where C_e is the equilibrium concentration of the solution after adsorption (mg/L), x/m is the adsorbed metal ion amount per unit mass of adsorbent (mg/g), V_m is the maximum adsorption uptake (mg/g), and K is the equilibrium constant related to the energy of adsorption (L/mg). The parameters K and V_m can be determined graphically.

Eq. (6) presents the Freundlich model, while the linear form of the Freundlich equation can be written as describes in Eq. (7):

$$\frac{x}{m} = K_f \cdot C_e^{1/n} \quad (6)$$

$$\log\left(\frac{x}{m}\right) = \log(K_f) + \frac{1}{n} \cdot \log(C_e) \quad (7)$$

where K_f ((L/mg)^{1/n} mg/g) and n are empirical constants, related to the capacity of maximum adsorption and the intensity of adsorption. Both parameters can be determined graphically.

2.4. Column tests

In fixed bed adsorption, concentrations in fluid phase and solid phase vary within time and the bed depth. When wastewater flows through the column, pollutants (in this case heavy metals) gradually separate when wastewater descends through the column, thus, forming a mass transfer zone [27]. The progressive movement of this zone can be observed through the representation of breakthrough curves, which correspond to the representation of the pollutant concentration at the column output during the experiment time [28].

A very important design parameter in columns operation is the maximum adsorption capacity of metals until the saturation point. This capacity of the bed can be represented by the area above the breakthrough point and is given by Eq. (8) [29]:

$$N_0 = G \cdot \int_0^{t_s} (C_0 - C) dt \quad (8)$$

where G is the solution flow rate in L/min, C_0 and C are the metal concentrations in the input and output of the column at time t in mg/L, respectively, and t_s is the time needed to reach the saturation point.

Fixed bed column adsorption experiments were conducted in 1-cm diameter glass columns, which were packed with 8 g mixture composed of brine sediments and sawdust. The metal ion solution containing 44 mg/L (zinc) and 34 mg/L (copper) was fed to the column at a constant flow rate of 0.2 mL/min. The solution leaving the bottom of the column was collected at various time intervals and filtered at vacuum through a membrane filter of 0.45 μm. The quantity of the remaining metal was quantified by through AAS. The input pH value was adjusted with HNO₃, maintaining output pH values of about 7.0 for zinc and 6.0 for copper. From the experimental curves, the saturation time was determined using Eq. (9):

$$BC = G \cdot (C_0 - C^*) \cdot t_s \quad (9)$$

where BC is the bed capacity for heavy metals retention (mg) and C^* is the metal concentration of the solution in equilibrium with fresh adsorbent.

3. Results and discussion

3.1. Materials characterization

3.1.1. Brine sediments

Brine sediments characterization by XRD (Table 1) showed that the sediments are constituted by NaCl (halite) and CaCO₃ (calcite) as main compounds, while SiO₂ (quartz), Fe₂Si (iron siliceous) and CaO (calcium oxide) were determined as marginal components.

XRF analysis showed that the main elements present in brine sediments are Ca (4.02%) and Fe (1.08%). Copper was not detected, whereas trace quantities of Zn were found in the analyzed samples (140 μg/g).

The main exchangeable cations in brine sediments were found to be sodium (659.4 cmol+/kg), calcium (12.1 cmol+/kg), magnesium (4.5 cmol+/kg) and potassium (0.6 cmol+/kg). These results are according to the XRD and XRF characterization.

Brine sediments showed an effective cationic exchange capacity (CEC_{eff}) of 22.2 cmol+/kg. This value is similar to those reached by some soils which have a CEC of 21.3 cmol+/kg (like andisols from the Azores, Portugal) [30] and 44.4 cmol+/kg (volcanic ash-derived soils in Nicaragua) [31]. Bearing in mind brine sediments are industrial wastes that presents disposal problems and that it is a potential material for the removal of heavy metals, it can be said that this material presents a considerable cation exchange capacity.

3.1.2. Sawdust

The main cation exchanged in sawdust is calcium (1.5 cmol+/kg), followed by magnesium (1.1 cmol+/kg), sodium (1.0 cmol+/kg) and potassium (0.6 cmol+/kg). Compared to the values obtained for brine sediments, those from sawdust are lower (except for potassium).

Table 1
Compounds identified by XRD in brine sediments.

Quantitative estimated formula	Name
NaCl ^a	Halite
CaCO ₃ ^a	Calcite
SiO ₂ ^b	Quartz
Fe ₂ Si ^b	Iron silicide
CaO ^b	Calcium oxide

^a Main compound.

^b Marginal compound.

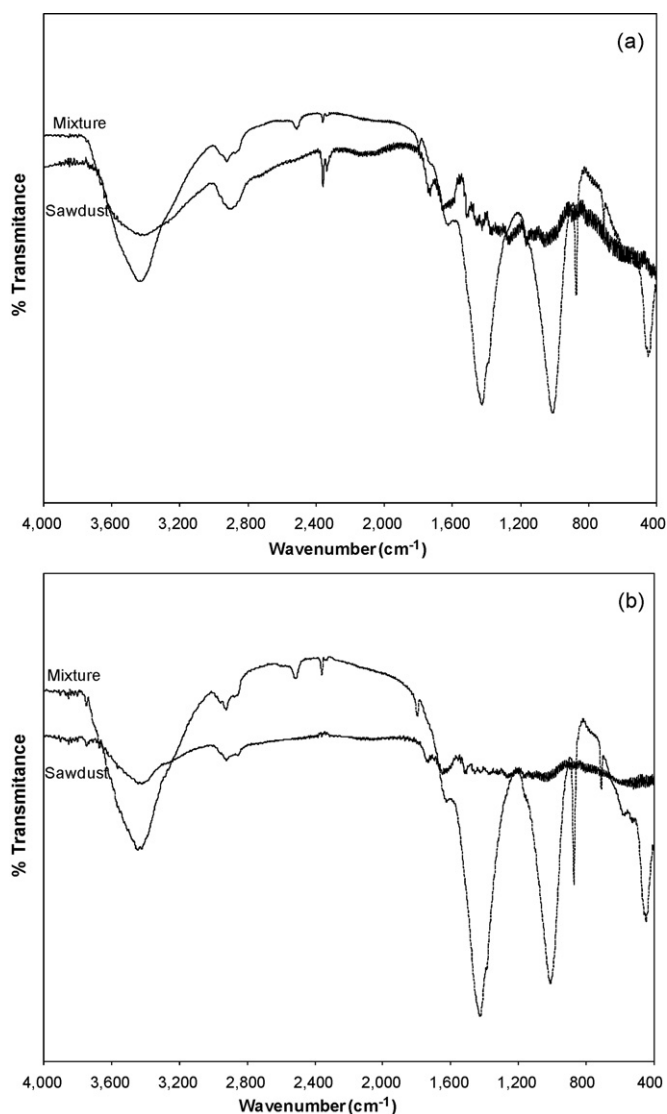


Fig. 1. FT-IR sawdust and mixture spectra without adsorbed metal: (a) pH 7.0; (b) pH 6.0.

The intensities and changes produced in the bands of a FT-IR spectrum are related to the change in the chemical composition of functional groups and in the chemical structure of a sample. Fig. 1(a) and (b) show the different IR spectra for sawdust and brine sediment–sawdust mixture at pH 7.0 and 6.0, respectively. The use of brine sediments mixed with sawdust produced changes in the latter's structure. These changes are mainly reflected in the intensity of bands placed at 870, 1005, 1425, 1620 and 3400 cm^{-1} .

The band located at 870 cm^{-1} represents (CH) vibrations that can be attributed to aromatic compounds, while the band located at 1005 cm^{-1} is attributed to stretching (C–O) and (C–C) vibrations of alcoholic and phenolic groups. Bands located at 1425 and 1620 cm^{-1} are attributed to the formation of deprotonated and coordinated carboxylic groups, while the band located at 3440 cm^{-1} can be assigned to (O–H) stretching vibrations of phenolic groups. Generally, bands located at 870, 1005 and 1425 cm^{-1} are attributed to vibrations whose origin is cellulose [32,33], the latter band being attributed by other authors to (CH) vibrations of the methoxy group, whose origin would be lignin [34,35]. Other bands associated to lignin can be found at 1510, 1460, 1270 and 1130 cm^{-1} [36]. The presence of a band located at 1425 cm^{-1} and a band located at

1620 cm^{-1} is often associated to heavy metals removal [37]. In this case, the presence of a band located at 1425 cm^{-1} can be attributed to the exchange between sodium and calcium ions present in brine sediments through H^+ present in sawdust carboxylic groups. In this exchange, sawdust O–H alcoholic and phenolic groups may be also involved. As shown in Fig. 1, no significant differences between the IR spectra obtained with sawdust and mixture at pH 7.0 and 6.0 were detected.

3.2. Adsorption kinetics

In zinc and copper adsorption kinetics on brine sediments (Fig. 2), two phases can be observed. A first dynamic phase, during 5, 15 and 180 min for adsorbent/solution ratios of 1/10, 1/20 and 1/40, respectively, and a second phase where equilibrium is attained were observed. Additionally, a similar behavior in the adsorption kinetics of both heavy metals on the mixture was observed.

In the case of zinc and copper adsorption kinetics on sawdust (Fig. 2(b)), three phases were observed: a first dynamic phase of rapid retention, with contact times of about 5 min for all adsorbent/solution ratios, a second phase of fixation where equilibrium is attained, and a third phase where part of the metals previously adsorbed were desorbed.

On the one hand, at pH 6.0, copper removal could be assumed as the combination of adsorption and precipitation processes. This fact is in agreement with results obtained for zinc and copper removal by natural clays, where for pH values higher than 6, copper presented higher removal efficiency than zinc. According to Veli and Alyuz [38], this phenomenon was caused by the formation of copper hydroxyl complexes, which may precipitate inside the adsorbent structure. On the other hand, at pH 7.0 no formation of hydroxyl complexes with zinc is expected [39], so zinc precipitation was not considered as a possible removal mechanism in adsorption kinetics trials.

Another important phenomenon was that as the adsorbent dosage increased, the adsorbed metal quantity increased, reducing equilibrium time. This is due to a higher number of available active sites and thus, a higher quantity of cations and functional groups are available to be exchanged [40–42]. It is also important to point out that as the adsorbent dosage increased, the metal removal efficiency increased but the metal amount per mass unit decreased, due to the incomplete use of adsorption sites or particles interaction such as aggregation, as a result of a high-sorbent concentration. Such aggregation state may result in a decrease in the total surface area of the sorbent and an increase in diffusional path length [22].

Besides copper precipitation during adsorption kinetics, the behavior observed of both metals is very similar. Equivalent results have been obtained in cadmium, copper and zinc removal by cassava tuber bark waste, where the minimum degree of removal for cadmium – compared with removal achieved for copper and zinc – is attributed to its ionic size (ionic radius of $\text{Cd}^{2+} = 0.97\text{ \AA}$; $\text{Zn}^{2+} = 0.74\text{ \AA}$; $\text{Cu}^{2+} = 0.73\text{ \AA}$) [43].

3.3. Adsorption isotherms

In Fig. 3, adsorption isotherms are shown for the different adsorbent materials using three different adsorbent/solution ratios. The predominant form according to Giles' classification [44] corresponds to type L isotherms or Langmuir isotherm. This characteristic form of isotherm becomes more evident as the quantity of adsorbent in the solution decreases. This phenomenological classification is based on simple observation and does not reveal the processes leading to the different shapes of an isotherm, and may give a notion of the mathematical model better adjusting to the obtained data [45].

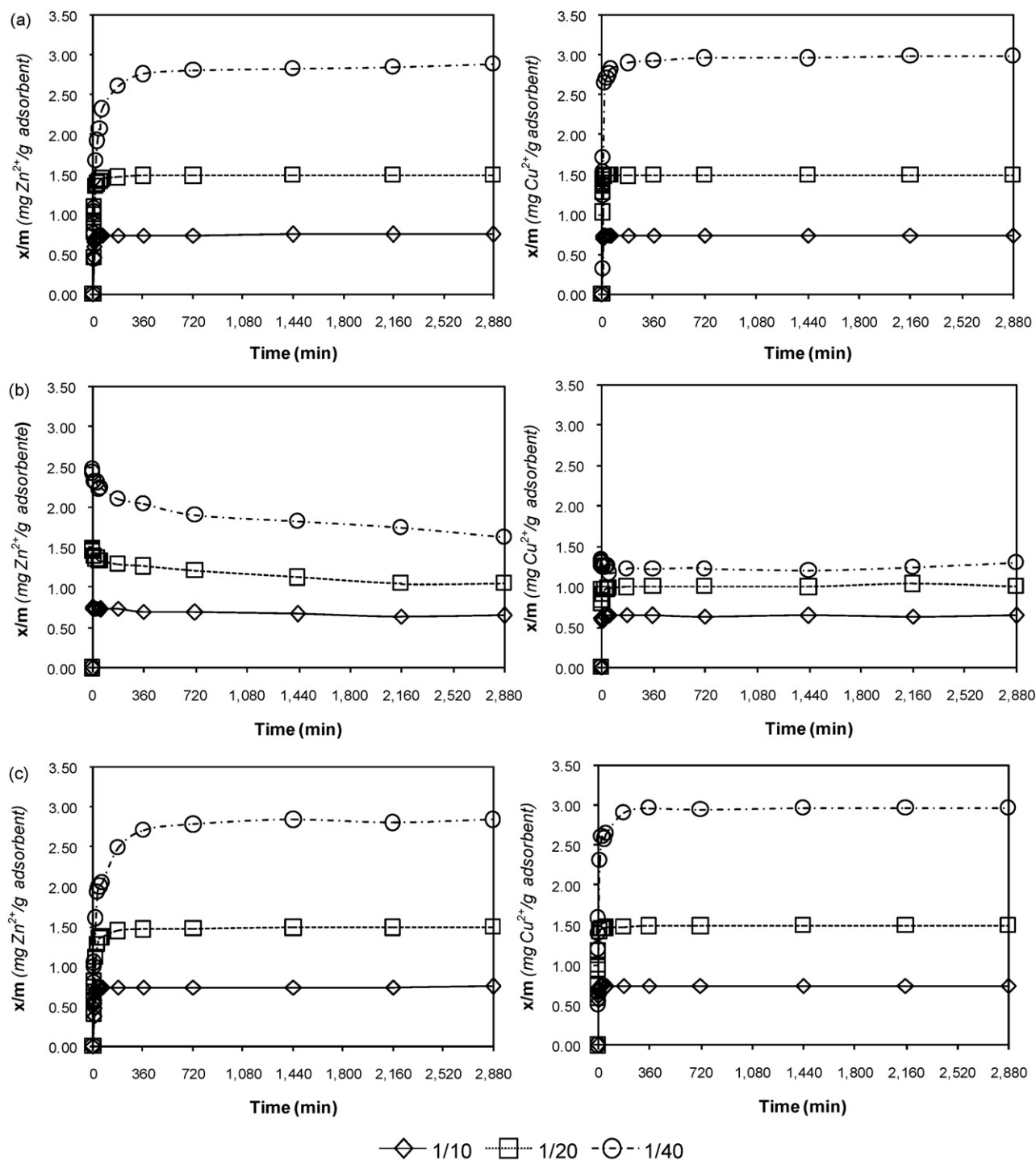


Fig. 2. Zinc and copper adsorption kinetics on brine sediments (a), sawdust (b) and mixture (c). Adsorbent/solution ratios 1/10, 1/20, 1/40; $T = 25^\circ\text{C}$; initial metal concentration 75 mg/L; pH 7.0 (zinc) and 6.0 (copper).

Langmuir (K and V_m) and Freundlich (K_f and n) isotherm parameters, as well as regression coefficients (R^2) were obtained. As shown in Table 2, regression coefficients between 0.92 and 1.00 (except for one value) indicated that both, Langmuir and Freundlich models are well adjusting the experimental data, the former presenting slightly higher regression coefficients. Added to the obtained isotherm shapes, it can be assumed that the experimental data adjusted better to the Langmuir model, indicating that molecules are adsorbed in well defined sites, energetically equivalent and distant enough

from each other, avoiding interaction between adsorbed molecules of adjacent sites [46,47].

The zinc maximum adsorption capacity of brine sediments was determined to be 0.97, 2.04 and 4.85 mg/g for adsorbent/solution ratios of 1/10, 1/20 and 1/40, respectively. In sawdust, the obtained values were 1.32, 1.95 and 2.58 mg/g for adsorbent/solution ratios of 1/10, 1/20 and 1/40, respectively. The zinc maximum adsorption capacity in mixture was higher than the maximum adsorption capacity obtained in brine sediments and sawdust, achieving val-

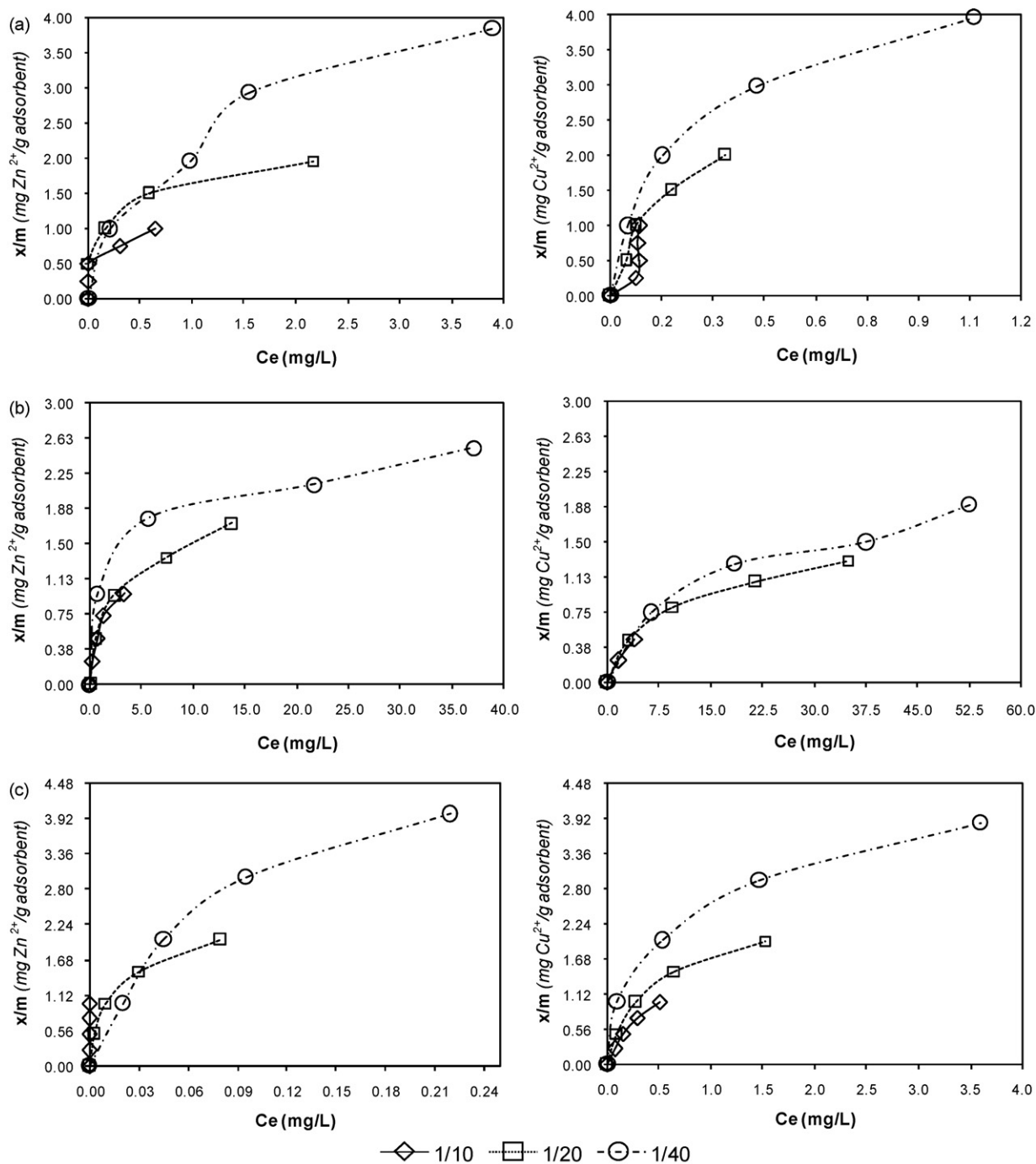


Fig. 3. Zinc and copper adsorption isotherms on brine sediments (a), sawdust (b) and mixture (c). Adsorbent/solution ratios 1/10, 1/20, 1/40; $T=25^{\circ}\text{C}$; initial metal concentration 0, 25, 50, 75 and 100 mg/L; pH 7.0 (zinc) and 6.0 (copper).

ues of 2.29 and 5.59 for adsorbent/solution ratios of 1/20 and 1/40, respectively.

Values obtained for zinc adsorption capacity are comparable to those of zinc adsorption capacity observed in *Mucor rouxii* (4.9 mg/g) [48], jute fibres (3.5 mg/g) [49], montmorillonite (4.9 mg/g) [50], kaolinite (between 1.3 and 1.8 mg/g) [51,52], and clinoptilolite and chabazite (2.7 and 5.5 mg/g, respectively) [53]. Nevertheless, the obtained values are far below the maximum zinc adsorption capacity of chitosan (75 mg/g) [54], *Thiobacillus thiooxidans* and *Thiobacillus ferrooxidans* (43.3 and 82 mg/g, respectively) [55,56], carrot residues (29.6 mg/g) [57], and bentonite (52.9 mg/g) [58].

In the case of copper, the maximum adsorption capacity of brine sediments was found to be 3.15 and 4.69 mg/g for adsorbent/solution ratios of 1/20 and 1/40, respectively. In sawdust, the obtained values were 1.23, 1.57 and 2.31 mg/g for adsorbent/solution ratios of 1/10, 1/20 and 1/40, respectively. Mixture maximum adsorption capacity for copper, on the contrary as zinc adsorption, was determined to be slightly inferior than the maximum adsorption capacity obtained in brine sediments, achieving values of 1.88, 2.48 and 4.33 mg/g for adsorbent/solution ratios of 1/10, 1/20 and 1/40, respectively.

Experimental values obtained for copper adsorption are comparable to those obtained in *Aspergillus niger* (4.9 mg/g) [59], jute

Table 2
Langmuir and Freundlich isotherm parameters for the adsorption of zinc and copper.

Heavy metal	Adsorbent	Adsorbent/solution ratio	Langmuir			Freundlich		
			V_m (mg/g)	K (L/g)	R^2	K_f ((L/mg) ^{1/n} mg/g)	n	R^2
Zn ²⁺	Brine sediments	1/10	0.97	54.16	0.98	1.17	2.67	1.00
		1/20	2.04	8.45	0.99	1.64	3.85	0.99
		1/40	4.85	0.94	0.97	2.11	2.10	0.98
	Sawdust	1/10	1.32	0.84	1.00	0.55	1.79	0.97
		1/20	1.95	0.44	0.99	0.63	2.56	0.99
		1/40	2.58	0.43	0.99	1.09	4.33	0.98
	Mixture	1/10						
		1/20	2.29	87.20	1.00	5.66	2.56	0.99
		1/40	5.59	11.93	1.00	18.62	1.73	0.96
Cu ²⁺	Brine sediments	1/10						
		1/20	3.15	5.28	0.95	4.30	1.59	0.92
		1/40	4.69	4.84	1.00	2.65	3.95	0.53
	Sawdust	1/10	1.23	0.14	0.99	0.19	1.75	0.98
		1/20	1.57	0.12	0.99	0.29	2.34	0.99
		1/40	2.31	0.07	0.96	0.35	2.40	0.98
	Mixture	1/10	1.88	2.29	0.98	1.79	1.39	0.98
		1/20	2.48	2.51	1.00	1.73	2.02	0.98
		1/40	4.33	1.96	0.99	2.47	2.69	1.00

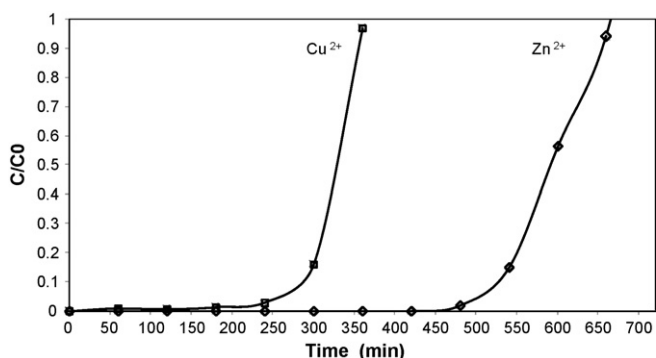


Fig. 4. Zinc and copper adsorption breakthrough curves onto the mixture. C_0 : metal concentration in column input (mg/L), C : metal concentration in column output (mg/L).

fiber (4.2 mg/g) [49], kaolinite (1.9 mg/g) [3], clinoptilolite (between 1.6 and 3.8 mg/g) [53,60], in fly ash (between 1.18 and 1.39 mg/g) [61], and oak sawdust (3.6 mg/g) [40]. However, the obtained values are far below the maximum copper adsorption capacity of chitosan (222 mg/g) [54], seaweed biomass (between 52 and 114 mg/g) [62–64], *Thiobacillus thiooxidans* (30.8 mg/g) [56], alfalfa (20 mg/g) [65], carrot residues (32.7 mg/g) [57], palygorskite (30.7 mg/g) [66], and clinoptilolite of 25.7 (mg/g) [67].

3.4. Column tests

Breakthrough curves and maximum adsorption capacity values for zinc and copper in the mixture showed that zinc presented a higher adsorption capacity than copper (see Fig. 4 and Table 3), as obtained previously in batch experiments (see Table 2). Nevertheless, fixed bed adsorption capacities were found to be considerably lower for both heavy metals, mainly due to the fact that in batch systems, a good adsorbent–solute interaction is achieved, showing solid particles a rapid movement in the solution, increasing solute

Table 3
Zinc and copper columns adsorption parameters.

Heavy metal	Affluent metal concentration (mg/L)	Adsorbed amount (g)	Saturation time (min)	Adsorbed amount at bed exhaustion point	
				Total (mg)	(mg/g)
Zinc	44	8	690	6.072	0.759
Copper	34	8	360	2.448	0.306

concentration near the adsorbent surface and increasing solute diffusion from the boundary layer to the adsorbent's surface [40]. On the contrary, in fixed bed adsorption systems, the adsorbent is packed in the column hiding part of solid particles surface, resulting in a poor solid–solute interaction. Furthermore, liquid channeling, which results in poor adsorbent–solute contact and less hydraulic retention time may occur in the column [68].

Once the saturation point was reached at 690 min for zinc and 360 min for copper adsorption trials, zinc and copper concentration increased in the output of each column, reaching concentrations higher than the input concentration. This increase of metal concentration may be caused by a partial desorption of the previously adsorbed metal. In fact, once the adsorbent was completely saturated with metals, it may be acted as a regenerator agent, replacing previously adsorbed metals by H^+ cations present in the solution.

3.5. Possible adsorption mechanisms

As previously mentioned, in FT-IR characterization of sawdust and the brine sediment–sawdust mixture, brine sediments caused modifications mainly in carboxylic, alcoholic and phenolic groups present in sawdust surface. Once metals were adsorbed in the mixture, the existence of the same bands could be observed, and the 1005 and 1425 cm^{-1} band presented a lower intensity (Fig. 5). These results are similar to other ones reported by [69] in juniperus bark and wood, where bands intensity obtained by FT-IR decreased after cadmium adsorption.

Generally, and as shown in IR spectra, zinc and copper adsorption by sawdust presented subtle variations in bands located at 1510, 1460, 1270 and 1130 cm^{-1} , corresponding to lignin functional groups [36]. Most often, metal adsorption in sawdust does not produce a major modification in its structure as seen in the brine sediment–sawdust mixture. This could be explained because zinc and copper adsorption processes are dynamic processes.

As determined by XRD, XRF and exchangeable cations, brine sediments are mainly composed by sodium and to a lesser extent

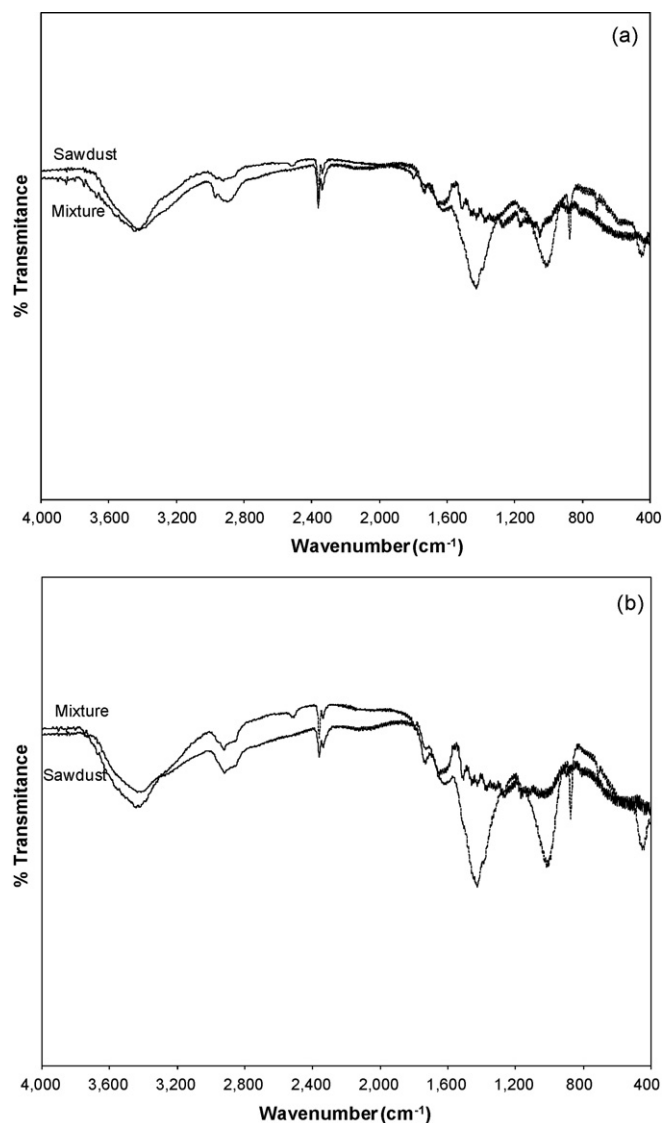
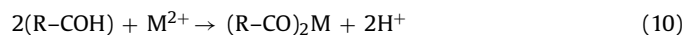


Fig. 5. FT-IR sawdust and mixture spectra with adsorbed zinc (a) and copper (b).

calcium. So, it could be assumed that the main mechanism involved in the removal of metals is the ionic exchange between sodium and to a lesser extent calcium, present in the material, through zinc and copper present in the solution.

In the case of sawdust, heavy metals removal is attributed to the adherence of the metal to adjacent hydroxyl groups. In case of a divalent metal such as zinc and copper, hydroxyl groups can donate two pairs of electrons to the metal (M), forming a coordination number four and freeing two hydrogen ions into the solution [6]. This can be reflected through the following equation:

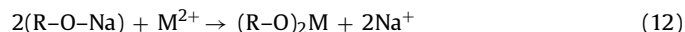
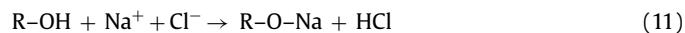


This ionic exchange acidifies the aqueous solution, which results in the desorption of previously adsorbed metals [23,70]. This behavior is expected as previously freed H^+ competes with the metals for exchange sites [18,47,71].

The increase in zinc removal capacity using the brine sediment-sawdust mixture, compared to the removal achieved using sawdust and brine sediments, may be due to an exchange between Na^+ and Ca^{2+} ions present in brine sediments by H^+ cations present in sawdust surface, which are later exchanged by zinc and copper present in the solution. Similar results have been obtained in the removal of zinc and copper with sawdust mixed with Na_2CO_3 and NaOH ,

with a sixfold removal capacity increment for zinc and a twofold increment for copper [72]. Additionally, in the removal of zinc, copper and nickel using sawdust treated with NaCl and CaCl_2 , the removal capacity of these metals increased with the treatment [73].

The probable mechanism can be represented in Eqs. (11) and (12) [18], where R is sawdust matrix:



4. Conclusions

Brine sediments are mainly constituted by NaCl (halite) and CaCO_3 (calcite), being sodium the main available cation to be exchanged (659.4 cmol+/kg).

Zinc and copper adsorption kinetic curves in brine sediments showed two phases: a first retention phase and a second fixation phase. However, in the case of sawdust, three phases could be observed: a first fast retention phase, a second fixation phase and a third phase where part of the adsorbed zinc was desorbed. This desorption was not observed for brine sediment-sawdust mixture under batch conditions.

Adsorption isotherms adjusted better to Langmuir model, indicating that heavy metals were adsorbed in well-defined places, energetically equivalent and distant enough from each other to prevent interaction among adsorbed molecules in adjacent sites. A maximum zinc adsorption value of 5.59 mg/g was obtained in the brine sediment-sawdust mixture. In the case of copper, a maximum fixation value of 4.69 mg/g was obtained for brine sediments.

Columns reached their saturation point at 690 min (zinc) and 360 min (copper). However, after reaching this saturation point, metals desorption was observed. This desorption was not observed in the brine sediment-sawdust mixture under batch conditions, while in columns trials, once the adsorbent was completely saturated with metals, it may be acted as a regenerator agent, replacing previously adsorbed metals by H^+ cations present in the solution.

Brine sediment-sawdust mixture produced some changes in sawdust surface, mainly attributed to carboxylic, alcoholic and phenolic groups. Once metals were adsorbed in the mixture, the presence of the same bands with lower intensity was observed in FT-IR spectra. Besides, metal adsorption in sawdust did not produce a major change in its functional groups.

The main mechanism involved in the removal of metals in both materials was determined to be ionic exchange between metal cations and sodium and calcium ions present in brine sediments, as well as H^+ present in carboxylic, alcoholic and phenolic groups of sawdust surface.

The use of brine sediments, sawdust and the mixture of these residues may present an interesting alternative as a possible non-conventional adsorbent for the removal of heavy metals from wastewater.

Acknowledgement

This research was funded by the DIUFRO project no. 120519 of the University of La Frontera, Temuco, Chile.

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