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ADSORPTION OF Zn^{2+}, Cd^{2+} AND Cu^{2+} ON ZEOLITES COATED BY MANGANESE AND IRON OXIDES

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Abstract: Adsorption of copper, cadmium and zinc on manganese and iron oxide coated zeolite from aqueous solution was investigated in a batch mode. Experiments were conducted to investigate the effects of the initial concentration of metals, initial pH, contact time and temperature on the adsorption of ions. According to the results, adsorption of ions on manganese and iron oxide coated zeolite increased with the enhancement of initial Cu^{2+}, Zn^{2+} and Cd^{2+} concentrations and contact time and also with increase of temperature. The results showed that at the beginning, the adsorption rate of Cu^{2+} and Cd^{2+} was more than 90 %. This rate continued to be slower for Zn^{2+} in both zeolites. Furthermore, the amount of Cu^{2+}, Zn^{2+}, and Cd^{2+} adsorption on the manganese oxide coated zeolite (q_e) was equal to 14 mg/g, 9 mg/g and 16 mg/g and on the iron oxide coated zeolite it was 11 mg/g, 7 mg/g and 13mg/g, respectively. It was shown that at the concentrations below 100 mg/dm^3 adsorption was rapid and almost all heavy metals were adsorbed. As a result, the significant factor affecting q_e is the proportion of weight to liquid and pH in the solutions. Finally, the results showed that the adsorption of Zn^{2+}, Cu^{2+} and Cd^{2+} onto the manganese oxide coated zeolite followed both the Langmuir and Freundlich isotherm models.

Keywords: *adsorption, wastewater, manganese oxide, iron oxide, zeolite*

Introduction

There are many natural and synthesized adsorbents used in various applications (Bao et al., 2013; Ciesielczyk et al., 2013; Farghali et al., 2013; Merrikhpour and Jalali, 2013; Sen and Khoo, 2013; Arshadi et al., 2014; Dawodu and Akpomie, 2014; Mehdizadeh et al., 2014; Bartczak et al., 2015; Klapiszewski et al., 2015). Some natural minerals such as zeolites are known as low-cost adsorbents (Babel and Kurniawan, 2003; Han et al., 2006). Due to the low capacity of these natural minerals, activation of zeolites is commonly carried out using chemical reagents such as metal oxides (Al-Degs et al., 2000; Al-Ghouti et al., 2005; Han et al., 2006). Natural zeolite

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modified by iron oxide (FeOCZ) has a high capability to adsorb high concentrations of heavy metals from solutions. According to literature, the FeOCZ has a higher specific surface area. This characteristic results in a higher amount of adsorption of this modified zeolite than that of unmodified zeolites (Doula and Dimirkou, 2008). With respect to some studies (Doula, 2007; Doula and Dimirkou, 2008), the FeOCZ surface has a high negative charge and this makes heavy metal cations adsorb on the adsorbent under acidic conditions. For instance, the iron-modified system could adsorb higher amount of Cu^{2+} and Mn concentrations in comparison with natural zeolite (Maria, 2006; Doula, 2007). The successful elimination of Mn^{2+} and Zn^{2+} ions was carried out using the clinoptilolite-iron oxide system (Dimirkou and Doula, 2008). Such a system was used to eliminate Cu^{2+} and Zn^{2+} from drinking water (Dimirkou, 2007; Doula and Dimirkou, 2008). In addition, lead can be efficiently removed from solutions using iron-modified zeolite (Kragovic et al., 2012).

Manganese oxide has the capability of metal adsorption (Catts and Langmuir, 1986; Fu et al., 1991). The pure manganese oxide cannot be applied to remove ions due to economic reasons and its undesirable chemical and physical properties. Thus, it is used as a coating layer on the surface of adsorbents. This coating provides an effective surface for heavy metal adsorption removal from aqueous solution (Taffarel and Rubio, 2010). In this regard, Taffarel and Rubio (2010) investigated Mn^{2+} removal from aqueous solution using zeolite coated by manganese oxide (MnOCZ). In a similar research, Cu^{2+} and Pb^{2+} were adsorbed from aqueous solutions using MnOCZ (Han et al., 2006; Zou et al., 2006). In addition, MnOCZ has been used to remove uranium(VI) from aqueous solutions (Han et al., 2007; Zou et al., 2009). All of the literature thus far shows the efficient usage of MnOCZ in heavy metal ions elimination.

In this paper, two modified adsorbents, namely manganese oxide coated zeolite (MnOCZ) and iron oxide coated zeolite (FeOCZ) were used to remove heavy metal ions from model solutions. Copper, zinc and cadmium ions as contaminated metals in the aqueous environment were chosen to be removed by modified zeolites. The paper specifically shows the effect of experimental parameters such as pH, contact time, metal concentration, and temperature on the adsorption process. The adsorption isotherm and competitive effects between copper, zinc and cadmium ions on the sorption capability of MnOCZ, FeOCZ and the description of the kinetics of metal removal by MnOCZ are the main aims of this research.

Material and methods

Materials

Samples of natural zeolite were taken from the Abegarm mine (Semnan, Iran) as an affective adsorbents. According to the XRD analysis, the crystalline phase composition of the natural zeolite used in this work was almost 75 % clinoptilolite and the remainder consisted of quartz and gypsum. The exchange cations were Ca^{2+}, Mg^{2+},

Na^+, and K^+ with prevalence of the later. The chemical composition of the sample was obtained using XRF as presented in Table 1. As can be seen, natural clinoptilolite contained high levels of SiO_2 (61.0 %) and Al_2O_3 (9.3 %). The contents of the other metal oxides were less than 10 %. Furthermore, $Fe(NO_3)_3$, KOH, $MnCl_2·4H_2O$ and $KMnO_4$ from Merck were used in modification systems. In order to obtain sulfate solutions containing various metal ions, $CuSO_4·5H_2O$, $3CdSO_4·8H_2O$, $ZnSO·7H_2O$ were purchased from Merck Co. All of the salts were dissolved in deionized water. The other chemical materials used in this study were purchased from Merck Co.

Sample preparation

Modification of natural zeolite with iron oxide

The aim of chemical conditioning is removing certain cations from the structure of the zeolite and substituting more easily removable ones before any application. The Fe-modified sample was made by following the method of pure goethite preparation. The sample was prepared by mixing 30 g of clinoptilolite, 100 cm^3 of 1 M $Fe(NO_3)_3$ solution, and 180 cm^3 of 5 M KOH solution in a polyethylene flask. The pulp was diluted to 2 dm^3 with water and was kept at 70 °C for 60 h. Then, the precipitate was washed (until free of NO_3^- ions) and finally dried for one day.

Modification of natural zeolite with manganese oxide

The preparation of MnO_2 coated zeolite was performed as follows: (a) the raw zeolite was sieved to obtain different particle size fractions (0.42-0.50 mm); (b) the zeolite was washed with deionized water, filtered and dried at 70 °C for 1 h; (c) the obtained sample was ion-exchanged with $MnCl_2$ aqueous solutions (i.e. 0.1 M) with a liquid to solid ratio of 15:1 (i.e. 300 cm^3 solution per 20 g of raw zeolite) at 25 °C for 5 h; (d) the ion-exchanged zeolite was washed with deionized water, filtered and dried at 70 °C for 1 h; (e) 10 g of the obtained solid powder was agitated with 100 cm^3 of 0.1 M $KMnO_4$ solution with the initial pH of 6 for 1 h under shaking; (f) the final solid product (MnO_2 coated zeolite) was washed with deionized water, filtered and dried at 70 °C for 1 h. MnO_2 powder was synthesized in the absence of Mn by reacting aqueous solutions of $KMnO_4$ (100 cm^3, 0.1 M) and $MnCl_2$ (300 cm^3, 0.1 M) for 30 min.

Table 1. Chemical composition of natural clinoptilolite sample (wt. %)

Compound	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	SO_3	LOI (Loss of Ignition)
Weight (%)	61.0	0.23	9.30	1.30	3.58	0.68	3.58	2.58	2.70	13.90

Batch adsorption studies

In order to investigate the adsorption behavior of Zn^{2+}, Cu^{2+} and Cd^{2+}, an amount of 1.0 g modified clinoptilolite was agitated with 100 cm^3 of metal solution at a fixed agitation speed of 1000 rpm and appropriate time. According to the investigated parameter, the experiments were conducted at various temperatures (i.e. 20 °C, 40 °C and 60 °C), initial metal concentrations of 50 – 500 mg/dm^3, pH of 3 – 7, and time of 15 min to 90 min. In order to determine the amount of adsorption, aqueous solution obtained from the suspension were analyzed for Zn^{2+}, Cu^{2+} and Cd^{2+} concentrations using atomic absorption spectrometry (AAS) with an air-acetylene flame.

In order to construct adsorption isotherms, the following procedures were conducted. The amount of metal ion adsorbed on MnOCZ/FEOCZ (q_e) was calculated by Eq. (1):

$$q_e = \frac{C_i - C_e}{C}. \tag{1}$$

In this equation, C_i and C_e are the initial and equilibrated concentration ions in the solution (mg/dm^3), respectively. In addition, C is the concentration of adsorbent in the mixture (g/dm^3).

Determining the linear relationship of q and C_e was performed using Eq. (2)

$$q = a + b(C_e). \tag{2}$$

In order to find the constants a and b, linear regression was used. It is noteworthy that many sorbents exhibit linear isotherms at low concentrations.

Fitting data to the Langmuir isotherm model was based on Eq. (3)

$$\frac{C_e}{q_e} = \left(\frac{1}{bq_{max}}\right) + \left(\frac{1}{q_{max}}\right) C_e. \tag{3}$$

In this equation, C_e is the equilibrated concentration of ions (mg/dm^3), q_e is equilibrated ions adsorbed on unit mass of adsorbent (mg/g). Furthermore, q_{max} is considered maximum adoption capacity (mg/g) and b the adsorption energy (dm^3/mg). The Langmuir isotherm parameters q_{max} and b were determined from the slope ($1/q_{max}$) and intercept ($1/bq_{max}$) of the plot of C_e/q_e vs. C_e respectively.

Fitting data was done using the Freundlich model ND and Eq. (4):

$$Q = K_F C_e^{1/n}. \tag{4}$$

In this equation, K_F and $1/n$ are the Freundlich equilibrium and absolute constants, respectively. In order to determine the mentioned constants from the non-linear isotherms, the data was plotted in linear form by calculating the log of both sides of the equation:

$$\log(q) = \log K_F + 1/n \log C_e. \tag{5}$$

In this equation K_F is determined from intercept of linear plot and n can be obtained from the slope of equation.

Results and discussion

Effects of chemical treatment

In order to modify the surface of clinoptilolite, chemical treatment was carried out. This action makes certain cations easily exchangeable in the structure of the clinoptilolite (Irannajad et al., 2015). SEM micrographs illustrated in Fig. 1 show the morphological changes of the zeolite surface after chemical treatment with manganese and iron oxides. As shown in Fig. 1b, some places on the clinoptilolite surface were occupied by manganese dioxide after the coating process. It can also be seen that manganese oxide particles have grown in surface depressions and cracks. Furthermore, Fig. 1c illustrates iron oxide coating on the clinoptilolite surface. This figure also shows that iron oxide particles have formed clusters onto the clinoptilolite surface.

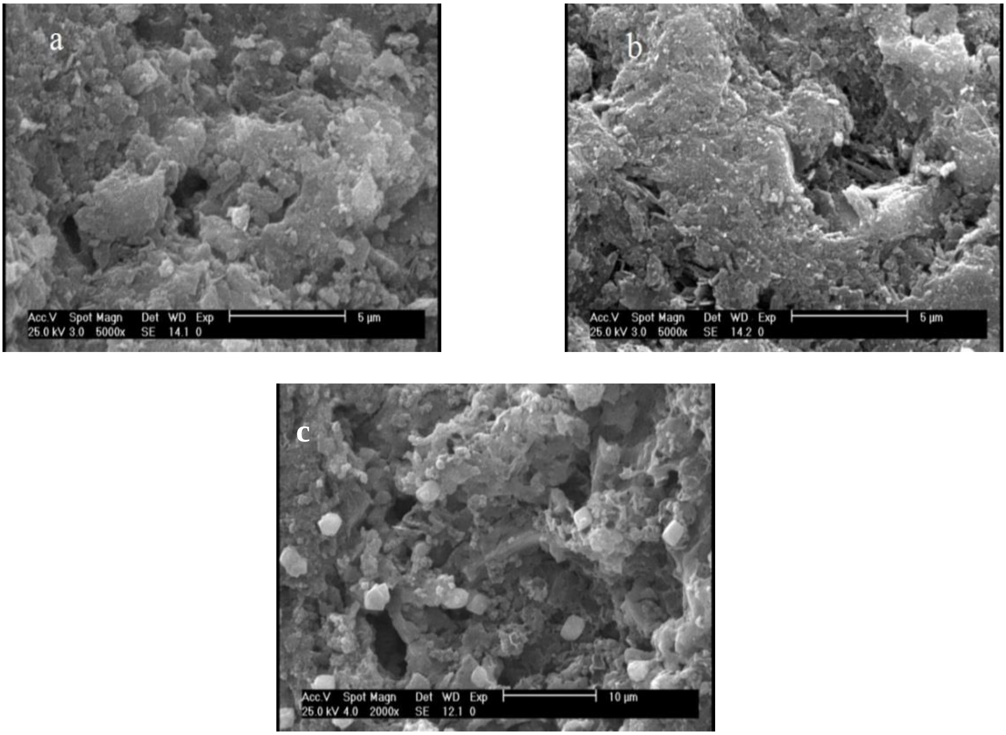

Fig. 1. SEM micrographs of: (a) natural, (b) MnCOZ and (c) FeCOZ clinoptilolite

According to literature, zeolites coated with manganese and iron oxide has higher specific surface area. This characteristic results in higher adsorption of this modified zeolite than that of unmodified zeolites (Doula and Dimirkou, 2008). Thus, it was predicted that the modified clinoptilolites efficiently adsorbed heavy metal ions from solutions.

Effect of equilibrium metal ion concentration

In order to find the effect of various initial concentrations of Cu^{2+}, Cd^{2+} and Zn^{2+} on the adsorption, a series of experiments was conducted at the condition being pH = 5.5, T = 20 °C, t = 30 min, FeOCZ = 1 g and Volume (V) =100 cm^3. The amount of metal adsorption by MnOCZ was plotted as a function of equilibrium concentration in Fig. 2a and 2b. It was clear that Cu^{2+}, Cd^{2+} and Zn^{2+} adsorption by MnOCZ and FeOCZ increased with an increase of the initial concentration. The reason is that by increasing the number of ions, the ion adsorption probability onto adsorbent increases. Furthermore, the higher availability of ions in solution increases q_e (Sen and Khoo, 2013). According to the maximum ion adsorption by MnOCZ and FeOCZ, the following was found: $Cd^{2+} > Cu^{2+} > Zn^{2+}$ (for FeOCZ), $Zn^{2+} > Cd^{2+} > Cu^{2+}$ (concentration < 200 mg/dm^3 for MnOCZ) and $Cd^{2+} > Cu^{2+} > Zn^{2+}$ (concentration > 200 mg/dm^3 for MnOCZ). As seen in these figures, the maximum amount of Cu^{2+}, Cd^{2+} and Zn^{2+} adsorption by FeOCZ was found to be 7.2 mg/g, 7.7 mg/g and 6.5 mg/g, respectively. In addition, the maximum amount of adsorption by MnOCZ for Cu^{2+}, Cd^{2+} and Zn^{2+} was determined to be 9.8 mg/g, 12.2 mg/g and 9.1 mg/g, respectively. These results indicate that the amount of adsorption of MnOCZ is higher than that of FeOCZ. As seen in Fig. 2a, the lower adsorption of zinc by FeOCZ in comparison with the other heavy metals can be seen. Similar results have been reported in literature (Langella et al., 2000; Panayotova and Velikov, 2002; Sheta et al., 2003; Peric et al., 2004; Hui et al., 2005; Oren and Kaya, 2006). With respect to the results, a metal concentration of 200 mg/dm^3 was selected as an optimum condition. This value was selected with respect to the removal efficiency. Since the removal efficiency inversely depends on metal concentrations; therefore, an initial concentration of 200 mg/dm^3 is the logical value. The removal efficiency at this concentration is higher than that at >200 mg/dm^3 and approximately close to the concentration of 100 mg/dm^3. At this initial concentration, metal ions with efficiency of > 90% were removed from both systems.

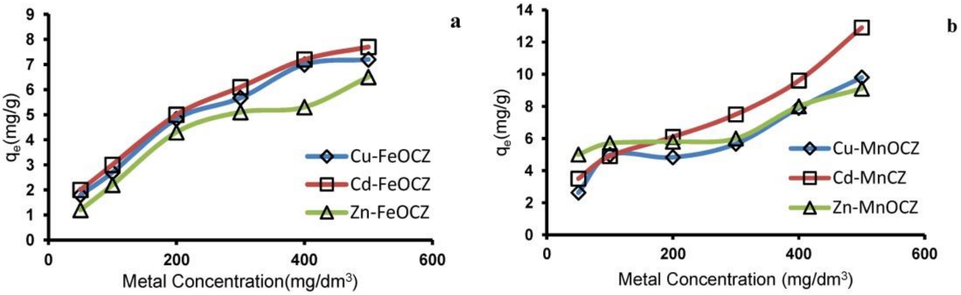

Fig. 2. Effect of initial concentration on adsorption of metal ions onto: (a) FeOCZ and (b) MnOCZ; pH_e = 5.5, T = 20 °C, t = 30 min, adsorbent = 1 g and V = 100 cm^3

Effect of contact time

Contact time is a significant factor because “this factor can reflect the adsorption kinetics” (Bao et al., 2013). The effect of contact time on the adsorption of Cd^{2+}, Cu^{2+} and Zn^{2+} on MnOCZ and FeOCZ was studied by changing time (15 – 120 min) in the initial ion concentration of 200 mg/dm^3. Figures 3a and 3b show the amount of ion adsorption as a function of time. As seen in Fig. 3a, Cd^{2+} adsorption by FeOCZ is high in the first 30 min of contact time. With prolonging time, the adsorption rate decreases and reaches a steady state. However, much more time is needed for Zn^{2+} and Cu^{2+} adsorption. In this regard, the appropriate time for all metal ions was found to be 60 min. In addition, as seen in Fig. 3b, adsorption of ions by MnOCZ reaches a steady state in 60 min of contact time. This is while 60 min is proper for Cd^{2+}, Zn^{2+} and Cu^{2+} adsorption. With respect to the mentioned figures, the adsorption of MnOCZ for all ions is higher than that of FeOCZ. According to the results, duration of 60 min was selected as an optimum condition for both systems. In order to compare the rate of adsorption of ions, the first-order kinetic model was used (Eq. 6):

$$\ln q_t = -kt + C \tag{6}$$

where q_t is the concentration of ion at time t, C is constant, and k is the first-order rate constant. Figures 4a and b show the first order kinetic models for adsorption of Cu^{2+}, Cd^{2+} and Zn^{2+} by FeOCZ and MnOCZ, respectively. As seen in Fig. 4a, the rate constants (k) of copper and zinc adsorptions by FeOCZ are approximately the same. However, the cadmium adsorption rate is lower than that of the other ions. Figure 4b shows the first-order kinetic equations for Cd^{2+}, Cu^{2+} and Zn^{2+} adsorption by MnOCZ. According to this figure, the adsorption rate constants of three ions are close together. However, the adsorption rate constant of copper is slightly higher than that of zinc and cadmium.

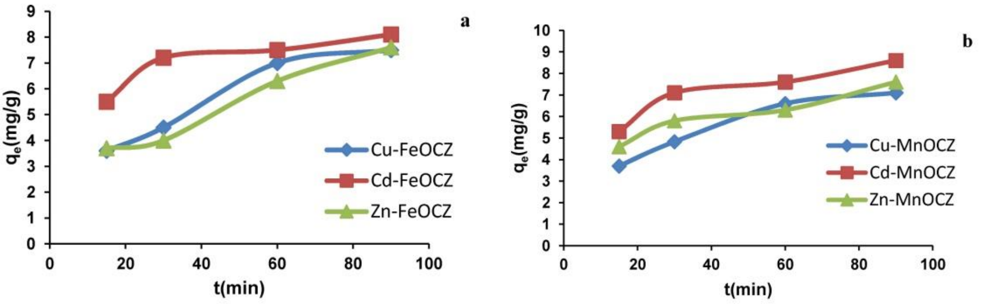

Fig. 3. Effect of contact time on adsorption of Cd^{2+}, Zn^{2+} and Cu^{2+} by: (a) FeOCZ and (b) MnOCZ; $pH_e = 5.5$, initial concentration of 200 mg/dm^3, $T = 20$ °C, adsorbent = 1 g and $V = 100$ cm^3

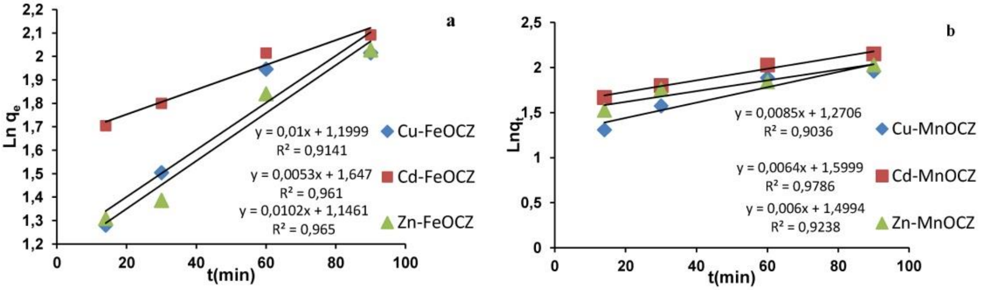

Fig. 4. The first-order kinetic equations for Cd^{2+}, Cu^{2+} and Zn^{2+} adsorption by (a) FeOCZ, (b) MnOCZ

Effect of pH

In order to study the effect of pH on adsorption, experiments were carried out in the pH ranges of 3–6 for Cu^{2+} and 3–7 for Zn^{2+} and Cd^{2+}. Figures 5a and 5b show that the adsorption of the metal ions was increased by increasing the initial pH of the solution and a maximum value was reached at pHs of 5.5, 7.0 and 6.0 for Cu^{2+}, Zn^{2+}and Cd^{2+}, respectively. In order to avoid the precipitation of metal ions in the form of their hydroxides, pHs above 5.5 for Cu^{2+} and 7 for Zn^{2+}and Cd^{2+} were not used. The suitable pH may change depending on the concentration of the metal ions in the solution. At a lower pH, adsorption of metal ions reduced due to their competition with H$^+$ ions for active adsorption sites (Farghali et al., 2013; Arshadi et al., 2014; Akpomie and Dawodu, 2015), whereas, at higher pHs, the presence of H$^+$ decreases on the adsorbent surface. Thus, the adsorption of metal ions increases (Kushwaha et al., 2012). Unmodified zeolite favorably tends to H$^+$ ions and adsorbs it from the solution in comparison to heavy-metal ions (Inglezakis et al., 2003; Sprynskyy et al., 2006). Thus, in acidic conditions, more H$^+$ ions are adsorbed. At higher pH values, with decreasing the H$^+$ ions, more heavy-metal ions are adsorbed from the solution as indicated by an enhancement in q_e (Moreno, 2001). According to this research, since “zeolites are not only affected by solution pH, but in turn are capable of affecting solution pH, they tend to have a higher internal pH”. Furthermore, the adsorption efficiency of ions generally enhanced when the initial pH of the solution was enhanced (Inglezakis et al., 2003; Hui et al., 2005; Sprynskyy et al., 2006; Coruh, 2008; Dimirkou and Doula 2008). As a result, the pH of 6 for both systems can be considered as an optimum condition because q_e of ions at this value is approximately high. After this pH, the precipitation of ions occurred and affected the systems.

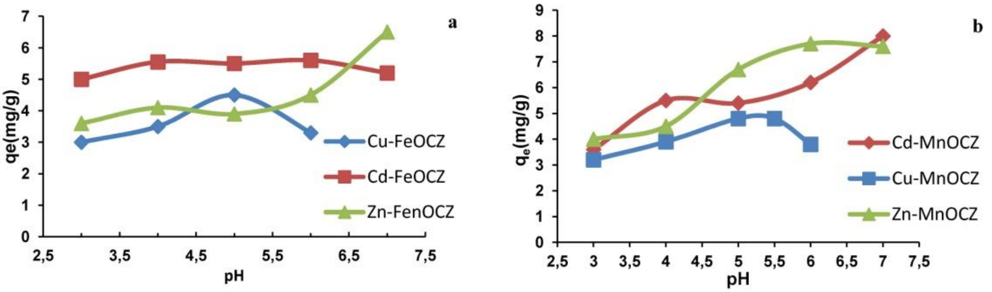

Fig. 5. Effect of pH on adsorption of Zn^{2+}, Cd^{2+} and Cu^{2+} onto: (a) FeOCZ and (b) MnOCZ; $T = 20$ °C, initial concentration = 200 mg/dm^3 $t = 60$ min, MnOCZ = 1 g and $V = 100$ cm^3

Effect of temperature

A series of experiments were determined to investigate the influence of temperatures (20 °C, 40 °C, 60 °C) on the metal adsorption. In these experiments, all other parameters were kept at their constant levels (Fig. 6a and 6b). A part of K^+ and Ca^{2+} was not exchangeable because it was associated with impurities in the clinoptilolite matrix (Cerjan-Stefanovic and Corkivic, 1997). With regard to these figures, the amount of adsorption by MnOCZ is higher than that of FeOCZ.

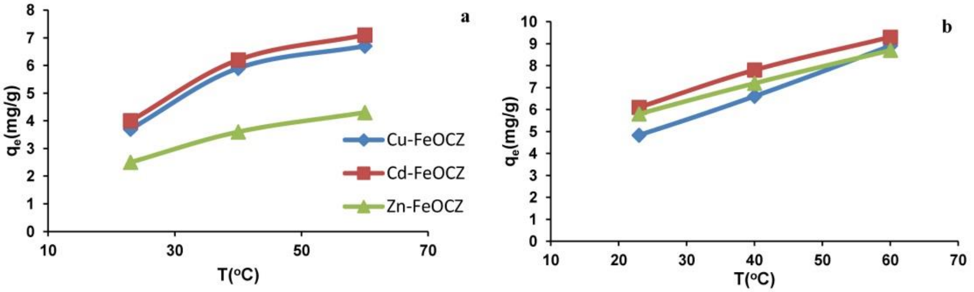

Fig. 6. Effect of temperature on adsorption of metal ions onto: (a) FeOCZ and (b) MnOCZ; initial concentration = 200 mg/dm^3, $t = 60$ min, $pH_e = 6$, MnOCZ = 1 g and $V = 100$ cm^3

As shown in Fig. 6a, with an enhancement in the temperature, the amount of adsorption (q_e) increased from 4 mg/g to 7.1 mg/g for $Cu^{2+}$and 3.7 mg/g to 6.7 mg/g for Cd^{2+} and 2.5 mg/g to 4.3 mg/g for Zn^{2+}. Similarly, the amount of adsorption (q_e) by MnOCZ increased from 4.83 mg/g to 8.7 mg/g for Cu^{2+} and 6.1 mg/g to 9.3 mg/g for Cd^{2+} and 5.8 mg/g to 8.7 mg/g Zn^{2+}. In addition, with respect to the results, a high temperature is more suitable for metal ions adsorption. With regard to these figures, the capacity of MnOCZ is higher than that of FeOCZ. Furthermore, the results showed that the adsorption reactions for both adsorbents are dependent to the temperature. According to the literature, such behavior occurred in the sorption processes with endothermic mechanism (Zou et al., 2006).

Adsorption isotherm

In order to study the sorption isotherms, the Freundlich and Langmuir isotherm equations were analyzed. The corresponding isotherms for ion adsorption by FeOCZ and MnOCZ were shown in Fig. 7 and Fig. 8. With respect to these figures, the adsorption isotherm studies indicate that the adsorption of Cu^{2+}, Zn^{2+} and Cd^{2+} ions follow both the Langmuir and Freundlich isotherms. The usage of two isotherm models for ion adsorption suggests that monolayer and heterogeneous surfaces are formed during the adsorption process (Dawodu and Akpomie, 2014). However, according to Fig. 7a and Fig. 8a, the experimental data (corresponding to MnOCZ) fits better with the Langmuir model. The values of $n > 1$ also indicated favourable adsorption conditions (Cerjan-Stefanovic and Corkivic, 1997). Furthermore, with regard to Fig. 7b and Fig. 8b, the experimental data (corresponding to FeOCZ) fits better with the Langmuir model. The corresponding values of each model such as q_{max}, b, K_F, n and R^2 were calculated and shown in Table 2. Similar results have been reported by various researchers who applied the Langmuir model to explain heavy metal removal by various types of zeolites (Taffarel and Rubio, 2010). With respect to the Langmuir isotherm, the sorption process is carried out at homogeneous sites of sorbent (Jamil et al., 2010). With respect to q_{max} (mg/g) shown in Table 2, the monolayer capacity of FeOCZ is approximately the same for all ions, whereas the capacity of MnOCZ is in the following order: $Cd^{2+} > Zn^{2+} > Cu^{2+}$. Table 3 illustrates the comparison of copper, zinc and cadmium removal by various adsorbents mentioned in the literature. As seen in this table, the value of adsorption capacity for the adsorption of these three ions by various adsorbents is close together except some adsorbents such as silica/kraft lignin composite.

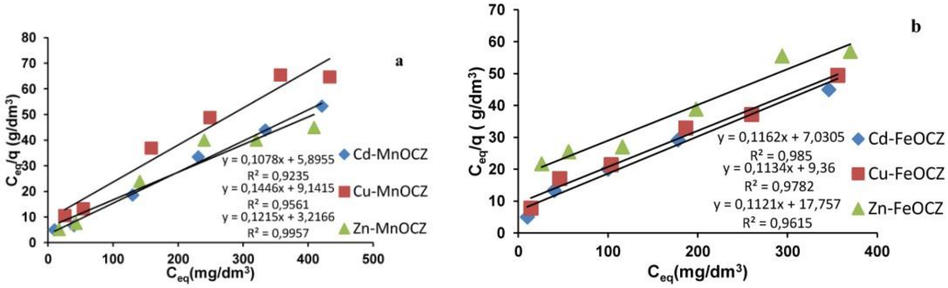

Fig. 7. Langmuir isotherm model for adsorption of Cu^{2+}, Cd^{2+} and Zn^{2+} on: (a) MnOCZ, and (b) FeOCZ; initial concentration = 200 mg/dm^3, t = 60 min, pH_e = 6, MnOCZ = 1 g, V = 100 cm^3 and T = 60 °C

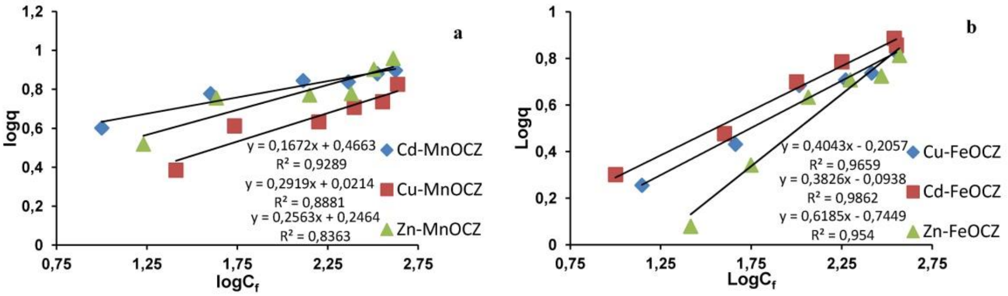

Fig. 8. Freundlich isotherm model for adsorption of Cu^{2+}, Cd^{2+} and Zn^{2+} onto: (a) MnOCZ and (b) FeOCZ, initial concentration = 200 mg/dm^3, t = 60 min, pH$_e$ = 6, MnOCZ = 1 g, V = 100 cm^3 and T = 60 °C

Table 2. The corresponding values of Langmuir and Freundlich models for FeOCZ and MnOCZ

Adsorbent type	Metal ion	Langmuir parameters			Freundlich parameters		
		q_{max} (mg/g)	b (L/mg)	R^2	n (L/mg)	K_F	R^2
FeOCZ	Cd^{2+}	8.61	0.82	0.9850	10.66	0.81	0.9659
	Cu^{2+}	8.82	1.06	0.9882	2.47	0.62	0.9862
	Zn^{2+}	8.92	1.99	0.9615	1.62	0.18	0.954
MnOCZ	Cd^{2+}	9.28	0.64	0.9235	5.98	2.93	0.9289
	Cu^{2+}	6.92	1.32	0.9561	3.43	1.05	0.8881
	Zn^{2+}	8.23	0.39	0.9957	3.90	1.76	0.8363

Conclusions

This research describes a method for the Cu^{2+}, Cd^{2+} and Zn^{2+} ion adsorption process using zeolite modified with manganese and iron oxide. The iron and manganese oxides coating was characterized by SEM. The corresponding results proved the formation of iron and manganese oxides coating on the surface of natural zeolite. The adsorption of ions by zeolite samples was studied as a function of initial concentration, time, pH and temperature. In this regard, the optimum condition of initial concentration, time and temperature was found to be 200 mg/dm^3, 60 min and 60 °C, respectively. As a result, the optimum pH for the adsorption of Cu^{2+}, Cd^{2+} and Zn^{2+} was found to be 5.5, 6 and 7, respectively. In order to compare the rate of adsorption of ions, the first-order kinetic model was used. According to the results, the rate constants (k) of copper and zinc adsorptions by FeOCZ are approximately the same. However, the cadmium adsorption rate is lower than that of the other ions. Furthermore, the rate constants of ion adsorptions by MnOCZ are close together; however, the adsorption rate constant of copper is slightly higher than that of zinc and cadmium. The adsorption isotherm studies indicate that the adsorption of Cu^{2+}, Zn^{2+} and Cd^{2+} ions follow both Langmuir and Freundlich isotherms. However, with respect to the R^2 values, the experimental data corresponding to both modified zeolites had a good correlation with the Langmuir isotherm. The usage of two isotherm models for ion adsorption suggests that monolayer sorption and heterogeneous surfaces are formed during the adsorption process. In addition, with respect to the results of the Langmuir model, the monolayer capacity of FeOCZ is approximately the same for all ions. This is while the capacity of MnOCZ is in the following order: $Cd^{2+} > Zn^{2+} > Cu^{2+}$.

Table 3. Comparison of zinc and cadmium adsorption using various adsorbents

Adsorbents	q_m maximum capacity (mg/g)			References
	Zn^{2+}	Cd^{2+}	Cu^{2+}	
Manganese oxide modified	–	26.6	9.9	(Al–Degs et al., 2000; Eren, 2008; Iqbal et al., 2009)
Peat	–	10.23	6.54	(Mckay and Porter, 1997)
Eucalyptus black liquor lignin	–	16.12	9.95	(Mohan et al., 2006)
clinoptilolite	–	4.22	25.69	(Sprynskyy et al., 2006)
Natural mongolian zeolite	0.085–0.149 mmol/g	0.051–0.125 mmol/g	–	(Batjargal et al., 2011)
Phosphate rock	8.54	10.46	–	(Elouear et al., 2008)
Activated phosphate rock	12.26	13.56	–	(Elouear et al., 2008)
X–zeolite (containing N_2O 3.5 SiO_2 2.2) A–zeolite (containing N_2O 3.5 SiO_2 2.2)	0.63 mmol/g 0.44 mmol/g	0.824 mmol/g 0.635 mmol/g	–	(Ibrahim et al., 2010)
Red Mud	2.22 mol/g	1.16 mol/g	–	(Gupta and Sharma, 2002)
Magnesium–silicon (Mg–Si) binary oxide adsorbent	–	18.23	–	(Ciesielczyk et al., 2015)
Silica–kraft lignin composite	–	84.66	–	(Klapiszewski et al., 2015)
MnOCZ	8.23	9.28	6.92	This study
FeOCZ	8.92	8.61	8.82	This study

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