

## REMOVAL OF $\text{Co}^{2+}$ , $\text{Ni}^{2+}$ , AND $\text{Pb}^{2+}$ BY MANGANESE OXIDE-COATED ZEOLITE: EQUILIBRIUM, THERMODYNAMICS, AND KINETICS STUDIES

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**Abstract**—The removal of  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Pb}^{2+}$  from aqueous solutions using a modified zeolite was investigated because of the need to eliminate toxic contaminants from wastewaters. In the present study the ways in which equilibrium, thermodynamics, and kinetics parameters affected the removal of heavy metals were evaluated and compared. An Iranian clinoptilolite with a Si/Al ratio of 6.5 was used as an adsorbent. In order to increase the adsorption capacity of the adsorbent, it was converted to a manganese oxide-coated zeolite (MOCZeol) using various Mn solutions. The initial concentration of metals, pH, contact time, and temperature were the variables studied and optimal conditions were established. The maximum amount of  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Pb}^{2+}$  adsorption on MOCZeol was ascertained. A thermodynamics study, using  $\Delta G$ ,  $\Delta H$ , and  $\Delta S$  state functions showed that adsorption of  $\text{Pb}^{2+}$  was more spontaneous than that of  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$  ions. The adsorption of these ions on MOCZeol was an endothermic reaction. Investigation of the adsorption models revealed that the adsorption of  $\text{Pb}^{2+}$ ,  $\text{Co}^{2+}$ , and  $\text{Ni}^{2+}$  on MOCZeol followed both the Langmuir and Freundlich models. Kinetics studies showed that the adsorption of  $\text{Pb}^{2+}$ ,  $\text{Co}^{2+}$ , and  $\text{Ni}^{2+}$  on MOCZeol followed the pseudo-second order kinetics model with a high correlation coefficient.

**Key Words**—Ion-exchange Adsorption, Manganese Oxide, Wastewater, Zeolite Kinetics and Thermodynamics.

### INTRODUCTION

Heavy-metal contamination arises through the disposal of industrial materials from a variety of industrial processes, including the paper industry and iron and steel manufacturing plants (Inglezakis *et al.*, 2002, 2007). Dealing with the wastewater discarded from industrial processes is a critical environmental issue. Some metals included in the discarded material are toxic (Moattar and Hayeripour, 2004; Rahmani *et al.*, 2004), and nickel can have serious effects on human and animal health (Turtureanu *et al.*, 2008). The small amounts of Pb present may have adverse effects on the human brain and central nervous system (Inglezakis *et al.*, 2007). Finding ways to improve the quality of industrial wastewaters was, therefore, the main motivation for the present study. Cobalt, Ni, and Pb ions were selected here because of their wide use in various industries and adverse effects on the aqueous environment.

The elimination of heavy metals from industrial effluents has been studied extensively. Several processes such as liquid-liquid extraction, membrane extraction, filtration, ion exchange, and adsorption have been developed to remove dangerous species from wastewater. Of these methods, adsorption processes are acknowledged as being the simplest and most economical. Activated carbon, activated carbon composites, silicates (Erto *et al.*, 2013; Karnib *et al.*, 2014; Azari *et*

*al.*, 2015), kaolins and ball clays (Chantawong *et al.*, 2004), leaf powders (Li *et al.*, 2013), mixed Fe-Al oxides (Violante *et al.*), activated carbon fibers (Park *et al.*), silica gels (Tzvetkova *et al.*, 2009), Na-purified natural clays (Fröhlich, 2015; Ghorbel-Abid and Trabelsi-Ayadi, 2015), bentonites (Wu *et al.*, 2015), attapulgites (Guo *et al.*, 2014), fruit peels (Mallampati *et al.*, 2015), zeolite X/chitosans (Lu *et al.*, 2015), montmorillonites (Kalantari *et al.*, 2015), clinoptilolite (Miličević *et al.*, 2013; Irannajad *et al.*, 2015), agricultural soils (Zhang and Zheng, 2007), and coal bottom ash (Asokbunyarat *et al.*, 2015) are some of the adsorbents that have been or are applied in remediation of contaminated water. Of these adsorbents, natural zeolites are considered to be the cheapest, having large adsorption capacities and appropriate selectivities (Al-Degs *et al.*, 2000; Irannajad *et al.*, 2016c). Zeolites are also more readily available than some of the other adsorbents such as montmorillonite. Several studies have been performed on the removal of various species using a natural zeolite (Doula, 2006; Ören and Kaya, 2006; Taffarel and Rubio, 2010; Mehdizadeh *et al.*, 2014a; Irannajad *et al.*, 2016c). The activation of natural zeolites, using various chemical reagents, is done to increase the adsorption capacities of natural minerals. The literature shows that modification of a zeolite with manganese oxide increases the adsorption capacity significantly to levels which are greater than that of minerals such as montmorillonite, for example.

The chemical modification of natural zeolites has also been investigated (Doula, 2006; Taffarel and Rubio, 2010; Gonzalez *et al.*, 2015; Irannajad *et al.*, 2016c). One of the chemical reagents used to modify zeolites is

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manganese oxide, a coating of which creates an effective surface for element adsorption (Taffarel and Rubio, 2010). Many studies have focused on the uptake of metals by the manganese oxide-coated zeolite (MOCZeo). Results indicated that MOCZeo was effective at adsorbing Mn<sup>2+</sup>, Cu<sup>2+</sup>, and Pb<sup>2+</sup> ions from aqueous solutions, using both fixed-bed column and batch equilibrium experiments (Han *et al.*, 2006; Zou *et al.*, 2006b). Kinetics studies on the uptake of Cu<sup>2+</sup> and Pb<sup>2+</sup> ions by MOCZeo from aqueous solution were carried out by Zou *et al.* (2006a) in which a pseudo-second order model was selected as the most appropriate. Adsorption by ion exchange of U(VI) by MOCZeo was also carried out in two studies (Han *et al.*, 2007; Zou *et al.*, 2009). An Fe-Mn-modified clinoptilolite was used to eliminate As<sup>3+</sup> and As(V) from aqueous solution (Jiménez-Cedillo *et al.*, 2011). MOCZeo has also been used to remove the Fe species and other impurities contained in a uranium leach liquor (Nouh *et al.*, 2015). In a previous study by the present authors, the simultaneous elimination of Cu, Cd, and Zn by MOCZeo was studied (Irannajad *et al.*, 2016c).

In the present study, the removal of three hazardous heavy metals (Co<sup>2+</sup>, Ni<sup>2+</sup>, and Pb<sup>2+</sup>) from aqueous solutions using MOCZeo was studied and compared. The behavior of MOCZeo in the removal of these metals was described by means of equilibrium thermodynamics and kinetics. The influence of experimental variables such as contact time, metal concentration, and temperature on the adsorption process was tested in the application of adsorption isotherms to model the adsorption of Co<sup>2+</sup>, Ni<sup>2+</sup>, and Pb<sup>2+</sup> ions on MOCZeo.

## MATERIALS AND METHODS

### Material

Clinoptilolite from the Semnan region in Iran, characterized previously by Irannajad *et al.* (2015, 2016a, 2016b, 2016c) was used here as the adsorbent. The chemical composition of the zeolite was obtained using X-ray fluorescence (XRF) analysis (PW1480 instrument, Phillips, Amsterdam, The Netherlands): SiO<sub>2</sub> 61.0%, TiO<sub>2</sub> 0.23%, Al<sub>2</sub>O<sub>3</sub> 9.30%, Fe<sub>2</sub>O<sub>3</sub> 1.30%, CaO 3.58%, MgO 0.68%, K<sub>2</sub>O 3.58%, Na<sub>2</sub>O 2.58%, SO<sub>3</sub> 2.70%, and LOI 13.90%. The cation exchange capacity (CEC) of the zeolites is due to the isomorphous substitution of Al<sup>3+</sup> for Si<sup>4+</sup> in their tetrahedral structure. With increasing Si/Al ratio in the zeolite framework, hydrothermal stability and hydrophobicity are enhanced. In the present study, the Si/Al ratio was ~6.5. The exchange capacity of the natural zeolite, with particle size in the range 400–500 μm, was 0.086 mmol/g for Co<sup>2+</sup>, 0.083 mmol/g for Ni<sup>2+</sup>, and 0.1 mmol/g for Pb<sup>2+</sup>.

The MnO<sub>2</sub>-coated zeolite was synthesized as follows:

(1) The natural zeolite was ground using a laboratory stirred-ball mill for 60 min. The ground zeolite was sieved by a mechanical sieve shaker (Daneshfaravaran

Co., Iran) with aperture sizes in the range of 0 to 500 μm for 20 min, followed by washing of the samples with deionized water. In order to dewater the washed samples, they were filtered through Whatman filters (WH1001-085) followed by drying at 70°C for 1 h in an electric oven. Finally, dried samples were sieved and a sample with a particle size of >400 μm was collected for further analysis.

(2) 10 g of the dried zeolite was added to 300 mL of a 0.1 M MnCl<sub>2</sub> aqueous solution followed by addition of 4.59 g of KMnO<sub>4</sub> to this solution at a temperature of 25°C and pH of 6; they were mixed using a mechanical stirrer (RW20 Digital, IKA, Germany) for 5 h. The pulp obtained was washed using deionized water, filtered through a Whatman filter (WH1001-085), and dried at 70°C in an electric oven. The aim of this stage was to precipitate MnO<sub>2</sub> onto the zeolite surface to obtain the MnO<sub>2</sub>-coated zeolite.

(3) The MnO<sub>2</sub>-coated zeolite was washed with deionized water, filtered, and dried at 70°C as above. All reagents (MnCl<sub>2</sub>·4H<sub>2</sub>O, KMnO<sub>4</sub>, CoCl<sub>2</sub>·6H<sub>2</sub>O, Pb(NO<sub>3</sub>)<sub>2</sub>, and NiSO<sub>4</sub>·6H<sub>2</sub>O) used in the present study were purchased from Merck, Darmstadt, Germany.

### Adsorption

The Co-, Ni-, and Pb-removal experiments were conducted in batch mode using a beaker. A mechanical stirrer was used to agitate the system. The concentrations of the metals in the liquid phase were measured by atomic adsorption spectrophotometry (AAS) (Varian<sup>®</sup> AA240 spectrometer, Palo Alto, California, USA). The amount of metal ion adsorbed onto MOCZeo ( $q_e$ ) was calculated using equation 1 (El-Kamash, 2008):

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

where  $C_0$  is the initial concentration (mg/L),  $C_e$  is the ion concentration at equilibrium (mg/L),  $q_e$  is the amount of ions per unit mass of adsorbent (mg/g) at equilibrium,  $m$  is the adsorbent mass (g), and  $V$  is the solution volume (L).

### Langmuir isotherm

The Langmuir isotherm shows monolayer adsorption, written in its linear form as equation 2 (Langmuir, 1916):

$$\frac{C_e}{q_e} = \frac{1}{bq_{\max}} + C_e \left( \frac{1}{q_{\max}} \right) \quad (2)$$

where  $q_{\max}$  is the Langmuir constant corresponding to the uptake capacity (mg/g), and  $b$  is the adsorption energy as well as the equilibrium constant of the adsorption-desorption process (L/mg). The constants in the Langmuir model,  $q_{\max}$  and  $b$ , were evaluated using the slope ( $1/q_{\max}$ ) and the intercept ( $1/bq_{\max}$ ), respectively, of the plot of  $C_e/q_e$  vs.  $C_e$ .

### Freundlich isotherm

The Freundlich isotherm represents a direct relationship between concentration and adsorption. Many organic and inorganic adsorbents follow this sorption behavior. The equation for the Freundlich isotherm is (equation 3):

$$q_e = K_F C_e^{1/n} \quad (3)$$

where  $K_F$  is the Freundlich equilibrium constant and  $1/n$  is an arbitrary constant determined from the linear form obtained from equation 3. As  $1/n$  approaches 1, equation 3 becomes linear. The more general expression for its linear form, however, is (Freundlich, 1906):

$$\log(q) = \log K_F + (1/n)\log C_e \quad (4)$$

### Kinetics of adsorption by ion exchange

*Pseudo-first order kinetics model.* The general equation for a pseudo-first order kinetics model is:

$$\log(q_e - q_t) = \log q_e - k_1 t / 2.303 \quad (5)$$

where  $q_e$  and  $q_t$  represent the amount of the ions removed by the zeolite ( $\text{mg g}^{-1}$ ) at equilibrium time and at any time  $t$ , respectively. Furthermore,  $k_1$  is the rate constant of this model ( $\text{min}^{-1}$ ). By plotting  $\log(q_e - q_t)$  vs.  $t$ , the rate constant  $k_1$  and the equilibrium capacity  $q_e$  can be obtained by calculating the values of the slope and intercept, respectively.

*Pseudo-second order kinetics model.* If the sorption reaction is more complex, it may follow a second-order mechanism and be described by the equation for a pseudo-second order reaction kinetics (Gupta *et al.*, 2012):

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (6)$$

when  $q_t$  varies from 0 to  $q_e$ . The integrated form of equation 6 is:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t \quad (7)$$

This equation is the integrated rate law for a pseudo-second order reaction. Equation 7 can be rewritten to obtain a linear equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (8)$$

The constants can be determined by plotting  $t/q_t$  vs.  $t$ . Similar to previous models, the sorption rate constant,  $k_2$  ( $\text{g mg}^{-1} \text{min}^{-1}$ ), and  $q_e$  ( $\text{mg g}^{-1}$ ) can be found using the intercept and the slope of the plot, respectively.

*Intra-particle diffusion.* Intraparticle diffusion has an essential role in ion-exchange adsorption, which can be described as follows (Kocaoba *et al.*, 2007):

$$q_t = k_i t^{0.5} + I \quad (9)$$

Here,  $q_t$  is the concentration of an ion adsorbed at time  $t$  ( $\text{mg/g}$ ), and  $k_i$  is the 'intraparticle diffusion rate constant' ( $\text{mg/g/min}^{0.5}$ ). The values of  $I$  represent mass-transfer residence because of the boundary-layer thickness (Ismadji *et al.*, 2015). In fact, the plot includes three linear portions and one general slope. The first line goes from the origin which is equal to 0 at initial time,  $t$ , confirming the external mass transfer at the primary stage (Bhattacharyya and Ray 2015). At  $t = 0$  no adsorption had occurred.

## RESULTS AND DISCUSSION

### Material characterization

Scanning electron microscopy (SEM) (Model S-4160, Hitachi, Japan) was used to characterize the morphologies of the samples. Images of raw and modified zeolite particles show that the latter were more porous and rougher than the former (Figure 1a,b), as also found in previous studies (*e.g.* Zou *et al.*, 2006a). More SEM images were obtained after adsorption by ion exchange of Pb, Co, and Ni on MOCZeo (Figure 1c–e). The pores in MOCZeo were smaller and fewer. The average pore sizes decreased after ion exchange, from 28 to 26 Å. According to previous studies by the present authors (Irannajad *et al.*, 2015, 2016a, 2016b, 2016c), the X-ray diffraction (XRD) pattern of the raw zeolite indicated that it was clinoptilolite. A minor amount of gypsum was observed.

### Effect of pH

The removal of ions was examined over the pH range of 3–5.5 for  $\text{Pb}^{2+}$  and 3–8 for  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$ . The results showed that the adsorption of metals by ion exchange was enhanced by increasing the initial pH of the solution (Figure 2): the maximum adsorption by ion exchange was obtained at a pH of 5.5 for  $\text{Pb}^{2+}$  and at 6–7 for  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$ . Experiments at pH values >5.5 for  $\text{Pb}^{2+}$  and >8 for  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$  were invalid because the precipitation of ions of these metals occurred in the hydroxide form. Note also that the pH of precipitation is related to the metal concentration. For example, for a solution with a concentration of Ni = 100 mg/L, the pH can be increased up to 8 while for concentrations above 500 mg/L, precipitation occurs at pH values of <7. At acidic pH values, ion-exchange adsorption is reduced due to the competition of these ions and  $\text{H}^+$  ions for dynamic ion-exchange adsorption sites (Farghali *et al.*, 2013; Arshadi *et al.*, 2014). With decreasing  $\text{H}^+$  ions in the solution at higher pH values, however, the surface of the zeolite is deprotonated and subsequently the uptake of the metal ions is enhanced (Kushwaha *et al.*, 2017).

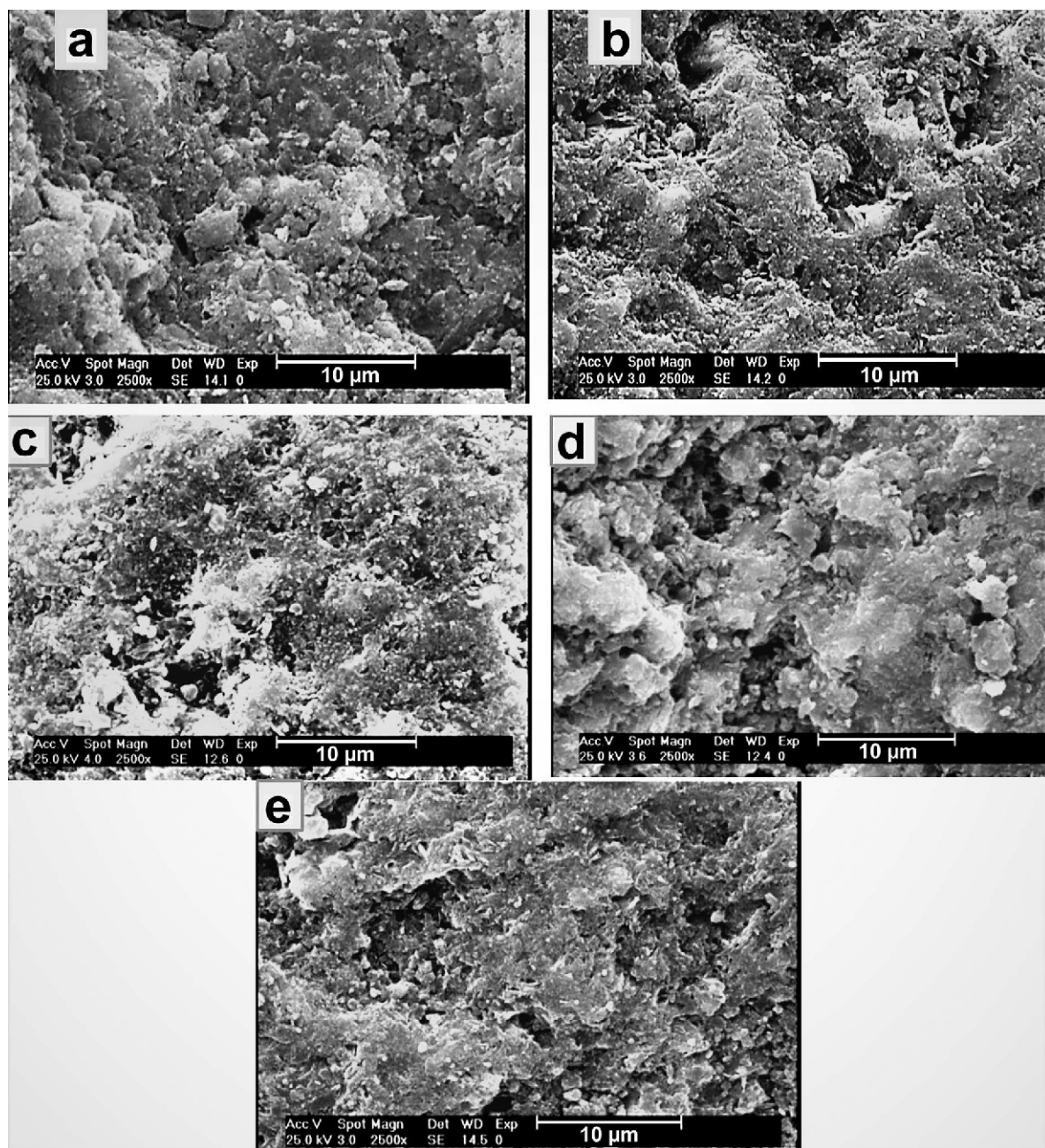


Figure 1. SEM images of zeolite particles (a) before and (b) after modification as well as the MOCZeo micrographs after adsorption of (c)  $\text{Pb}^{2+}$ , (d)  $\text{Co}^{2+}$ , and (e)  $\text{Ni}^{2+}$ .

#### *Effect of initial concentration on ion-exchange adsorption*

To examine the effect of the concentrations of  $\text{Pb}^{2+}$ ,  $\text{Co}^{2+}$ , and  $\text{Ni}^{2+}$  on ion-exchange adsorption, a series of the experiments was performed and the results are shown in Figure 3. The amount of  $\text{Pb}^{2+}$ ,  $\text{Co}^{2+}$ , and  $\text{Ni}^{2+}$  ions adsorbed on MOCZeo was increased following an increase in the initial ion concentration. The order of this adsorption was as  $\text{Pb}^{2+} > \text{Co}^{2+} \geq \text{Ni}^{2+}$ .

For maximum ion-exchange adsorption by MOCZeo, the order  $\text{Pb}^{2+} > \text{Co}^{2+} \geq \text{Ni}^{2+}$  was noted. As seen in Figure 3, the maximum amounts of  $\text{Pb}^{2+}$ ,  $\text{Co}^{2+}$ , and  $\text{Ni}^{2+}$  removed at a concentration of 500 mg/L were 38 mg/g (0.19 mmol/g), 7.9 mg/g (0.13 mmol/g), and 7.9 mg/g (0.13 mmol/g), respectively. A metal concentration of 200 mg/L was selected as optimal in terms of removal efficiency. The adsorption efficiency at this concentration was greater than at >200 mg/L and equal to the

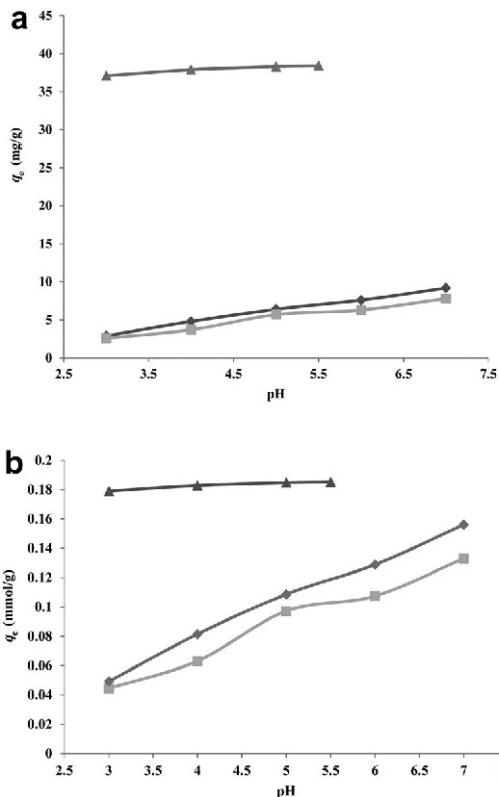


Figure 2. Effect of pH on the adsorption of  $\text{Pb}^{2+}$ ,  $\text{Co}^{2+}$ , and  $\text{Ni}^{2+}$  on MOCZeolite.  $T = 20^\circ\text{C}$ ,  $C_0 = 500 \text{ mg/L}$ ,  $t = 30 \text{ min}$ , MOCZeolite = 1 g, and  $V = 100 \text{ mL}$  (part a in mg/g, part b mmol/g).

efficiency of ion-exchange adsorption at a concentration of 100 mg/L.

#### Effect of contact time

To understand the influence of contact time on ion-exchange adsorption of heavy metals on MOCZeolite, a series of the experiments was conducted at an initial concentration of 200 mg/L and various durations of 15–120 min (Figure 4). The greatest rate of the ion-exchange adsorption was for  $\text{Pb}^{2+}$  and occurred within 30 min. This rapid adsorption may have occurred due to Pb adsorption by an ion-exchange reaction on the surface sites rather than in the pores (Lu *et al.*, 2005). Rapid diffusion onto the surface takes place by slow pore diffusion into the mineral structure (Bišćup and Subotić, 2004). The zeolite affinity for Pb, the extent of Pb hydration, and the energy of dehydration of Pb have significant roles to play in its rapid adsorption (Merrikhpour and Jalali, 2013). Equilibrium was reached at 60 min.

#### Temperature effect and thermodynamic evaluation

In order to investigate the influence of temperature on adsorption of  $\text{Pb}^{2+}$ ,  $\text{Co}^{2+}$ , and  $\text{Ni}^{2+}$  on MOCZeolite, a series of experiments was conducted at initial concentrations of 200 mg/L at temperatures of 23°C, 40°C, and

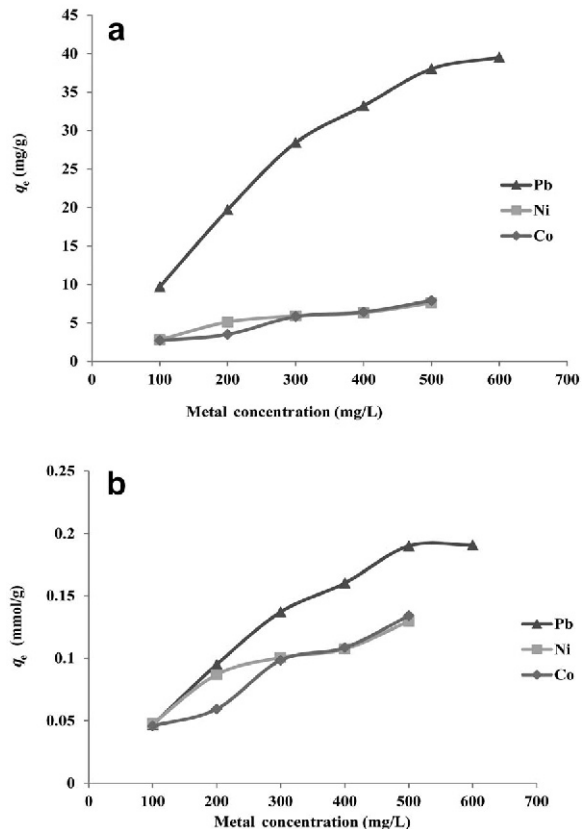


Figure 3. Effect of initial concentration on the adsorption of metals;  $T = 20^\circ\text{C}$ ,  $t = 30 \text{ min}$ , MOCZeolite = 1 g,  $V = 100 \text{ mL}$ , and pH = 5.5 (a in mg/g, b in mmol/g).

60°C. The ion-exchange adsorption percentage of each metal ion increased with increasing temperature (Figure 5a) and was, therefore, endothermic. The hydration shell of the heavy metals was interrupted (*i.e.* the reduction in the strength of hydrated bonds between water molecules and metal ions) at high temperatures (Tahir and Rauf, 2003) and produces an increase in the adsorption extent. The thermodynamic state functions of Gibbs free energy ( $\Delta G^\circ$ ), enthalpy ( $\Delta H^\circ$ ), and entropy ( $\Delta S^\circ$ ) were examined using equations 10 and 11 (Laylin, 1993):

$$\ln\left(\frac{q_e m}{C_e}\right) = \frac{\Delta S^\circ}{R} + -\frac{\Delta H^\circ}{RT} \quad (10)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (11)$$

In the equations above,  $m$  is the adsorbent dosage (g/L);  $q_e$ , the metal-ion adsorption at equilibrium per adsorbent unit mass (mg/g);  $C_e$ , the concentration of metal ions at equilibrium (mg/L);  $q_e/C_e$ , the ion-exchange adsorption affinity;  $R$ , the universal gas constant, 8.314 J/mol/K; and  $T$ , the temperature (K). These thermodynamic functions were evaluated by plotting  $\ln(q_e m/C_e)$  as a function of  $1/T$  (Figure 5b,

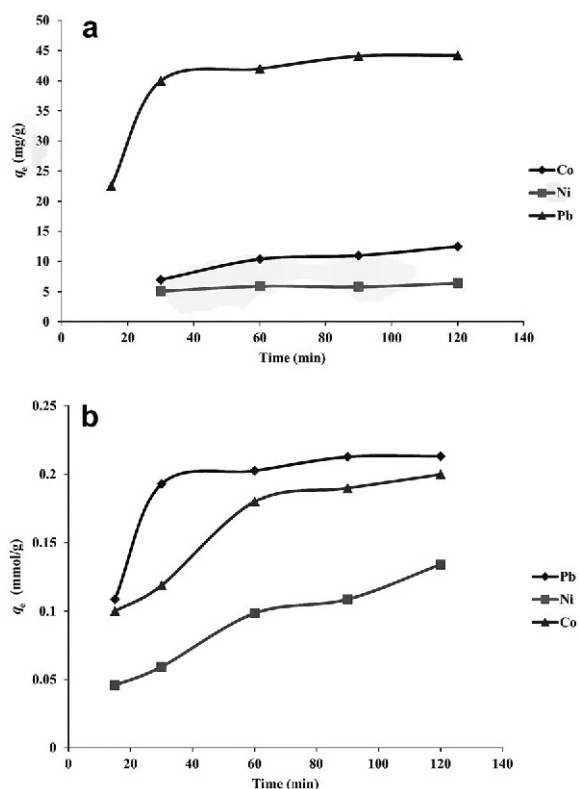


Figure 4. Effect of contact time on the adsorption of  $\text{Pb}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Co}^{2+}$ ; concentration = 200 mg/L,  $T = 60^\circ\text{C}$ , MOC-Zeo = 1 g,  $V = 100$  mL, and  $\text{pH} = 5.5$  (part a in mg/g, part b in mmol/g).

Table 1). The  $\Delta G^\circ$  values were negative and increased with increasing temperature, indicating that high temperature favored ion-exchange adsorption of  $\text{Pb}^{2+}$ ,  $\text{Co}^{2+}$ , and  $\text{Ni}^{2+}$  on MOCZeo. Under such conditions, ion-exchange adsorption reactions occurred spontaneously. The enthalpy ( $\Delta H^\circ$ ) of ion-exchange adsorption was positive for all ions, indicating that the ion-exchange adsorption reaction of these ions on MOCZeo was endothermic. The endothermic reaction of heavy-metal adsorption onto various zeolites has been reported previously (Irannajad *et al.*, 2015). A positive  $\Delta S^\circ$  value suggested that ions were not consistent in terms of the uptake sites of the adsorbent, probably due to the increase in the ‘translational energy’ of ions meaning the kinetic energy related to direct motion.

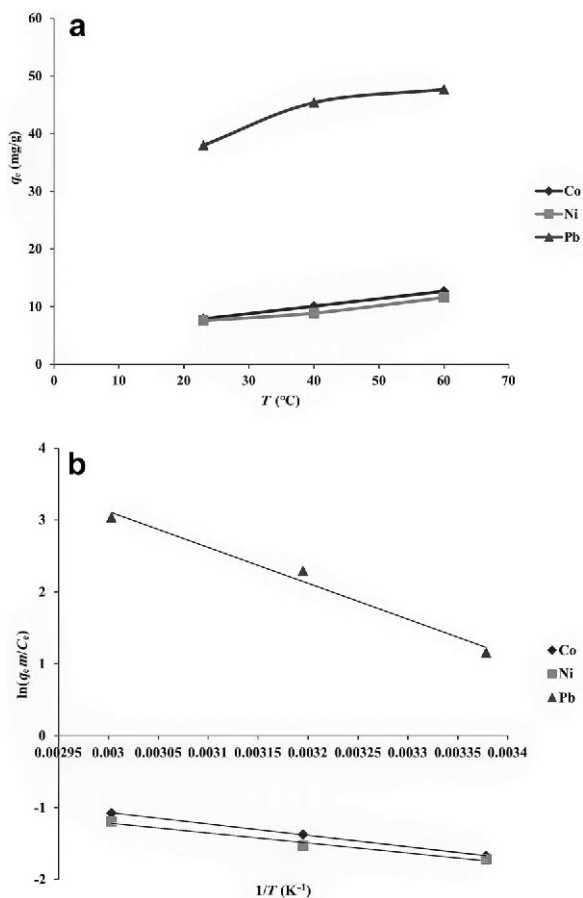


Figure 5. (a) Effect of temperature on adsorption and (b) plot of  $\ln(q_e m/C_e)$  vs.  $1/T$  for the adsorption of  $\text{Pb}^{2+}$ ,  $\text{Co}^{2+}$ , and  $\text{Ni}^{2+}$  on the MOCZeo composite; concentration = 200 mg/L,  $t = 30$  min,  $\text{pH} = 5.5$ , MOCZeo = 1 g, and  $V = 100$  mL.

*Ion-exchange adsorption isotherm and kinetic models*

Ion-exchange adsorption was evaluated by plotting the data using the linear forms of the Langmuir and Freundlich isotherms (equations 2 and 4, respectively). The results indicated that the data for  $\text{Pb}^{2+}$ ,  $\text{Co}^{2+}$ , and  $\text{Ni}^{2+}$  onto MOCZeo all fitted both the Langmuir and Freundlich equations (Figure 5; Table 2). Use of the two isotherm models indicated that both monolayer ion-exchange adsorption and an heterogeneous MOCZeo surface were present. The affinity of the metal ions for MOCZeo decreased in the order:  $\text{Pb}^{2+} > \text{Co}^{2+} \geq \text{Ni}^{2+}$ .

Table 1. Thermodynamics parameters for adsorption of  $\text{Pb}^{2+}$ ,  $\text{Co}^{2+}$ , and  $\text{Ni}^{2+}$  on MOCZeo.

Metal ions	$\Delta H^\circ$ (kJ/mol)	$\Delta S^\circ$ (Jmol/K)	$-\Delta G^\circ$ (kJ/mol)		
			296 K	313 K	333 K
$\text{Pb}^{2+}$	41.55	150.5832	-3.0226	-5.5835	-8.594
$\text{Co}^{2+}$	13.193	30.684	-4.11	-3.589	-2.975
$\text{Ni}^{2+}$	11.582	24.65	-4.2856	-3.86	-3.373

Table 2. Isotherm parameters for adsorption of  $\text{Co}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Ni}^{2+}$  on MOCZeo.

Metals ions	Langmuir constants			Freundlich constants		
	$q_{\text{max}}$ (mg/g)	$b$ (L/mg)	$R^2$	$K_F$ [ $\text{mg/g}(\text{mg/L})^{-1/n}$ ]	$n$	$R^2$
$\text{Pb}^{2+}$	40.65	0.11856	0.9974	10.556	3.882	0.7697
$\text{Co}^{2+}$	14.875	$2.44 \times 10^{-3}$	0.7438	0.1698	1.5926	0.9404
$\text{Ni}^{2+}$	10.515	$5.35 \times 10^{-3}$	0.9633	0.3242	1.9113	0.9434

Overall, the statistical correlation using the Langmuir isotherm was better than the Freundlich isotherm for  $\text{Pb}^{2+}$  and  $\text{Ni}^{2+}$ , with regression coefficients of 0.99 and 0.96, respectively, which agrees with the studies by Hui *et al.* (2005), Wingfelder *et al.* (2005), and Çoruh (2008). On the other hand, the Freundlich isotherm gave a better statistical correlation for  $\text{Co}^{2+}$ , with a regression coefficient of 0.94. As pointed out in previous studies (Treybal and Treybal Robert, 1968; Poots *et al.*, 1978; Ho and McKay, 1998), slopes of  $1/n \gg 1$  in the Freundlich model indicate that sorption is favored over the whole range of concentrations, whereas slopes of  $1/n < 1$  indicate that sorption is favored only at high concentrations. In the present study, the values of  $1/n < 1$  from the Freundlich model also confirmed the more favored ion-exchange adsorption at high concentrations. The capacity of MOCZeo was compared with that of other adsorbents mentioned in the literature, and the results are listed in Table 3. The capacity of MOCZeo is greater than that of adsorbents such as platinum nanoparticles/Zeolite-4A, nanoparticles of ferruginous sand, hydrous amorphous Fe oxides, chaba-

zites, and clinoptilolites. Other adsorbents, however, have capacities which are greater than that of MOCZeo, *e.g.*  $\text{Fe}_3\text{O}_4$ /bentonite nanocomposite, lemon peel as a biosorbent, and almond green hull. The best conditions for ion-exchange adsorption by platinum nanoparticles/zeolite-4A for heavy metals were: pH = 7, dose = 0.1 g/10 mL, contact time = 30 min. Ion-exchange adsorption of  $\text{Fe}_3\text{O}_4$ /bentonite nanocomposites depended heavily on the pH, as the removal efficiency increased with increasing pH, up to the alkaline range. The equilibrium contact time of poly(methoxyethyl)acrylamide for ion exchange adsorption of Pb was 60 min, near the equilibrium contact time of the adsorbent in the present study. In the case of dinitrophenyl-hydrazine (DNPH)-modified  $\alpha\text{-Al}_2\text{O}_3$ , the maximum simultaneous ion-exchange adsorption of  $\text{Pb}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Mn}^{2+}$ , and  $\text{Cr}^{3+}$  at a pH of 5.0 was obtained after 90 min. Ion-exchange adsorption was found to be heavily pH dependent which made the nanoparticles adsorb selectively these three metals from wastewater. Equilibrium ion-exchange adsorption of  $\text{Cr}^{6+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Ni}^{2+}$  was reached within 10 min and depended heavily on the pH.

Table 3. Comparison of  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ , and  $\text{Pb}^{2+}$  adsorption using various adsorbents.

Adsorbents	$q_m$ maximum capacity (mg/g)			References
	$\text{Ni}^{2+}$	$\text{Co}^{2+}$	$\text{Pb}^{2+}$	
Platinum nanoparticles/Zeolite-4A	0.839			(Mehdizadeh <i>et al.</i> , 2014)
$\text{Fe}_3\text{O}_4$ /bentonite nanocomposite		18.76		(Hashemian <i>et al.</i> , 2014)
Kaolinite		$1 \mu\text{mol/m}^2$		(Babel and Kurniawan, 2003)
Poly(methoxyethyl)acrylamide			81.02	(Şölenner <i>et al.</i> , 2008)
DNPH modified	18.18			(Afkhami <i>et al.</i> , 2010)
$\alpha\text{-Al}_2\text{O}_3$				
Hydrous amorphous	8.5			(Hu <i>et al.</i> , 2006)
Fe oxides				
Nanoparticles of iron oxide	14.7			(Babel and Kurniawan, 2003)
Nanoparticles of ferruginous sand	2.04			(Boujelben <i>et al.</i> , 2009)
Calcined phosphate			155	(Aklil <i>et al.</i> , 2004)
Nanoparticles of iron-modified sepiolite	18.30			(Lazarevic <i>et al.</i> , 2010)
Activated phosphate			4	(Mouflih <i>et al.</i> , 2005)
Bacillus-bacterial biomass	39.9		467	(Barakat, 2011)
Chabazite	4.50	5.8	6.0	(Ouki and Kavannagh, 1997)
Lemon peel as biosorbent		22		(Bhatnagar <i>et al.</i> , 2010)
Almond green hull		45.5		(Ahmadpour <i>et al.</i> , 2009)
Clinoptilolite	0.4	14.39	1.6	
Present study	10.52	14.88	40.65	

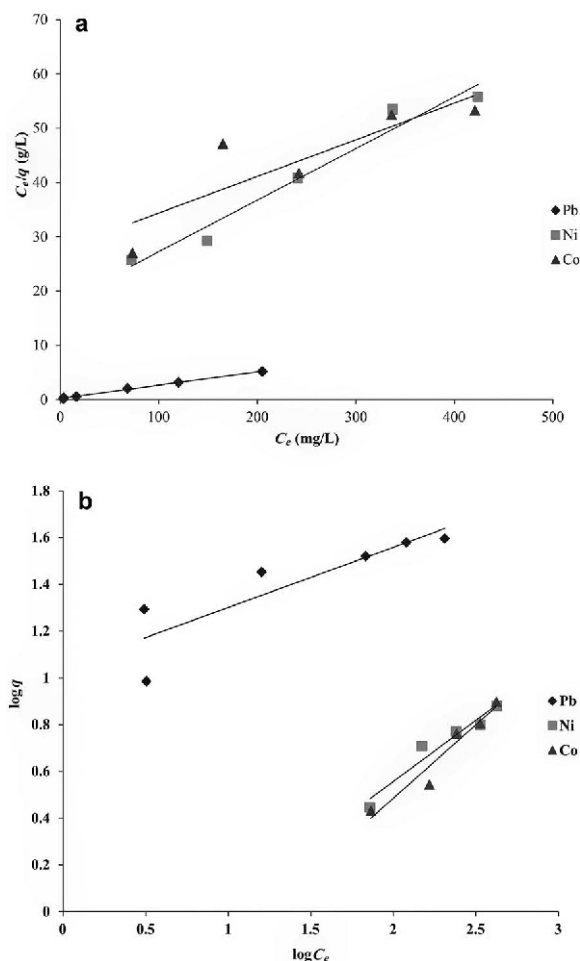


Figure 6. (a) Langmuir, and (b) Freundlich isotherm models for the adsorption of  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Pb}^{2+}$  on MOCZeo; concentration = 200 mg/L,  $T = 60^\circ\text{C}$ , MOCZeo = 1 g,  $V = 100$  mL, and  $\text{pH} = 5.5$ .

The maximum adsorption onto nano-iron oxide-coated sand was achieved at a pH of 4 and 7 for  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$ , respectively. The maximum adsorption of  $\text{Pb}^{2+}$  by calcined phosphate was found at a pH of 5. In addition, ion-exchange adsorption of Pb by activated phosphate is endothermic and more effective at high temperatures and at a pH of 3–4. In the case of chabazite, the selectivity order was  $\text{Pb} > \text{Cd} > \text{Zn} > \text{Co} > \text{Cu} > \text{Ni} > \text{Cr}$  and the

optimum pH was 5. Adsorption equilibrium of lemon peel as a biosorbent took place after 7 h which was much more than that of the natural adsorbents such as zeolites.

Ion-exchange adsorption kinetics is a major factor used in the study of such processes. Three well known models: pseudo-first order, pseudo-second order, and intraparticle diffusion were used. The kinetics plots of these models are shown Figure 6(a,b). In addition, the constants of all the kinetics models were examined and are listed in Table 4 where the correlation coefficients ( $R^2$ ) corresponding to the pseudo-second order model ( $>0.99$ ) were greater than those of the pseudo-first order model and intraparticle diffusion. The estimated values of  $q_e$  ( $q_{e,cal}$ ) from the pseudo-second order model agreed well (Table 4) with the experimental values of  $q_e$  ( $q_{e,exp}$ ).

Using equation 9, the intraparticle diffusion model (Srivastava *et al.*, 2006), possible reaction retardation due to intraparticle diffusion was evaluated by calculating the values corresponding to  $k_1$  and  $I$  from the slopes and intercepts, respectively. The results (Figure 6c, Table 4) revealed that the ion diffusion rates decreased in the order:  $\text{Pb}^{2+} > \text{Co}^{2+} > \text{Ni}^{2+}$ . The reason for this order corresponded to hydrated ionic radius and ionic movements (Ricordel *et al.*, 2001). The hydrated ionic radius of these metals increase in the order:  $\text{Pb}^{2+} < \text{Co}^{2+} < \text{Ni}^{2+}$  (Shannon, 1976). The smaller the radius, the greater the ionic movement and diffusion rate. According to the literature, if the plots do not cross the origin, intraparticle diffusion and other processes may control the rate of ion-exchange adsorption (Alver and Metin, 2012; Mahmoud *et al.*, 2012). The results show that the lines did not pass through the origin (Figure 6b). The results showed that both the surface uptake and the intraparticle-diffusion mechanisms play a major role in the ion-exchange adsorption process.

### CONCLUSIONS

In the present study MOCZeo was used as a modified adsorbent for the removal of  $\text{Pb}^{2+}$ ,  $\text{Co}^{2+}$ , and  $\text{Ni}^{2+}$  from aqueous solutions. Characterization of the samples showed that the natural zeolite modified by manganese oxide was more porous than the unmodified version. The capacity of MOCZeo was compared with that of other

Table 4. Kinetics parameters for adsorption of  $\text{Pb}^{2+}$ ,  $\text{Co}^{2+}$ , and  $\text{Ni}^{2+}$  on MOCZeo.

Metal ions	– Pseudo-first order –				– Pseudo-second order –			Intraparticle diffusion		
	$q_{e,exp}$ (mg/g)	$q_{e,cal}$ (mg/g)	$k_1$ ( $\text{min}^{-1}$ )	$R^2$	$q_{e,cal}$ (mg/g)	$k_2$ (g/mg/g)	$R^2$	$k_i$ (mg/g/ $\text{min}^{0.5}$ )	$I^*$	$R^2$
$\text{Co}^{2+}$	13	12.858	0.025	0.9537	16.28	$1.6 \times 10^{-3}$	0.993	1.0971	0.8637	0.677
$\text{Pb}^{2+}$	45	19.86	0.03	0.8837	49.5	$1.634 \times 10^{-3}$	0.991	2.611	18.953	0.9528
$\text{Ni}^{2+}$	8	4.384	0.0088	0.8155	7.107	$9.252 \times 10^{-3}$	0.992	0.3906	2.3476	0.8078

\*  $I$  = mass-transfer residence time.



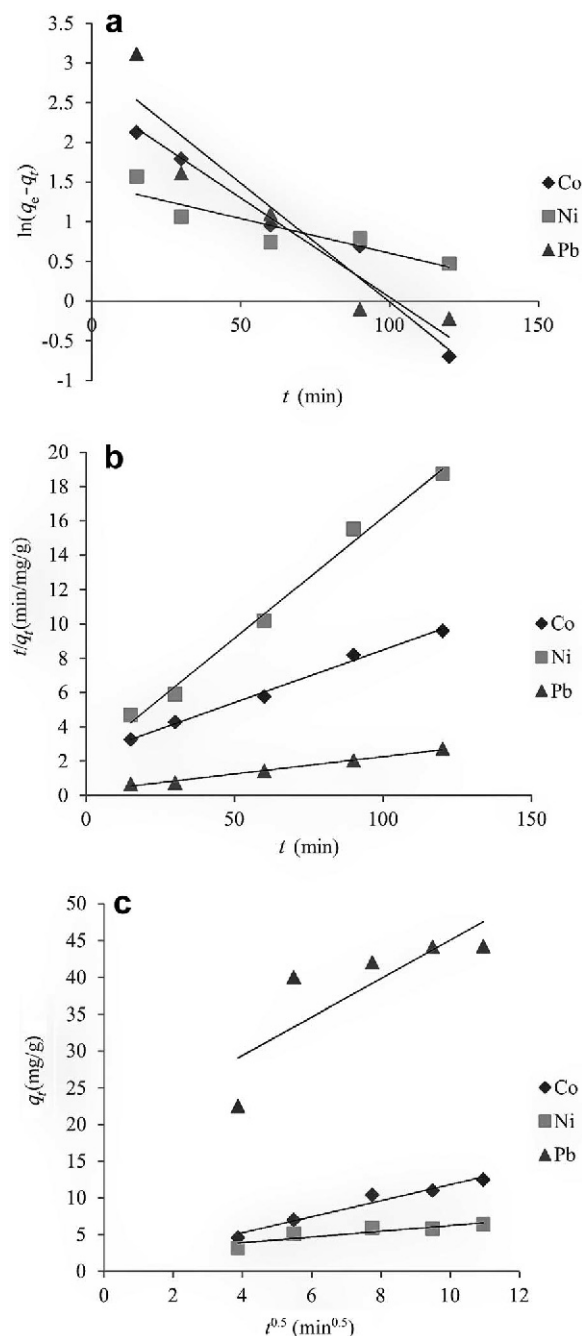


Figure 7. (a) Pseudo-first order, (b) Pseudo-second order, and (c) intraparticle diffusion kinetics models for the adsorption of Pb<sup>2+</sup>, Co<sup>2+</sup>, and Ni<sup>2+</sup> on MOCZeo; concentration = 200 mg/L,  $T = 60^\circ\text{C}$ , MOCZeo = 1 g,  $V = 100$  mL, and pH = 5.5.

adsorbents and the results showed that the removal of the heavy metals by MOCZeo is enhanced by the modification with manganese oxide. The influence of variables such as initial concentration, initial pH, contact time, and temperature on ion-exchange adsorption was investigated. The degree of removal of metal ions was improved by increasing the initial pH of the metal-ion

solution; the maximum value was reached at a pH of 5.5 for Pb<sup>2+</sup> and at 7–8 for Co<sup>2+</sup> and Ni<sup>2+</sup>. The ion-exchange adsorption selectivity was in the following order: Pb<sup>2+</sup> > Co<sup>2+</sup> > Ni<sup>2+</sup> for MOCZeo in the present study, similar to the pure zeolite. The thermodynamics study showed that the  $\Delta G^\circ$  values were negative and increased with increasing temperature. Higher temperatures favored uptake of heavy metals on MOCZeo, therefore, with spontaneous ion-exchange adsorption. The ion-exchange adsorption of Pb<sup>2+</sup>, Co<sup>2+</sup>, and Ni<sup>2+</sup> on MOCZeo was best described by both the pseudo-first order and pseudo-second order kinetics models. Correlation coefficients ( $R^2$ ) corresponding to the pseudo-second order model were greater than those of the pseudo-first order model and of intraparticle diffusion. The estimated values of  $q_e$  ( $q_{e,cal}$ ) from the pseudo-second order model were in agreement with the experimental values of  $q_e$  ( $q_{e,exp}$ ).

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