International Journal of Engineering

Removal of Fe^{2+} from Aqueous Solution Using Manganese Oxide Coated Zeolite and Iron Oxide Coated Zeolite

M. Khashij[a], S. A. Mousavi*[b], M. Mehralian[c], M. R. Massoudinejad[a]

[a] Department of Environmental Health Engineering, Shahid Beheshti University of Medical Sciences, Tehran, Iran.
[b] Department of Environmental Health Engineering, Research Center for Environmental Determinants of Health (RCEDH), Kermanshah University of Medical Sciences, Kermanshah, Iran.
[c] Department of Environmental Health Engineering, Kermanshah University of Medical Sciences, Kermanshah, Iran.

A B S T R A C T

The adsorption of Fe^{2+} by the manganese oxide coated zeolite (MOCZ) and iron oxide coated zeolite (FOCZ) was studied. Surface properties of adsorbents have been investigated for monitoring their changes and morphology for both of the MOCZ and FOCZ. Main variables namely; contact time, pH, initial concentration of Fe^{2+}, size and dosage of adsorbent have been optimized, and the results contrasted with isotherm and kinetic models for finding best fit. The best fit of the adsorption isotherms was obtained using the Langmuir model (R^2=0.96 and 0.92) using MOCZ and FOCZ. The rates of adsorption were found to conform to the pseudo-second-order kinetic with a good correlation (R^2=0.98 and 0.82 for MOCZ and FOCZ, respectively). The results indicated that MOCZ has good ability (80% removal of Fe^{2+}) for the removal of Fe from water. The MOCZ exhibited the porous structure with high surface area rather than FOCZ, and the percentage removal of Fe^{2+} by MOCZ was better than FOCZ.

doi: 10.5829/idosi.ije.2016.29.11b.13

1. INTRODUCTION

Nowadays groundwater as main source of drinking water need to be tested for different pollutants especially metals such as Iron components. Excessive amounts of Fe^{2+} in water lead to unfavorable odor, taste, fouling and scaling in pipe that followed ferrous bacteria growth and public health difficulties [1]. Ground water can be polluted by wastewaters from different sources such as electroplating, metal finishing, metallurgy, chemical manufacturing, mining and battery manufacturing [2, 3]. The high amounts of heavy metals (like Fe) in drinking water identified as a potential source of numerous diseases and disorders related to kidney, lung and intestinal damage [4]. Furthermore, they can cause irreversible damages to the nervous system and other pathologies as pneumonia, circulatory collapse, edema of the respiratory treating [2, 5].

Therefore, responsible agencies such as WHO recommended a maximum level of 0.3 mg/L for Fe in dirking water [6].

Among different methods that have been performed for Fe removal form aqueous solutions, adsorption due to simple application, cost effectiveness and reliable technique widely can be used [7]. Variety of absorbents have been developed to remove different pollutant especially heavy metals, that among them Clinoptilolite (natural zeolite) as a natural porous mineral shows high sorption [8] and ion-exchange behavior [9] that because of its low-cost and nontoxic nature as well as their wide availability on the earth, has been widely applied for removal of different water pollutants [10-12] such as Pb, Zn and dye [13, 14]. Nowadays, researchers in order to improve the efficiency of natural adsorbents, have applied several methods to modify natural zeolites by either physical or chemical reactions.

Among materials that can be used to improve natural zeolites; manganese oxide and iron oxide with high ability to reduce trace metal in water via high oxidation

Corresponding Author's Email: seyyedarm@yahoo.com (S. A. Mousavi)

power and co-precipitation processes have been examined in previous studies [15, 16]. But, they are only available as fine powder and their use in the form of powder is limited by high head loss, difficulty in separation of the solid from solution and leaching of the metal oxide in the treated water [17]. In order to overcome these shortcomings, modification of zeolite with manganese oxide and iron oxide, leads to the formation of the adsorbent with special properties for heavy metal adsorption removal from aqueous solutions.

The new approach shows high ability for cations adsorption due to chelating mechanism, dense functional group in adsorbent, high special surface [18]. Furthermore, many parameters such as adsorbent size, concentration of heavy metal, contact time, and pH of solution have effect on the removal efficiency of metals in adsorption systems which beside investigated the kinetics and isotherms their effects on process efficiency have been optimized as objects of this paper.

2. MATERIAL AND METODS

2. 1. Preparation of MnO$_2$ and FeO Coated Zeolite
All materials and reagents were prepared by Merck Company from Germany. MOCZ have been prepared by using KMnO$_4$ – (Scharlau) solution and HCl – (Synth). Fe (NO$_3$)$_2$– (Chemlab) was used for the preparation of iron synthetic solutions, and has been used directly without any further purification. The zeolite used in the preparation of MOCZ and FOCZ was prepared from mines that located in Semnan provinces, Iran. According to its chemical composition (Na$_{0.52}$K$_{2.44}$Ca$_{1.48}$) (Al$_{6.59}$Si$_{29.41}$O$_{72}$).28 (H$_2$O) this ratio of Si/Al was 4.46 which approximately is the ideal ratio (23). For determination of specific surface area of adsorbents methylene blue (MB) adsorption technique was used. The test has been done by adding 0.1 gr of zeolite into 100 ml methylene blue solution and the suspension was centrifuged after 1 hr and the residual of MB concentration was determined by spectrophotometer (Hach DR 5000 UV-Vis- Canada) at λ=665 nm. The amount of methylene blue adsorbed was calculated by difference in methylene blue concentration before and after adsorption (Equation (1)).

$$SSA = X_m \times N \times A \tag{1}$$

where X is the monolayers capacity in mole/g; N is Avagadro number (6.019 × 10^{23}) and A is area per molecule on the surface. So, specific surface area of adsorbents is converted from 12.23 to 87.5 and 123.89 m^2/g with MnO$_2$ and FeO coated zeolite, respectively. The raw zeolite was sieved in order to achive different sets of mesh size.

Afterward, zeolite (Clinoptilolite) was converted to Na formed by suspended 30 g of zeolite in 500 ml of a 1 M NaCl solution for 24 h. Na–zeolite from pervious step was dried in oven (70 BSO-2006, Germany) at 100 °C for 24 h. For enriching and ion exchange increasing of the zeolite, potassium permanganate was added into a beaker, and then hydrochloric acid (37.5%) droped on the KMnO$_4$ slowly. The solution was stirred for 1 h, suspension was filtered. For removing free potassium and chloride ions zeolite washed by deionized water. Finally, the composite was dried in oven at 100 °C for 24 h.

For the preparation of iron oxide-coated zeolite, firstly 30 g Clinoptilolite was mixed with 60 ml of solution containing 2% Iron (III) nitrate. Then pH of the mixture adjusted to the desired value with NaOH. The pH was measured by pH meter (WTW-720 Inolab-Germany). For covering substance on zeolite, the solution was stirred for 1h, and dried at 105 °C for 20 h. After coating, the zeolite washed with deionized water to remove unattached and extra metals oxide until the pH reached to a constant value (7–8). Eventually, the FOCZ was dried at 105 °C for 24 h and stored in a capped container.

2. 2. Batch Adsorption Study
The experiments have been performed in a glass beaker with total volume of 250 mL and working volume of 100 mL. The reactor consisted of a 7 cm in diameter by 9 cm in height. Agitation for achieving homogeneity in system was conducted by magnetic shaker (JENWAY SELECTA 1000, UK) at 120 rpm for all tests at room temperature. Batch experiments were performed with six controllable factors namely initial pH, adsorbent type, initial concentration (C$_0$), contact time, size and dosage of adsorbents. The levels of variables have been adjusted based on previous research works: initial concentration of Fe^{2+} (1–5 mg/L), pH (4–8), contact time (5–120 min), size of adsorbents 3.8, 4, 10 (mesh) (equal 1-3, 3-7 and 7-10 mm), dosage (1, 3, and 5 g). The uptake of Fe^{2+} (q) was expressed as Fe^{2+} removal per mass unit of adsorbents (mg Fe^{2+}/g) at time t using Equation (2):

$$q_t = \frac{(c_0 - c_t)v}{m} \tag{2}$$

where, C$_0$ and C$_t$ are the Fe^{2+} concentration and equilibrium concentration at time t (mg/L), V is the solution volume (L), and m is the adsorbent dose (g). Fe^{2+} concentration as mg Fe/L was detected using Atomic Absorption Spectrophotometer (Contra 700, Analytic Jena). In order to data analysis, Nonparametric Test (Mann Whitney) through SPSS ver.20 has been developed. In addition, interaction between Fe with two adsorbent toward the rate of Fe affinity of the modified zeolite and surface properties is described with different isotherm and kinetic models. Isotherm models and their parameters are illustrated in Table 1.

TABLE 1. Models of adsorption isotherms and kinetic

Isotherms	Equation	Parameters
Freundlich	$\log q_e = \log k_f + \frac{1}{n}\log c_e$	q_e ; adsorption equilibrium rate (mg/g)
Langmuir	$\frac{c_e}{q_e} = \frac{1}{bQ_{max}} + \frac{c_e}{Q_{max}}$	q_{max} ; maximum adsorbed concentration of Fe^{2+} (mg/g)
Temkin	$q_e = B.\operatorname{Ln} A + B.\ln c_e$	K_F; Constant (mg g^{-1}) (L/g)$^{-1/n}$
kinetics		b ; Langmuir constant (L/mg)
		n ; Freundlich constants
First-order	$\frac{dq_t}{dt} = k_1(q_e - q_t)$	C_e ; Final concentration (mg/g)
		A ; Temkin constant (L/g)
Second-Order	$\frac{dq_t}{dt} = k_2(q_e - q_t)^2$	B ; Heat of adsorption (J/mol)

3. RESULTS AND DISSCOSSION

3. 1. Characterization of Adsorbents The surface morphology of the zeolite before and after coating is shown in Figure 1 (a to c) using a KYKY (EM-3200) microscope. As can be noted from the Figure, the zeolite surface has a very rough and porous surface. Figure 1b and Figure 1c shows zeolite surface sites were apparently occupied with newborn manganese oxide and iron oxide. A clear difference in the surface morphology of MOCZ and FOCZ may relate to manganese oxide and iron oxide particles that appear to be growing together in surface depressions and coating cracks. This surface morphology of the modified zeolite has turned to show more dense, relatively porous surface and high affinity for diffusion of metal ion (Fe) in the case of modified zeolite composites that has been mentioned by Popov et al. [19]. Based on XRD analysis reported by Massoudinejad et al. [20], the oxide coverage on adsorbent surface is introduced as manganese (IV) oxide with chemical formula of MnO_2. According to survey on the zeolite structure, absorption behavior in zeolite is based on Louise acid theory in pore structure. Thus, existing oxygen atom in tetrahedral structure of zeolite (Si-O-Al) lead to negative charge on adsorbent surface that are available sites for Fe^{2+} absorption. Therefore, Si/Al ratio decline and presence of oxygen atom in zeolite structure is considered as two potential factors in Fe^{2+} adsorption process.

3. 2. Effect of pH In this study, a series of experiments was carried out for investigation on the effect of pH ranging from 4 to 8 and the data were presented in Figure 2. The Fe^{2+} removal decreased with increase of pH from 4 to 8 due to increase in static repulsion force. The best pH value for both adsorbents was 4 with maximum adsorption higher than 60% at contact time 15 min.
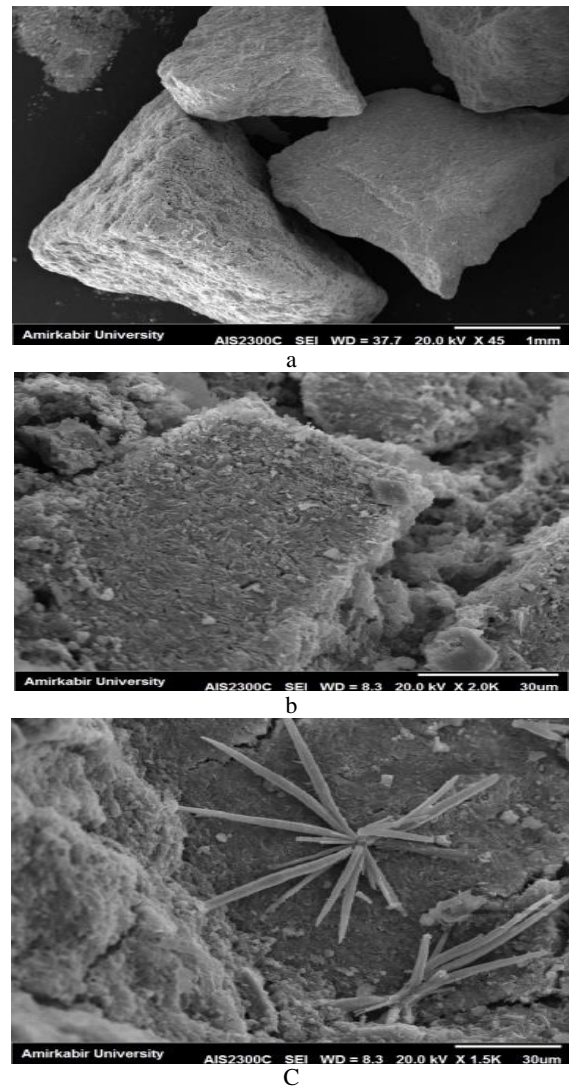

Figure 1. SEM micrograph of zeolite samples a: Raw zeolite; b: zeolite covered with MnO_2; c: zeolite covered with FeO

By using regression analysis, the results confirmed the reverse relationship between pH and Fe removal for both adsorbent, as with increasing one unit of pH, approximately %14.11 removal efficiency of system decreased with P-value <0.001. It is evident that pH has a strong influence on the Fe^{2+} removal, because solubility of the metal ions concentration can be affected by pH, resulting negative charge of the surface of MOCZ and FOCZ [21]. In comparison to FOCZ, the more negatively charged surface of MOCZ would have higher affinity towards Fe^{2+} that makes the adsorption more favorable, resulting a higher adsorption capacity [22]. In contrary to the results of the Massoudinejad et al. [20], the removal of Mn ion increased at high pH, because Fe has a low pK_a of 2.13 in comparison with pK_a=10.6 for Mn, which can hardly be removed by ion exchange. Indeed, at high pH values, both ion exchange and aqueous metal hydroxide formation may become

significant mechanisms in the metal removal process [23]. Besides, when the pH value increased, removal rate of Fe will decline due to that it is mainly in anion state (negative charge) in aqueous solution [24]. Therefore, inconsistent of our result can be explained that when pH is reduced, positive surface phenomena is predominated in the mass transfer and as a result, ion exchange of the Fe got excess. Thus, the solute has got enough time to get diffuse into the whole of the adsorbent mass [25].

3. 3. Effect of Fe Concentration   Effect of initial concentration of Fe^{2+} on the efficiency of the adsorbent was studied from 1 to 5 mg/L and the results are shown in Figure 3. As shown in Figure 3, the removal of Fe^{2+} was increased with increasing of Fe^{2+} concentration due to providing more Fe^{2+} cations for ion exchange in absorption processes. At a constant time of 15 min, the maximum removal of Fe^{2+} was 69% and 58% for MOCZ and FOCZ, respectively. It was observed that percentage removal of Fe^{2+} increased with increasing the amount of concentration that have a close similarity with recent study [26]. This result may be due to the adsorption sites unsaturation at lower concentrations of Fe^{2+}. The Fe^{2+} concentration provides an important driving force to dominate all mass transfer resistance [19]. In addition, at higher concentrations, the unoccupied active sites may available for sorption of cations [26].

3. 4. Effect of Contact Time   Figure 4 illustrates the effects of contact time on the adsorption process and unsaturation of the adsorption sites in lower times.
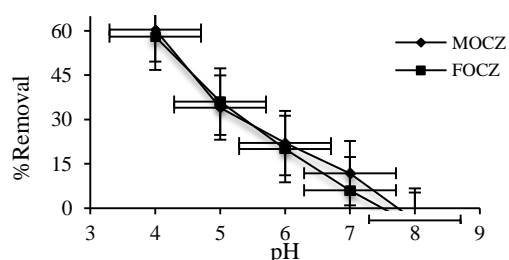

Figure 2. Effect of pH on the adsorption of Fe
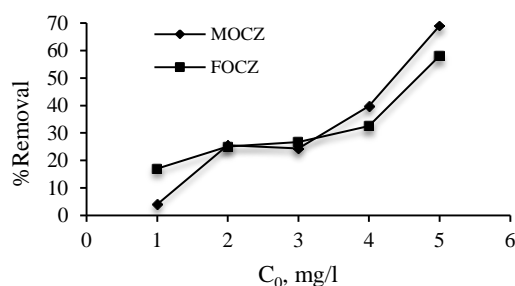

Figure 3. Effect of initial concentration of Fe in adsorption process

On the other hand, one factor affected in this phenomenon is the Fe^{2+} concentration that it provides an important driving force to dominate all mass transfer resistance [27, 28] and lead to higher adsorption of heavy metal with increased time. It was also observed that the adsorption capacity of the Fe^{2+} was increased with the increase of contact time due to giving enough time and more availability of binding sites for the removal of pollutant. As shown in Fig. 4, the Fe^{2+} removal of 75% and 71.6% occurred by MOCZ, and FOCZ, respectively, when contact time was 120 min at the pH 4. The statistical analysis of archived data demonstrated significant relationship between contact time and percentage removal of Fe^{2+} (p value=0.01). Therefore, increasing in the contact time showed increasing in the removal of Fe^{2+}. This result was supported by previous study when modified zeolite has been used to remove of Mn from water by Massoudinejad et al. [20].

3. 5. Effect of Adsorbent Size and Dosage   Figures 5 and 6 show the adsorption of Fe^{2+} as a function of size and dosage of MOCZ and FOCZ. Incontrovertible by increasing the adsorbent dose the percentage removal of Fe increased, but adsorption density, the adsorption per mass unit, decreased. It is readily intended that the number of accessible adsorption sites increases by increasing the adsorbent dose. The depression in adsorption density with an increase in the adsorbent dose is vigorously because of unsaturation adsorption sites through the adsorption process [29]. Another reason can be the inter-particle interaction (such as aggregation, resulting from high adsorbent dose), which that lead to decrease in the total surface zone of the adsorbent and an increasing in diffusion length path [11]. A similar behavior was observed in several previous investigations regard to aggregation properties for different adsorbents in absorption process [28, 30, 31]. The Fe^{2+} absorption mechanisms on modified zeolite carry out according to Equations (3) and (4).
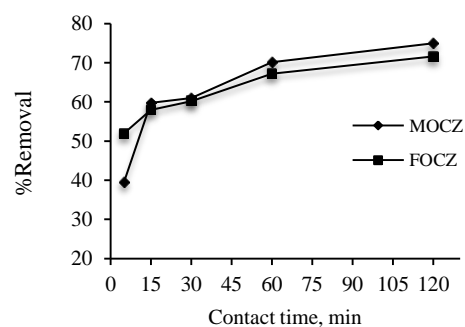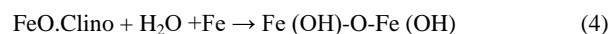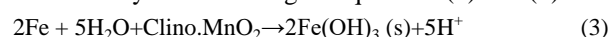
$$2Fe + 5H_2O + Clino.MnO_2 \rightarrow 2Fe(OH)_3 \ (s) + 5H^+ \qquad (3)$$

$$FeO.Clino + H_2O + Fe \rightarrow Fe \ (OH)\text{-}O\text{-}Fe \ (OH) \qquad (4)$$

Figure 4. Effect of contact time on the adsorption of Fe

According to Figures 5 and 6, the percentage removal of Fe^{2+} will happened when particle size of the adsorbents decreaded from 1-3 to 5-7 mm. Between the particles sizes considered in the study, the percentage elimination is highest for the particle size of 1–3 mm i.e. meshes of 10 for both MOCZ and FOCZ. For most adsorbents, the internal pore surface area is much bigger than the outer external surface area. Indeed, a reduction of the particle size lead to a higher total number of active sites available [32]. However, the higher corresponding number of sites at the external adsorbent surface leads in more favorable absorption [33]. Therefore, the reduction of particle size improved the percentage removal of Fe.

3. 6. Adsorption Isotherms and kinetics
Adsorption isotherm was used to description the reaction between absorbent and adsorbate. The results in Table 2 indicated Langmuir isotherm states the best interpretation of Fe by MOCZ and FOCZ with R^2=0.96 and 0.92, respectively. The high correlation to Langmuir isotherm implies the existence of heterogeneous surface toward monolayer adsorption. This result have been pointed out by researchers; Shavandi et al. [34] where used natural materials with different modification to Fe adsorption.

To understand the dynamics of adsorption reaction or rate-limiting step was used kinetics models like pseudo first-order and pseudo second-order as shown in Figure 7. Results of absorption kinetics according to Table 3 showed that the second order model with R^2

TABLE 2. Isotherms parameters for Fe^{2+} adsorption

Adsorbent	Freundlich		
	R^2	n	k
MOCZ	0.94	1.58	-0.142
FOCZ	0.89	1.66	-0.187
	Langmuir		
	R^2	b	Q(max)
MOCZ	0.96	0.094	1.119
FOCZ	0.92	0.081	1.410
	Temkin		
	R^2	K_t	B
MOCZ	0.077	0.038	0.05
FOCZ	0.243	0.041	0.039

A (MOCZ)

B (MOCZ)

C (FOCZ)

D (FOCZ)

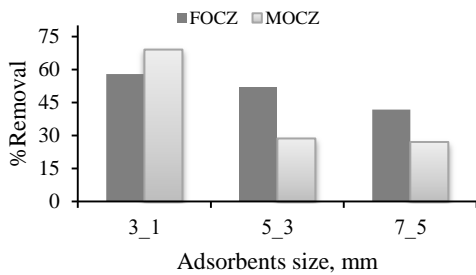**Figure 7.** Kinetics modeling: 1st order kinetic (A-C) and 2nd order kinetic (B-D)

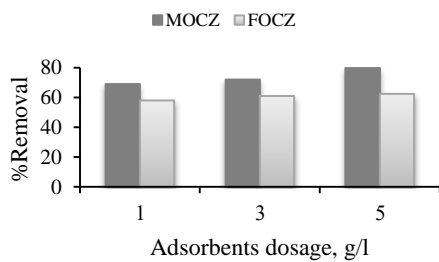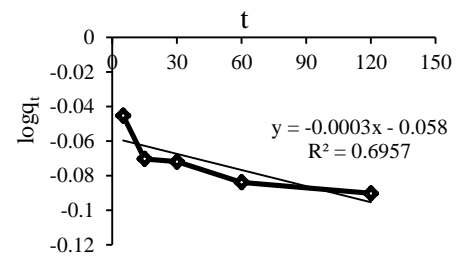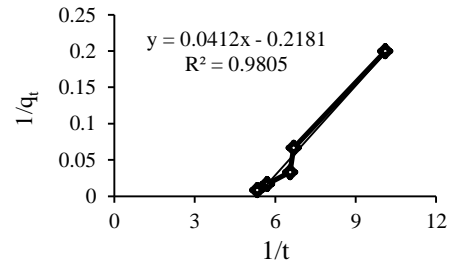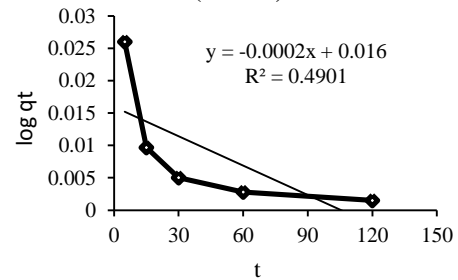**Figure 5.** Effect of zeolite size of on the efficiency removal of Fe

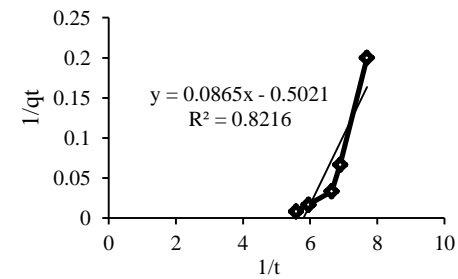**Figure 6.** Effect of zeolite dose in the efficiency removal of Fe

TABLE 3. kinetics study based on the 1st order and 2nd order equations

Models	Kinetics Parameters					
	MOCZ			FOCZ		
	q_1	K_1	R^2	q_2	K_2	R^2
1st order	0.1	0.0003	0.69	0.061	0.0002	0.49
2nd order	0.14	0.04	0.98	0.092	0.086	0.82

equal 0.99 and 0.91 is the best model to determine of reaction speed that supported with Shavandi et al. [34] for simultaneously removal of Mn^{2+} and Zn^{2+} from palm oil mill effluent. In addition, the absorption kinetics correspond with the study by Kan et al. [35], which showed Langmuir and Freundlich adsorption isotherm due to homogeneity as well as monolayer adsorption [36]. In addition, these models implies the chemisorptions might be occurred which involved electrons between Fe and adsorbents via sharing bonds [37-39]. Moreover, b value represents the enthalpy of adsorption process and affinity of Fe^{2+} to sites of exchange. The highest amount of this parameter is 0.094 and related to MOCZ because of more exchange sites. However, this rate for FOCZ was obtained 0.081 that illustrated less affinity of Fe to absorb on the surface. Nonetheless, Kan et al. [25] reported that high amount of b for adsorbents with low number of exchange sites could be observed during adsorption process.

4. CONCLUSION

Removing Fe^{2+} from water by adsorption is not a simple, and the efficiency is dependent on different variables. The great efforts have been made to find ways to improve the Fe removal from aqueous solution in previous researches that their results have confirmed best way for high removal of Fe can be achievable by using integrated system, rather than single one. The oxide coated zeolite and iron oxide coated zeolite have been used to remove Fe^{2+} from an aqueous solution. The MOCZ exhibited the porous structure with high surface area rather than FOCZ and therefore Fe^{2+} uptake with MOCZ was better than FOCZ. The removal rate of Fe^{2+} ions is the result of combination of various reactions namely; ion exchange, chemisorption and adsorption. The modified zeolite as a low-cost material, show a good potential to removal of Fe^{2+} from aqueous solution.

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Removal of Fe^{2+} from Aqueous Solution Using Manganese Oxide Coated Zeolite and Iron Oxide Coated Zeolite

M. Khashij[a], S. A. Mousavi[b], M. Mehralian[c], M. R. Massoudinejad[a]

[a] Department of Environmental Health Engineering, Shahid Beheshti University of Medical Sciences, Tehran, Iran.
[b] Department of Environmental Health Engineering, Research Center for Environmental Determinants of Health (RCEDH), Kermanshah University of Medical Sciences, Kermanshah, Iran.
[c] Department of Environmental Health Engineering, Kermanshah University of Medical Sciences, Kermanshah, Iran.

چکیده

جذب آهن محلول به وسیله زئولیت های اصلاح شده با اکسیدهای آهن و منگنز مورد مطالعه قرار گرفته است. ویژگی های سطحی جاذب به منظور تعیین مشخصات ساختاری و مورفولوژی MOCZ و FOCZ بررسی شده است. متغیرهای اساسی شامل زمان تماس، pH، غلظت اولیه آهن محلول، اندازه و مقدار جاذب بهینه سازی شده است و نتایج در غالب ایزوترم و مدل های سنتیکی ارائه شده است. بهترین مدل ارائه نتایج با ایزوترم جذب لانگمویر با ضریب همبستگی به ترتیب ۰/۹۶ و ۰/۹۲با MOCZ و FOCZ بدست آمد. سنتیک جذب از مدل شبه درجه دوم با ضریب همبستگی بالا ۰/۹۸ و ۰/۸۲ تبعیت می کند. نتایج نشان دهنده ی این است که MOCZ با ۸۰٪ حذف آهن محلول، توانایی بیشتری در حذف آلاینده از آب دارد. ضمن اینکه MOCZ به دلیل ساختار متخلخل ترو سطح ویژه بالاتر نسبت به FOCZ، کارایی حذف بالاتری نسبت به FOCZ دارد.

doi: 10.5829/idosi.ije.2016.29.11b.13