Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2014.927333

55 (2015) 1523–1533
July

Taylor & Francis
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Adsorption behaviour of the zeolite, Controll M.F. 574® in removing iron and manganese from natural water

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Received 1 November 2013; Accepted 13 May 2014

ABSTRACT

In this work, zeolite, Controll M.F. 574® was characterized and its adsorption properties were evaluated for the removal of iron (Fe) and manganese (Mn) from natural water, compared with a synthetic solution. Characterization by dispersive X-ray and X-ray diffraction identified a semi-crystalline structure and the presence of magnesium aluminium silicate, quartz and iron and manganese oxides. The results of the adsorption isotherms verified that the adsorption of iron followed a linear model indicating that physisorption occurred. The adsorption of manganese was better adjusted to the Langmuir model, indicating the formation of a monolayer on the surface of the adsorbent. The kinetic results were best adjusted to the pseudo-second-order model with a correlation coefficient of 0.99 for adsorption of both elements. The results showed that the zeolite studies showed good adsorption capacity for Fe (74%) and Mn (66%) in natural water. The concentrations of these metals were below the values permitted by Brazilian legislation.

Keywords: Adsorption studies; Zeolite; Controll M.F. 574®; Iron; Manganese; Natural water

1. Introduction

The removal of trace elements from surface water, groundwater and wastewaters is an essential social and environmental subject because of their detrimental effects to water quality and their toxic characteristics for living beings. Many studies investigated environmental effects associated with these elements such as arsenic [1–4], zinc [5], silver [6], mercury [7], chromate [8] and cadmium [9]; however, studies of Fe and Mn are less reported for the treatment of potable water.

Some substances in the water may change their organoleptic and aesthetic properties, for example Fe

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1944-3994/1944-3986

and Mn salts. These salts are present in many fresh waters but may also be present because of underground pollution. Excess Fe and Mn in potable water cause operational and aesthetic problems such as taste, odour and high turbidity and can stain kitchen utensils, bath accessories and laundered clothes. [10,11]. According to Resolution RDC No. 269/2005 of the Brazilian National Agency for Sanitary Surveillance (ANVISA), the Recommended Daily Intake of Fe and Mn for adults is approximately 14 and 2.3 mg, respectively [12]. Excess ingestion can cause lesions in the pancreas, lung inflammation, nausea and headaches [13,14].

The Health Ministry of Brazil [15] set by the governmental decree 2914/2011 a maximum acceptable drinking water concentration for Fe and Mn of 0.3 and 0.1 mg L^{-1}, respectively. These values are according to World Health Organization [16].

To achieve these limits, methods for removing these metals mainly consist of the physico-chemical process of aeration that accelerates the oxidation of soluble Fe and Mn species and subsequently removes hydroxides or oxides by sedimentation and filtration. However, this process produces a large volume of sludge for disposal [17]. Another useful but expensive method is oxidation with stronger oxidants (potassium permanganate, chlorine and ozone), which generates insoluble compounds of these metals which are removed via decantation and/or filtration. However, several of these reagents can form undesirable compounds, such as trihalomethanes, which are potentially carcinogenic and are harmful to the population [18,19].

An unconventional method to remove these metals involves a biological process that cultivates oxidant specific micro-organisms in a filter medium, thus the oxidized metals are retained in the medium. However, the disadvantages to this method are that the biological process requires a long period of time (a few months) for the development and stabilization of the culture of micro-organisms and the careful control of operating conditions because of the sensitivity of micro-organisms to environmental conditions [19,20].

There has been some research into finding a cost-effective method for the removal of these metals. For example, adsorption has been shown to be a low-cost technique when natural or synthesized materials are used as adsorbents. The adsorption process can reduce the downstream metal concentration to subparts per billion levels. Many adsorbents have been investigated for Fe and Mn in water including activated carbon [21], natural adsorbents [22,23], coal adsorbents [24], clay minerals [9] and zeolites [25,26]. These materials have different adsorption capacities that depend on the sorbent mass, pH, contact time and initial concentration of the metals in the solution.

Zeolites have received increasing attention in the context of potable water and wastewater treatment [1,27–30]. These materials occurring, naturally or synthetic, are aluminosilicates with a porous three-dimensional structure. Aluminium ions create negative places and to keep the crystal neutrally charged, other ions are present such as Na^+, K^+, Ca^{2+} or H^+. These cations are exchangeable with certain cations in solutions such as zinc, cadmium, lead, silver, arsenic and manganese [1,28,31,32]. Zeolites have good capacity of adsorption and this makes them a suitable material for the removal of metals in aqueous media. Furthermore, the possibility of the reuse of these adsorbents without losing the adsorption capacity is remarkable [31,32].

Some of these adsorbents had evaluate the removal of Fe and Mn at high concentrations. However, in Brazil, some surface water used for public supply has low concentrations of Fe and Mn (less than 1.0 mg L^{-1}), then it is necessary to evaluate the removal of these elements in this range. Even at these low concentrations, these metals can contribute to the hardness of the water and its accumulation in distribution networks.

The aim of this study was to evaluate the adsorption behaviour of Fe and Mn using a commercial zeolite, Controll M.F. 574®, in natural water, with a concentration below 1.0 mg L^{-1} in order to be applied for the treatment of water for public supply. Tests of the adsorption of iron and manganese in batches were performed to verify the adsorption capacity and adsorption rate by zeolite.

2. Materials and methods

2.1. Study area

Natural water evaluated in this study is from the source of supply of Water Treatment Plant, Jurere Internacional neighbourhood, located in Florianopolis-SC, Brazil.

2.2. Adsorbent material

The adsorbent material employed in this study was the commercial zeolite, Controll M.F. 574® supplied by the Controll Master Industrial located in Sete Lagoas, Minas Gerais, Brazil. The composition of this material is based in minerals of oxides of iron and manganese and the particle size used in adsorption experiments ranged from 0.355 to 0.850 mm according to the manufacturer.

2.3. Characterization of adsorbent material

2.3.1. Morphological and elemental analysis

The zeolite was characterized using a scanning electron microscope combined with an X-ray energy dispersive spectrometer (Philips XL 30). A sample of the adsorbent material was plated with a thin layer of gold plating on a P-S2 Diod Sputtering System.

2.3.2. X-ray diffraction

The chemical composition of the zeolite was obtained by X-ray diffractogram (XRD) from the powdered sample at room temperature on a Philips X'Pert diffractometer with Cu K_α radiation ($\lambda = 1.54056$ Å). The 2θ scan was performed at 0.01 degrees every 2 s.

2.4. Leaching test

This test was conducted to evaluate the characteristics of the zeolite wash effluent and to determine whether it satisfies the effluent requirements of Resolution 357/2005 of the Brazilian National Council on the Environment (CONAMA) [33].

In an Erlenmeyer (500 mL) flask, 10 g of zeolite was added to 200 mL of ultra-pure water (pH 6.21). This Erlenmeyer was constantly agitated (29 rpm) for 18 h at room temperature. After the test, the supernatant was filtered through a cellulose acetate membrane (0.45 μm porosity) to remove suspended solids, and then, the pH was determined (pH meter Alfakit—AT 310). The filtrate was placed in polyethylene bottles and acidified with HNO_3 (1.0%) for subsequent chemical analysis by Inductively Coupled Plasma-Mass Spectrometry (model Elan 6000 Perkin-Elmer Sciex, Thornhill, ON, Canada) [34].

2.5. Batch sorption experiments

As a first step, the batch tests may help in choosing the composition of new filter media, unlike conventional filter (sand + anthracite coal). For this, tests of adsorption isotherm and adsorption kinetic were conducted to evaluate the adsorption of Fe and Mn.

2.5.1. Adsorption isotherm

The adsorption isotherm of iron and manganese was determined to assess the potential for adsorption of these metals by zeolite because this could be used in filtration systems of water treatment processes for public supply.

In this test, a stock synthetic solution was prepared with $FeSO_4.7H_2O$ (160 mg L^{-1}) and $MnSO_4.H_2O$ (130 mg L^{-1}). The solution was pH-adjusted with Na_2HPO_4/NaH_2PO_4 buffer to approach the value found in natural waters. Fe and Mn were measured using the colorimetric methods Ferrozine® (L.D.: 0.009 mg L^{-1}) and PAN® (L.D: 0.007 mg L^{-1}), respectively, on a HACH Spectrophotometer—DR/4000U [35].

To perform the adsorption isotherm experiments, several solutions with different concentrations of Fe and Mn (0.05–100 mg L^{-1}) were prepared by dilution of the stock synthetic solution. In individual Erlenmeyer flasks (125 mL), 0.200 grams of zeolite was weighed and added to 50 mL of solution with different Fe and Mn contents. The solution was stirred for 24 h to ensure that equilibrium was reached. The supernatants were filtered through a cellulose acetate membrane (0.45 μm porosity) to remove suspended solids. The filtrates were placed in polyethylene bottles to directly determine the remaining concentrations of Fe and Mn using the colorimetric methods mentioned above.

The amount of metal adsorbed was calculated according to Eq. (1), in which q (mg g^{-1}) is the amount of metal, V (L) is the volume of the solution and m (g) is the weight of the adsorbent. C_0 and C_f are the concentrations (mg L^{-1}) at the initial and final time, respectively.

$$q = \frac{C_0 - C_f}{m(\mathrm{g})} \times V(\mathrm{L}) \tag{1}$$

Among the models used for the interpretation of the experimental adsorption data, a linear model is often used to describe the interactions between sorbent and sorbate. This model proposes that the accumulation of the metal in the adsorbent is directly proportional to the concentration of the metal in the solution, represented by Eq. (2):

$$q_e = k_d \times C_e \tag{2}$$

where q_e is the equilibrium amount adsorbed in mg g^{-1}, C_e is the equilibrium concentration of sorbate in solution in mg L^{-1} and k_d is the distribution constant in L g^{-1} of adsorbent.

Another model also widely used in interpreting the results of adsorption is the Langmuir isotherm model, which proposes a homogeneous surface and adsorption sites of the same energy to the material (i.e. a monolayer adsorption) consistent with a process of chemisorption [36]. This model is represented by Eq. (3):

$$q = \frac{q_m \times k_{\text{ads}} \times C_e}{1 + k_{\text{ads}} \times C_e} \tag{3}$$

where q is the amount adsorbed in mg g^{-1}, q_m is the maximum adsorption capacity in mg g^{-1}, k_{ads} is the equilibrium constant of adsorption and C_e is the equilibrium concentration in mg L^{-1}

With the linearization of (3), it is possible to calculate the values of q_m and k_{ads} through the graphs of (C_e/q) vs. C_e. The linear representation of this model is described by Eq. (4):

$$\frac{C_e}{q} = \frac{1}{k_{\text{ads}} \times q_m} + \frac{C_e}{q_m} \tag{4}$$

The essential characteristics of a Langmuir isotherm can be described by a dimensionless constant called an equilibrium parameter, R_L, which is usually defined by Eq. (5) [28]:

$$R_L = \frac{1}{(1 + C_0 \cdot k_{\text{ads}})} \tag{5}$$

where C_0 is the highest initial ion concentration (mg L^{-1}) and k_{ads} is the Langmuir constant that indicates the nature of the adsorption. The value of R_L indicates the type of adsorption isotherm to be either unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$).

2.5.2. Adsorption kinetics

Kinetics informs the rate of adsorption of metal ions on the adsorbent. These tests determine the minimum contact time required to achieve an adequate efficiency of the adsorbent because this material could be applied at large scales.

For kinetic experiments, a sample of natural water was collected (2,000 mL) from the water treatment plant in Jurere Internacional—Florianopolis, SC, Brazil. This sample was stored in a pre-cleaned plastic container and refrigerated.

For comparison, a combined synthetic solution of $FeSO_4.7H_2O$ and $MnSO_4.H_2O$ was prepared to determine how the possible presence of humic substances in natural water interferes with the removal of Fe and Mn by the adsorbent material. The pH of the synthetic solution was adjusted with a buffer solution Na_2HPO_4/NaH_2PO_4 to a value close to the pH of the natural water sample. Table 1 shows the physico-chemical properties of the samples used in kinetic experiments.

In individual Erlenmeyer flasks (125 mL), 0.500 g of zeolite was weighed and added to 50 mL of sample (NW or SS) with known concentration of Fe and Mn (Table 1). The shaking time varied from 5 to 300 min. The supernatants were filtered through a cellulose acetate membrane (0.45 μm porosity) to remove suspended solids. The filtrates were placed in polyethylene bottles to directly determine the remaining concentrations of Fe and Mn using the colorimetric methods Ferrozine® and PAN®, respectively, on a spectrophotometer HACH—DR/4000U [35].

Aiming to verify the kinetic mechanism governing the adsorption of Fe and Mn by the adsorbent material, the kinetic data were evaluated following the kinetic models of pseudo-first-order, pseudo-second-order and intraparticle diffusion.

The kinetic model of pseudo-first-order is represented by Eq. (6):

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} \times t \tag{6}$$

where k_1 (min^{-1}) is the rate constant for the pseudo-first-order adsorption, q_t and q_e (mg g^{-1}) is the amount adsorbed at time t (min) and at equilibrium, respectively. The graph of log ($q_e - q_t$) vs. t gives the values of k_1 and q_e.

The pseudo-second-order model based on the adsorption capacity at equilibrium can be expressed by Eq. (7):

$$\frac{t}{q_t} = \frac{1}{k_2 \times q_e^2} + \frac{1}{q_e} \times t \tag{7}$$

Table 1
Physico-chemical properties determined for the samples of the kinetic experiments

Parameters	Zeolite	
	NW*	SS*
pH	7.90	7.20
Conductivity (mS cm^{-1})	0.374	6.20
Turbidity (UT)	4.70	–
Temperature (°C)	20	20
Fe (mg L^{-1})	0.322	0.216
Mn (mg L^{-1})	0.123	0.136

*NW—natural water; SS—synthetic solution.

where k_2 (g mg^{-1} min^{-1}) is the pseudo-second-order adsorption rate constant. From the intercept and the slope of the (t/qt) vs. t graph, k_2 and q_e can be obtained.

It is important to have a material that removes large amounts of sorbate in a short period of time. Rearranging Eq. (7), the initial rate of adsorption can be determined for the adsorbent material [37].

Replacing the term ($k_2\ x\ q_e^2$) by h, we have Eq. (8). Therefore, the intercept ($1/h$) allows the initial adsorption rate to be calculated, which is given in mg g^{-1} min^{-1}.

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} \times t \tag{8}$$

The intraparticle diffusion kinetics consists of a simple model where the rate of intraparticle diffusion can be obtained by the linearization of the curve represented by Eq. (9):

$$Q_t = k \times t^{1/2} \tag{9}$$

The validity of these models can be interpreted by the linearity of the graphs $\log(q_e - q_t)$ vs. t, (t/q_t) vs. t and q_t *vs* $t^{1/2}$, respectively. A positive correlation of kinetic data can indicate the mechanism of adsorption of Fe and Mn by the adsorbent material.

3. Results and discussion

3.1. Characterization of adsorbent material

3.1.1. Morphological and elemental analysis

Fig. 1 shows the micrographs of the zeolite, Controll M.F. 574®. With a magnification of 33 times, Fig. 1(a) shows the variation of particle size of zeolite, the average value varies between 0.477 and 0.975 mm, an approximate value that is consistent with the size reported by the manufacturer. Fig. 1(b) represents a magnification of 10,000 times that reveals the irregular structure of the zeolite that may facilitate its adsorbent properties. The results obtained by semi-quantitative elemental analysis of the zeolite showed the presence of manganese, aluminium, iron, silicon and oxygen (64.57, 7.14, 3.25, 6.96 and 18.08% by weight, respectively), as majority elements.

3.1.2. X-ray Diffraction

This analysis evaluated the crystallinity of the adsorbent material. The XRD pattern obtained for the zeolite, Controll M.F. 574®, showed a semi-crystalline structure (i.e. a simultaneously crystalline and amorphous structure). As can be seen in Fig. 2, this is confirmed by the presence of well-defined peaks and small bands. Moreover, this analysis revealed principal minerals such as magnetite ($FeO.Fe_2O_3$), pyrope ($Mg_3Al_2(SiO_4)_3$), quartz (SiO_2), manganese oxide (Mn_3O_4), hematite (Fe_2O_3) cryptomelane ($K(Mn^{4+}, Mn^{2+})Mn_8O_{16}$) and groutite ($MnO(OH)$). These minerals suggest that the material is a zeolite. Furthermore, manganese oxides present in materials, such as zeolites, quartz sand, glauconite, anthracite, sulpho-coal, clinoptilolite and chabazite can act as catalysts for the oxidation of Mn^{2+} assisting in the removal of this metal [29].

3.2. Leaching test of the adsorbent material

Table 2 presents the concentrations of elements in the leachate of the zeolite, Controll M.F. 574®, and their maximum allowed values (MAV) for the effluent discharge as established in Resolution CONAMA 357/2005. The pH of the leachate (pH 5.15) was lower

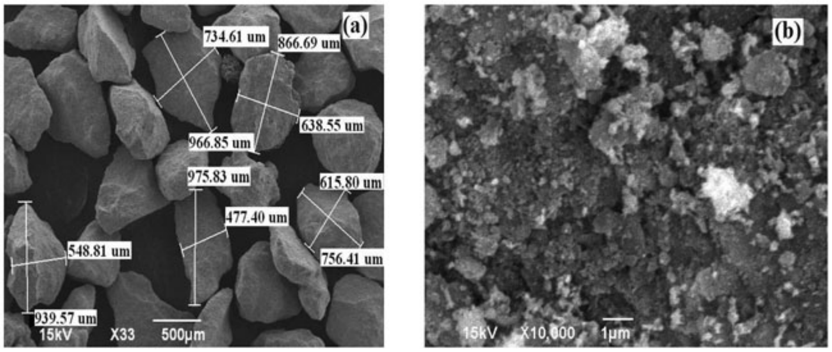

Fig. 1. Scanning electron micrograph of zeolite, Controll M.F. 574®; with a magnification of 33 times (a) and 10,000 times (b).

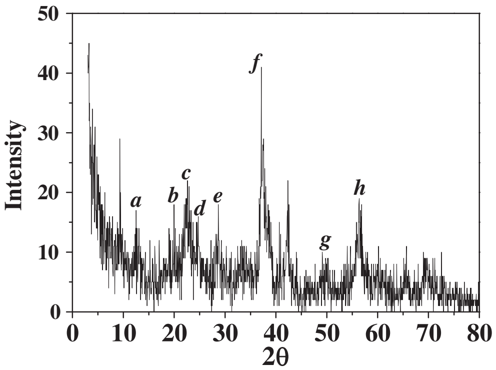

Fig. 2. XRD of the zeolite sample. (a) cryptomelane; (b and d) quartz; (c) hematite; (e) magnetite; (f) manganese oxide; (g) pyrope and (h) groutite.

than the initial pH of the water (pH 6.21). Among all the analysed elements, Mn was the metal that showed higher leaching. However, all values are in accordance with the parameters determined by CONAMA 357/2005. Under the conditions employed in this assay, the elements present and their concentrations in the leachate allow its discharge in a water receptor body without causing environmental problems.

3.3. Adsorption experiments

The present study focuses to determine the ability of the zeolite to remove iron and manganese from natural water for public supply, whose recommended pH is 6–9.5 [15]. In this pH range, adsorption mechanism is prevalent. At higher pH values result in precipitation of the metallic hydroxides and lower pH values could result in predominant ion exchange processes. For these reasons, studies about effect of pH on the adsorption of iron and manganese and determination of ion exchange capacity were not developed, just studies about adsorption (isotherm and kinetics) [28,38,39].

3.3.1. Adsorption isotherm

Fig. 3 represents the relationship between the amount of Fe and Mn adsorbed on the surface of zeolite, Controll M.F. 574®, and the concentration remaining in solution at equilibrium. Only the adsorption of Fe onto the zeolite followed the linear isotherm model, indicating a process of physical adsorption (Fig. 3(a)). As the concentration of metals increases, the adsorption by the zeolite also increases. This indicates that the material used has a good adsorption capacity for this metal. This model fits well with the experimental data because the linearization of the equation has a good correlation coefficient ($R^2 = 0.999$). Other adsorbent materials, such as decomposed leaf matter, activated carbon and clinoptilolite-rich tuff, for iron, manganese and iron–manganese systems, showed a different behaviour from this zeolite. Some materials showed a Freundlich [10] or Langmuir [40,41] model isotherm. These models suggest a saturation of the materials because they determine a maximum adsorption capacity for the metals.

Table 2
Results of the leaching tests for zeolite

	Standards for effluent discharge (mg L^{-1}) Resolution CONAMA 357/2005[a]	Concentration in the leachate (mg L^{-1}) Zeolite
pH	5–9	5.15
As	0.5[b]	0.12×10^{-3}
Cd	0.2[b]	0.04×10^{-3}
Cr	0.5[b]	3.84×10^{-3}
Cu	1.0[c]	1.25×10^{-3}
Fe	15.0[c]	0.01
Mn	1.0[c]	0.45
Ni	2.0[b]	0.05
Pb	0.5[b]	0.07×10^{-3}
Se	0.3[b]	<LOD[d]
Zn	5.0[b]	0.02

[a] Standard for discharging effluent into water bodies (Resolution CONAMA—357/2005).

[b] Total metal.

[c] Concentration of metal.

[d] <LOD—below the limit of detection of the technique.

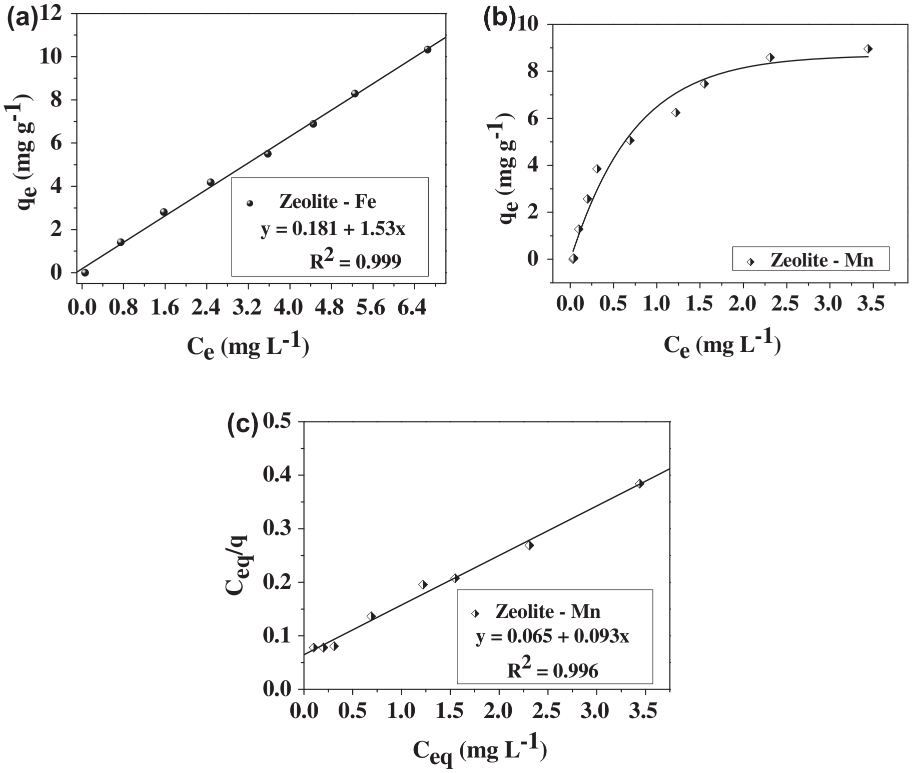

Fig. 3. Amount of Fe (a) and Mn (b) adsorbed at equilibrium by the zeolite, Controll M.F. 574®; (c) linearization of the Langmuir equation for the adsorption of Mn by the zeolite.

By contrast, the Mn adsorption by the zeolite, Controll M.F. 574®, was better adjusted to the Langmuir model (Fig. 3(b)). This indicates the formation of a monolayer on the surface of the adsorbent. The linearization of the model, Fig. 3(c), indicates a maximum capacity ($q_m = 10.75\,\mathrm{mg\,g^{-1}}$) and the value for k_{ads} was 1.43 L $\mathrm{mg^{-1}}$. Thus, the value R_L was found to be 0.017, which indicates a favourable adsorption process. Taffarel and Rubio [28] evaluated the adsorption of manganese in a Chilean natural zeolite and also observed the same behaviour for the adsorption of metal, but with a lower adsorption capacity ($q_m = 7.14\,\mathrm{mg\,g^{-1}}$) than that observed in the present study. García–Mendieta et al. [10] founded that the best model describing the adsorption of iron and manganese in the Mexican clinoptilolite-rich tuff was the Freundlich model. However, the adsorption capacity of this material ($q_m\mathrm{Fe} = 6.49\,\mathrm{mg\,g^{-1}}$ and $q_m\mathrm{Mn} = 3.82\,\mathrm{mg\,g^{-1}}$) was lower when compared to the Controll M.F. 574® zeolite.

3.3.2. Adsorption kinetics

The adsorption kinetics describes the rate of adsorption of Fe and Mn in the adsorbent. This rate refers to the contact time of ions at the solid–liquid interface. Three models of adsorption kinetic were applied to evaluate the experimental data for adsorption of Fe and Mn onto zeolite, Controll M.F. 574®, from natural water and synthetic solution; the results are shown in Fig. 4 and Table 3. After 5 min of contact, the zeolite adsorbed 56% of Fe from the natural water and only 6% from the synthetic solution (Fig. 4(a)). The kinetics of the adsorption of Fe from synthetic solution was faster than that in natural water, but the zeolite removed a greater amount of Fe from natural water. Equilibrium was reached at 200 min and the Fe removal from the synthetic solution and natural water was 30 and 74%, respectively. Fig. 4(b) shows the kinetic profile of adsorption of Mn onto zeolite from two water samples. A similar behaviour for both samples was observed. It should be noted that the adsorption of Mn in the first 5 min was more efficient from the synthetic solution (30%) than from natural water (12%). Although the adsorption kinetics was also faster for the synthetic solution than for natural water, in both cases equilibrium was reached approximately 120 min, obtaining a removal of 65% and 59% from the natural water and synthetic solution, respectively.

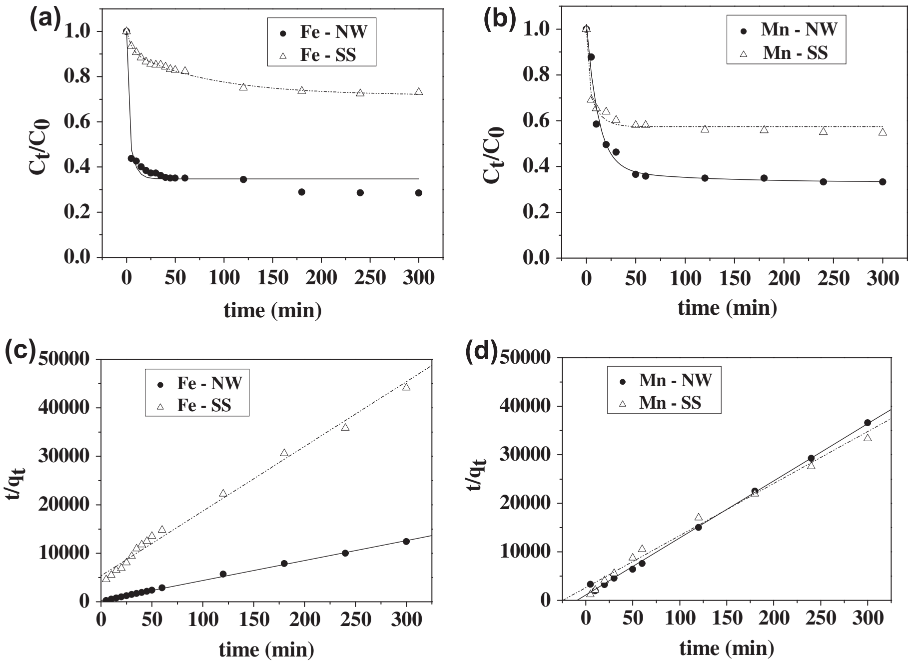

Fig. 4. Kinetics of the adsorption of Fe (a) and Mn (b) by zeolite over time. Linearization of the pseudo-second-order model of Fe (c) and Mn (d) for the natural water samples and synthetic solution.

At 300 min, the removal of Mn (66%) for both water samples reached a maximum.

The percentage of Fe removal was higher for the natural water than that for the synthetic solution, whereas the percentage of Mn removal was the same for both samples. After treatment, the concentrations of Fe and Mn in natural water were (0.08 and 0.04 mg L^{-1}), below the MAV established by Brazilian legislation (0.3 and 0.1 mg L^{-1}, respectively) for drinking water [15].

Table 3 presents the data for the adsorption models of Fe and Mn by zeolite both from the natural water and the synthetic solution. A comparison of the correlation coefficients indicates that Fe and Mn adsorption onto the zeolite does not follow a pseudo-first-order reaction for both samples. The $q_{e,\mathrm{cal}}$ values obtained from the pseudo-first-order kinetic model were not satisfactory and the values were also low when compared with the $q_{e,\mathrm{exp}}$ values. Additionally, the intraparticle diffusion model presents a non-linear distribution and therefore cannot be considered as a determining model in the Fe and Mn adsorption rate on zeolite. However, the correlation coefficients for the pseudo-second-order kinetic model were $R^2 = 0.99$ for the adsorption of Fe and Mn in both samples, and the $q_{e,\mathrm{cal}}$ values agreed well with the $q_{e,\mathrm{exp}}$ data. The relative error was less than 10% for adsorption of Fe and less than 3.7% for the adsorption of Mn. Therefore, the pseudo-second-order model best fit the experimental data. The graphs representing t/q_t vs. t (Fig. 4(c) and (d)) show the linearization of Eq. (7) obtained through the pseudo-second-order model for the adsorption of Fe and Mn, respectively, in the zeolite for both samples. This model is based on the assumption that the rate-limiting stage can be a chemical adsorption process involving valence. This model is consistent with the data obtained by Taffarel and Rubio [28].

Among the values for the rate constants (k_2) calculated using the pseudo-second-order model for the zeolite, the process that showed higher adsorption was the adsorption of Mn from natural water (12.7 g mg^{-1} min^{-1}). Regarding the initial rates of adsorption, Fe ($h = 3.79 \times 10^{-3}$ g mg^{-1} min^{-1}) from the natural water was the most rapidly adsorbed to the zeolite. This speed was 20 times faster than the initial rate of adsorption of Fe in the synthetic solution. The initial rate of adsorption of Mn from natural water by zeolite was two-times higher than the rate of adsorption of the synthetic solution. These results are tentatively attributed to the presence in the natural water of humic compounds, capable of complexing metallic ions, thus facilitating their removal, and whose study is now being carried out.

Table 3
Kinetic models and their parameters obtained from the kinetic adsorption of Fe and Mn in the zeolite from natural water and the synthetic solution

	NW*		SS*	
	Fe	Mn	Fe	Mn
Pseudo-first-order				
Equation	$y = -2.21-5.1 \times 10^{-3}x$	$y = -2.55-8.3 \times 10^{-3}x$	$y = -2.23-6.0 \times 10^{-3}x$	$y = -2.25-4.7 \times 10^{-3}x$
R^2	0.929	0.849	0.949	0.954
k_1[a]	0.012	0.019	0.014	3.0×10^{-4}
$q_{e,\text{cal}}$[b]	6.0×10^{-3}	3.0×10^{-3}	5.9×10^{-3}	55.9×10^{-4}
$q_{e,\text{exp}}$[c]	0.024	8.2×10^{-3}	6.8×10^{-3}	9.0×10^{-3}
R_e(%)[d]	74.7	65.6	13.3	37.8
Pseudo-second-order				
Equation	$y = 263.3 + 41.18x$	$y = 1{,}092 + 117.7x$	$y = 5{,}359 + 133.5x$	$y = 2{,}633 + 107.2x$
R^2	0.999	0.999	0.992	0.989
k_2[e]	6.44	12.68	3.32	4.36
$q_{e,\text{cal}}$[b]	24.3×10^{-3}	8.5×10^{-3}	7.5×10^{-3}	9.3×10^{-3}
$q_{e,\text{exp}}$[c]	24.2×10^{-3}	8.2×10^{-3}	6.8×10^{-3}	9.0×10^{-3}
h[f]	3.8×10^{-3}	9.2×10^{-4}	1.9×10^{-4}	3.9×10^{-4}
R_e%	0.40	3.68	10.2	3.6
Intraparticle diffusion				
Equation	$y = 0.02 + 3.7 \times 10^{-4}x$	$y = 4.5 \times 10^{-3} + 2.8 \times 10^{-4}x$	$y = 1.1 \times 10^{-3} + 3.5 \times 10^{-4}x$	$y = 3.5 \times 10^{-3} + 3.2 \times 10^{-4}x$
R^2	0.967	0.720	0.988	0.975
k[g]	3.0×10^{-4}	3.0×10^{-4}	4.0×10^{-4}	3.0×10^{-4}

*NW—natural water; SS—synthetic solution.

[a] k_1: adsorption rate constant of pseudo-first-order (min^{-1}).

[b] $q_{e,\text{cal}}$: amount calculated adsorbed in equilibrium (mg g^{-1}).

[c] $q_{e,\text{exp}}$: amount experimental adsorbed in equilibrium (mg g^{-1}).

[d] R_e: relative error (%).

[e] k_2: adsorption rate constant of pseudo-second-order ($\text{g mg}^{-1}\,\text{min}^{-1}$).

[f] h: adsorption initial velocity ($\text{mg g}^{-1}\,\text{min}^{-1}$).

[g] k: adsorption rate constant of intraparticle diffusion ($\text{mg g}^{-1}\,\text{min}^{-1/2}$).

4. Conclusions

Characterization tests employing EDX and XRD identified magnesium aluminium silicate, quartz and various oxides of manganese and iron, in zeolite, Controll M.F. 574®.

The results for the parameters evaluated by the leaching test showed that the leachate from the zeolite is in accordance with the effluent discharge standards set by Resolution CONAMA 357/2005. Therefore, the leachate can be disposed off in receptor water bodies.

In adsorption tests, the adsorption of Fe onto the zeolite followed a linear isotherm model indicating a process of physical adsorption. However, the adsorption of Mn was better adjusted to the Langmuir model, indicating the formation of a monolayer on the surface of the adsorbent.

Regarding kinetic parameters, the pseudo-second-order model best fit the results because the correlation coefficient was $R^2 = 0.99$ in adsorption of Fe and Mn in both samples. The adsorption of the metals showed a chemical interaction (chemisorption) that depends on the concentration of metal ions on the surface of adsorbent and adsorbed ions in equilibrium.

Finally, tests performed for the adsorption of Fe and Mn employing a commercial zeolite, Controll M.F. 574®, showed good adsorptive capacity and good efficiency for removal Fe (74%) and Mn (66%) in natural water, with concentrations lower than $1.0\,\text{mg L}^{-1}$, according to Brazilian legislation.

According to these results, this material could be tested on a pilot scale in order to evaluate the efficiency in a continuous flow, and further be applied in real scale as an alternative material and increase the efficiency of removal of these metals.

Acknowledgements

This research was supported by Foundation for Coordination of Personal Improvement in Higher

Education (CAPES) and the Department of Environmental and Sanitary Engineering of University Federal of Santa Catarina (UFSC). We thank the Controll Master Industrial located in Sete Lagoas, Minas Gerais—Brazil for supplying a sample of the zeolite, Controll M.F. 574®.

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