Removal of Cd, Cu and Zn ions from aqueous solutions using natural and Fe modified sepiolite, zeolite and palygorskite clay minerals

Fatemeh Nasseri Bahabadi, Mohammad Hady Farpoor and
Majid Hejazi Mehrizi

ABSTRACT

Metal ions such as Cu, Cd, and Zn are toxic and considered as hazardous pollutants due to their stability in the environment. In this study, the natural and Fe (III) modified sepiolite, palygorskite, and zeolite clay minerals were used for the removal of Cu, Zn, and Cd ions from aqueous solutions. The iron chloride 1 M was used for mineral modification and the capacity of sorbent was assessed in a batch experiment containing six starting concentration of sorbents ranging from 10 mg L^{-1} to 140 mg L^{-1}. Results of the study showed higher removal efficiency for modified compared to natural clays. Removal efficiency of Cd, Cu, and Zn for zeolite was increased by 15.5, 30.2 and 21.4%, respectively, after modification. Zn removal by sepiolite remained unchanged after surface modification, whereas Cu and Cd removal was increased respectively by 13.6 and 21.2%. Palygorskite modification process also increased 38.14% of Cu, 25.5% of Zn, and 28.4% of Cd sorption compared to its unmodified form. Equilibrium sorption isotherm studies showed that the experimental data were better fitted by the Freundlich sorption isotherm ($r^2 > 0.99$) than the Langmuir ($r^2 > 0.82$). In general, the investigated minerals are suggested as efficient sorbents for the removal of Cd, Cu, and Zn ions from contaminated aqueous solutions.

Key words | fibrous minerals, heavy metals, isotherm, removal efficiency

Fatemeh Nasseri Bahabadi
Mohammad Hady Farpoor
 (corresponding author)
Majid Hejazi Mehrizi
Department of Soil Science, Faculty of Agriculture,
Shahid Bahonar University of Kerman,
Kerman,
Iran
E-mail: *farpoor@uk.ac.ir*

INTRODUCTION

Environmental pollution by heavy metals such as Cd, Cu, and Zn has received great concern in the recent years. Heavy metals, which are discharged into the environment either naturally or as a result of industrial and mining processes, are non-degradable in nature and highly toxic to plants, animals and human beings (Alloway & Jackson 1991). They accumulate mainly in human skin, kidneys, pancreas, brain and liver, causing several diseases and disorders (Bailey *et al.* 1999). In recent years, several technologies and methods including filtration, chemical precipitation, membrane separation, solvent extraction, ion exchange and adsorption on activated carbon are developed to remove heavy metals from aqueous solutions (Bergaya *et al.* 2006; Wang & Chen 2009). Each method has some significant drawbacks in practice such as sludge production and high operational cost. That is why simplicity, reasonable price and removal efficiency of heavy

metal sorption from wastewater have been regarded as selection criteria.

Palygorskite and sepiolite minerals are most likely to occur in arid and semiarid regions of the world. Due to the large surface area and porosity, these minerals have shown remarkable ability for sorption of inorganic and organic pollutants (Galan 1996; Murray 2007). Zeolites, hydrated aluminosilicate minerals with high cation exchange capacity (CEC), are able to sorb water and ions without any changes in their molecular structure. Among natural zeolites, clinoptilolite has been used for heavy metal removal more often due to its abundance, low cost, high affinity to heavy metals and stability in different environmental conditions. Sorption of heavy metals by clay minerals is focused on by several studies. Shirvani *et al.* (2006) studied cadmium sorption by palygorskite, sepiolite and calcite minerals. They concluded that the

sorption capacity of minerals for Cd follows the trend: sepiolite > palygorskite > calcite. On the other hand, Sheikhhosseini *et al.* (2013), investigated the competitive sorption of nickel, cadmium, zinc and copper on palygorskite and sepiolite aluminosilicates. They showed, that the sequence of metal sorption on the minerals was Cu > Zn > Cd > Ni. They reported, that palygorskite and sepiolite can effectively remove Cu from solution regardless of the presence of other metals. Moreover, Doğan *et al.* (2008) assessed the metal affinity sequence of sorption on sepiolite as Zn (II) > Cu (II) ∼ Co (II) > Fe (III) > Mn (II) > Cd (II). Besides, Hamidpour *et al.* (2009) studied the kinetics and isotherms of cadmium sorption on bentonite and zeolite and found out that commercial Iranian bentonite and zeolite minerals showed a reasonable potential for the removal of Cd (II) from aqueous solutions.

Meanwhile, several methods have been developed to modify the surface and to increase heavy metal sorption of clay minerals. It is well known that Fe and Mn oxides display strong sorption affinities to heavy metals (Mustafa *et al.* 2009), and thus they are widely used for zeolite surface modification in order to enhance removal capacity (Doula 2006; Han *et al.* 2009). The modification of zeolite by Fe oxides increases the surface area and sorption affinity for heavy metals (Han *et al.* 2009; Noroozifar *et al.* 2009). Although several studies on the removal of heavy metals from aqueous solutions by sepiolite, palygorskite and zeolite minerals were performed, but little data about the effect of surface modification by oxides is available. Therefore, the objective of the present research was to determine the efficiency of natural and Fe (III) modified sepiolite, palygorskite and zeolite clay minerals on the removal of Cu, Cd, and Zn from aqueous solutions.

MATERIALS AND METHODS

Sorbents

The natural clay minerals used in this study included palygorskite from Florida (Gadsden County, USA), sepiolite from Fariman (Northeast Iran) and zeolite from Semnan (Central Iran). The mineral samples were powdered and passed through a 35 mesh standard sieve. Deionized water with the ratio of 1:10 (clay sample to water) was used to remove the impurities from the clay minerals and the samples were dried at 60 °C for 2 days (Han *et al.* 2009). A Philips X'pert High Score diffractometer operating at 40 kV and 30 mA was used for X-ray diffraction (XRD)

analyses. The surface morphology and the chemical composition of samples were investigated using a 'MIRA3 TESCAN' scanning electron microscope (SEM) equipped with X-ray energy dispersive detector (EDS).

$FeCl_3.6H_2O$ solution was used as the source of Fe (III) for mineral modification. To perform modification process, 50 g of clay was mixed with 1 M $FeCl_3.6H_2O$ solution (50 mL) and 50 mL 3 M NaOH solution in a 2 L container. The container was incubated at 80 °C for 48 h. The suspension was then filtered and washed out until no NO_3^- ions were detected. The resulting sample was dried at 105 °C to constant weight (Han *et al.* 2009; Eren *et al.* 2010).

Sorption equilibrium experiments

Sorption of cadmium, zinc and copper on natural and Fe-modified clay minerals was studied using a batch experiment. Certain amounts of mineral samples (0.3 g) were individually equilibrated with 30 mL of Cd (II), Zn (II), and Cu (II) solutions with the initial concentration of 10, 20, 40, 60, 80 and 140 mg L^{-1}. Equilibration process was carried out in two replications at room temperature (25 ± 1 °C) for 24 h on an orbital shaker (180 rpm). Centrifuge (3,000 rpm for 10 min) was used for the separation of the supernatant from the solid phase. Atomic adsorption spectrometer (AAS Vario 6-Analytikjena) was used to determine heavy metal concentrations in the supernatants (C_e).

The quantity of metal ions sorbed on clay minerals (q_t) and the removal percentage were calculated using Equations (1) and (2) (Bedoui *et al.* 2008), where C_0, C_e, m, and V are initial concentration (mg L^{-1}), equilibrium concentration (mg L^{-1}), sorbent mass (g), and volume of the solution (L), respectively.

$$q_t = \frac{(C_0 - C_e)V}{m} \tag{1}$$

$$\% \text{ removal } = \frac{(C_0 - C_e)}{C_0} * 100 \tag{2}$$

The equilibrium data were analyzed using Langmuir (1918) and Freundlich (1906) isotherms (Equations (3) and (4))

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \tag{3}$$

$$q_e = K_F C_e^n \tag{4}$$

where q_{max} and K_L are the Langmuir constants showing maximum sorption capacity and energy constant, respectively. K_F represents the Freundlich distribution coefficient and n is a correction factor. GraphPad Prism Ver. 5.0 software showed that the experimental data conformed to the non-linear form of Langmuir and Freundlich equations. The best model was selected on the basis of determination coefficient (R^2) and standard errors of estimate (SEE) by the following equation:

$$\text{SEE} = \left[\sum \frac{(q_e - q_e^*)^2}{(n-2)} \right]^{1/2} \tag{5}$$

where q_e and q_e^* represent measured and predicated amount of sorbed metal and n is the number of experimental points.

RESULTS AND DISCUSSION

Minerals characterization

Table 1 shows the chemical composition of clay minerals obtained by XRF analyses. The results showed that SiO_2 is the dominant component in all minerals; however, the SiO_2 content in zeolite (66%) was higher than sepiolite (37.4%) and palygorskite (56%) clay samples. Al_2O_3, CaO, MgO, Fe_2O_3, Na_2O, and K_2O were dominant components in all the minerals analyzed.

Table 1 | Chemical composition of studied clay minerals

Element %	Palygorskite	Sepiolite	Zeolite
SiO_2	56	37.44	66.5
Al_2O_3	8.0	0.42	11.81
Fe_2O_3	5.0	0.51	1.3
CaO	2.3	11.78	3.11
MgO	9.1	18.79	1.72
Na_2O	0.2	0.01	2.01
K_2O	0.9	0.02	3.12
P_2O_5	1.0	0.01	0.01
MnO	–	0.00	0.04
TiO_2	0.77	0.02	1.21
LOI[a]	16.5	30.77	12.05
CEC ($Cmol^+$/Kg)	38.41	15.65	89.63

[a]Loss on ignition.

Figure 1 shows the X-ray diffractograms of the investigated clay minerals. The high intensity 0.9 nm peak confirms the presence of zeolite as the dominant clay and quartz impurities in the analyzed sample (Figure 1(a)). Moreover, the sharp and intense 1.71 nm peak (Figure 1(b)) related to Fariman sepiolite sample proved the presence of a relatively pure sepiolite with quartz impurities. First (1.05 nm) and second (0.64 nm) order peaks of palygorskite together with feldspar and vermiculite impurities were investigated in palygorskite clay sample (Figure 1(c)).

Scanning electron microscopy and elemental analysis

Figures 2–4 show the scanning electron micrographs of natural and Fe modified minerals. Natural zeolite mineral with good crystallinity was not changed after modification and its ralubat morphology was preserved. EDS results
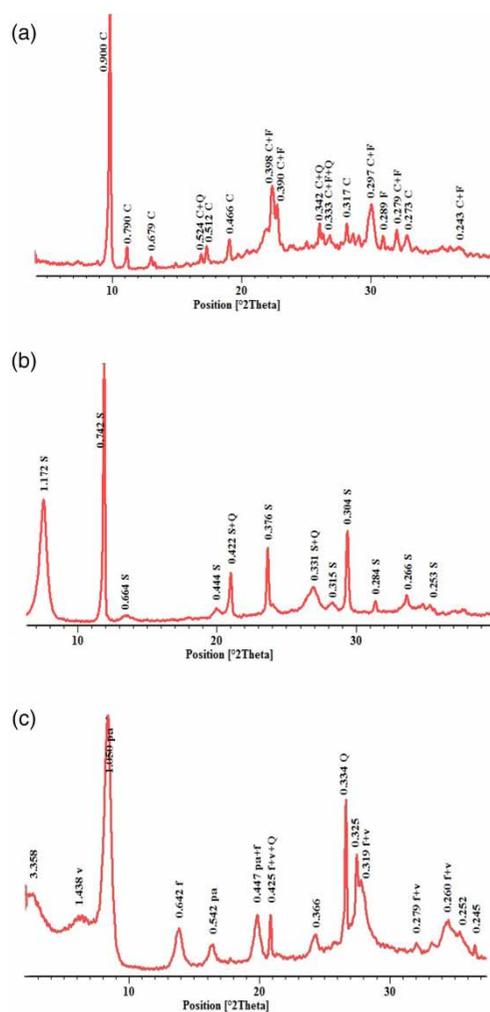

Figure 1 | XRD of zeolite (a), sepiolite (b) and palygorskite (c) clay samples. C, clinoptilolite; Pa, palygorskite; S, sepiolite; Q, quartz; F, feldspar; V, vermiculite.
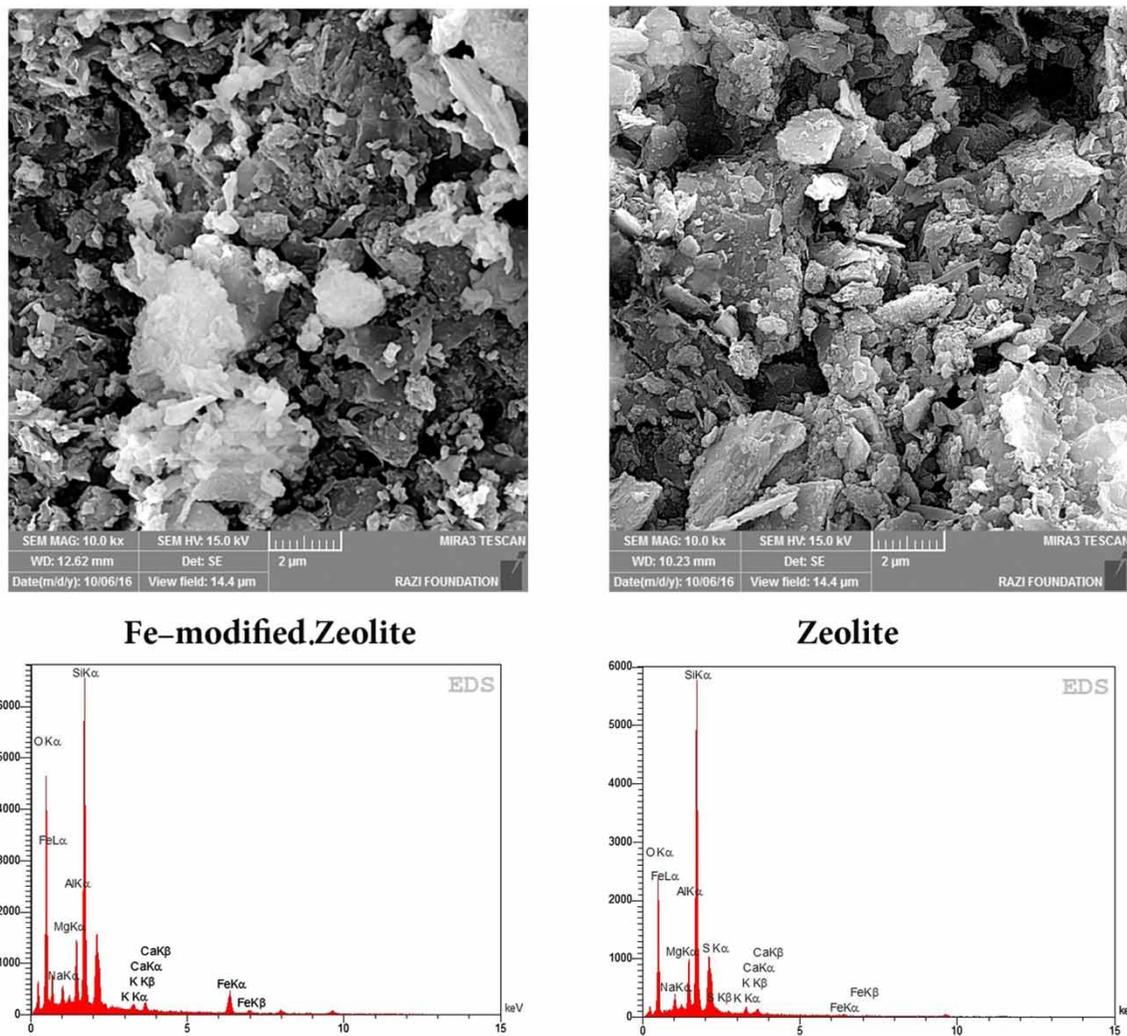
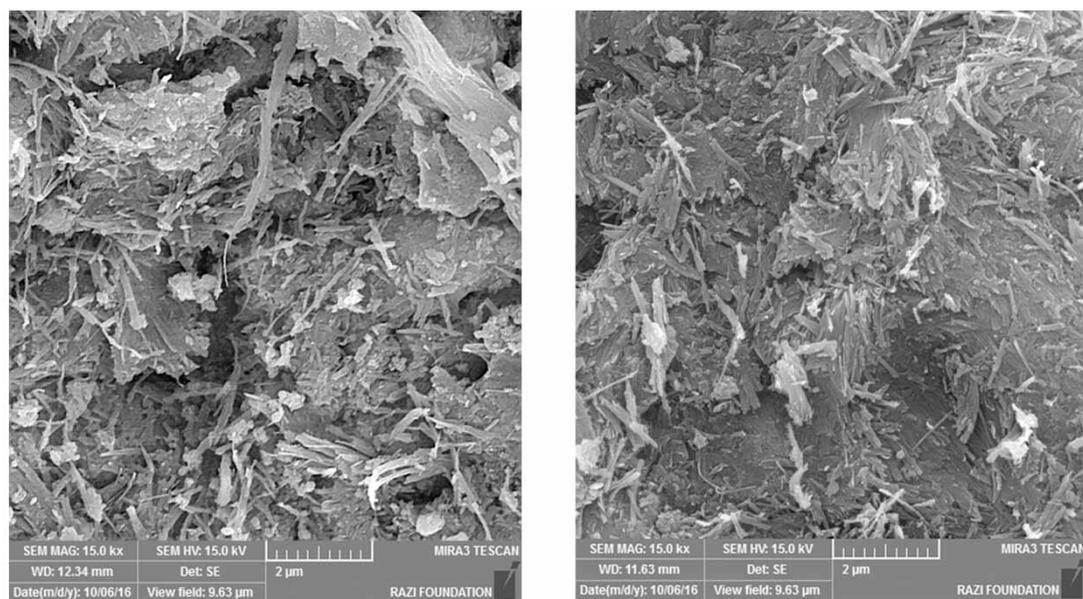**Figure 2** | SEM micrographs and EDS analysis of the natural and Fe-modified zeolite.

showed that Fe was increased after modification and mineral surface was coated by Fe. The same results were also reported by Doula & Dimirkou (2008). Besides, Kragović *et al.* (2013) also reported that zeolite form and size were preserved after Fe (III) treatment.

SEM micrographs for sepiolite mineral (Figure 3) showed that the surface roughness of sepiolite was increased after Fe modification. It seems that iron hydroxide was interfered with the mineral surface. The same result reported for metronidazole adsorption using Fe modified sepiolite by Ding & Bian (2014).

Figure 4 shows SEM micrographs and semi quantitative EDS analysis of palygorskite crystals. The same crystal morphology was observed before and after modification. EDS clearly showed that iron content was increased at the crystal surface and in the pore spaces after treatment.

Sorption study

Figure 5 shows the removal of different concentrations of Cu, Zn, and Cd by clay mineral treatments. The amount of metals sorbed by natural and Fe (III) modified minerals considerably increased with increasing initial metal concentration. For example, with the increase in the initial concentration of Cu (II), the amount of Cu sorbed by modified sepiolite (m.se) increased from 3.9 to 29.8 mg g^{-1} and for modified palygorskite (m.pa) varied from 2.9 to 23.8 mg g^{-1}. Previous studies reported that despite the low CEC of palygorskite and sepiolite clays, they are capable of sorbing heavy metals from aqueous solutions due to their porous structure (Wang & Chen 2009; Sheikhhosseini *et al.* 2013). Heavy metals are reported to be trapped by chemisorptions and/or cation exchange reactions in these
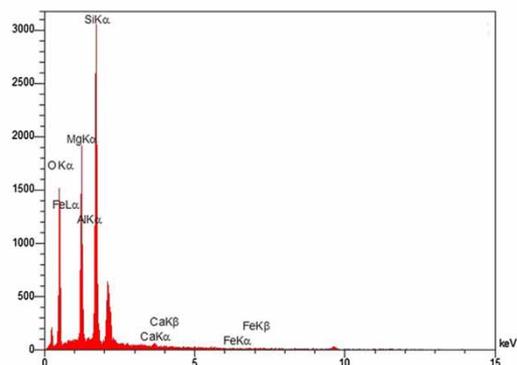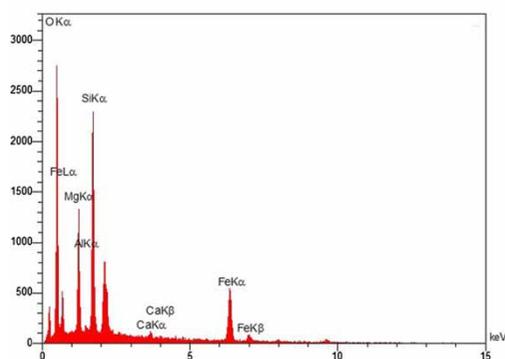
Figure 3 | SEM micrographs and EDS analysis of the natural and Fe-modified sepiolite.

fibrous clays (Wang *et al.* 2007). Zeolite also has large surface area and highly capable of ion exchange and sorption due to its particular tetrahedral pore framework (Han *et al.* 2009). However, lower metal sorption was observed in zeolite and Fe (III) modified zeolite (m.ze) treatments compared to other mineral treatments used. The results also showed that modified minerals could sorb Cu, Cd and Zn more than non-modified ones. It seems that Fe (III) ions could lie in the channels or form oxo- or hydroxo-complexes on the modified mineral surfaces causing an increase of the active sites.

Comparison of sorbent removal efficiency

A significant difference in Cu (II) removal was found between natural and Fe (III) modified minerals (Figure 6). The sorbents showed the following order of efficiency:

modified sepiolite > modified zeolite > modified palygorskite > sepiolite > zeolite > palygorskite. Surface modification of minerals using Fe (III) significantly ($p < 0.05$) increased the Cu removal efficiency of sorbents. As an example, Cu removal increased from 46.7% to 78% when sepiolite modified using Fe (III) ions. Eren & Gumus (2011) also reported higher efficiency of Fe (III) modified sepiolite in Pb (II) removal from aqueous solutions compared to natural sepiolite.

The removal of zinc by natural and Fe (III) modified sorbents is presented in Figure 7. Zinc removal by sepiolite and palygorskite was the same and higher than that of zeolite. However, the highest Zn removal was investigated for modified palygorskite. On the other hand, a significant increase in Zn removal was found when modified palygorskite and sepiolite were used instead of non-modified clays and no difference was found between Zn removal efficiency of
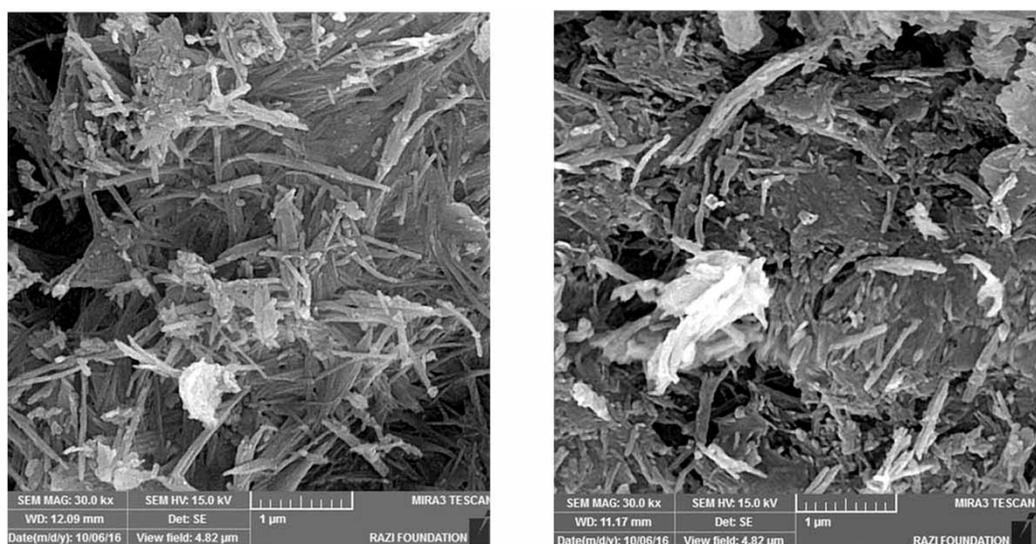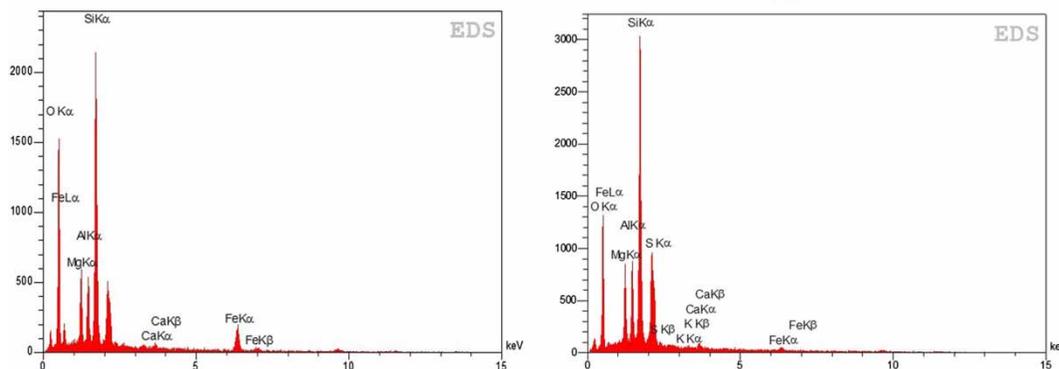
Figure 4 │ SEM micrographs and EDS analysis of the natural and Fe-modified palygorskite.

natural and modified zeolites. A higher amount of Zn removed by Fe (III) modified sorbents seems to be due to increasing number of active sites after modification. Kragović *et al.* (2012) also studied sorption of Pb (II) on natural and modified zeolites and reported that Fe (III) modified zeolite sorbed more Pb (II) than natural zeolite.

Significant differences among sorbents in the removal of Cd (II) from aqueous solutions were observed (Figure 8). Natural and Fe (III) modified sepiolites sorbed more Cd (II) than other natural and modified sorbents. Cadmium removal by sepiolite was 57% and significantly increased to 78.1% when modified with Fe (III). On the other hand, zeolite sorbed lower amounts of Cd (II) compared to other sorbents and sorption slightly increased from 21.8% to 37% after modification. Brigatti *et al.* (2000) also reported the suitable potential of sepiolite mineral for removing heavy metals from aqueous solutions. The tested minerals

clearly showed higher capacity of copper and cadmium sorption compared to zinc.

The comparison made for Figures 6–8 clearly showed that natural and modified sorbents removed higher amounts of Cu (II) than Zn (II) and Cd (II) from aqueous solutions. Sheikhhosseini *et al.* (2013) also showed that Cu and Zn sorption by natural palygorskite and sepiolite was more than that of Ni and Cd.

Sorption isotherms

The sorption isotherms represent the relations between the amounts of metal sorbed by a unit weight of sorbent and the amounts of metal remaining in the solution at equilibrium (El-Ashtoukhy *et al.* 2008). The isotherms are considered to be a suitable form of characterizing the sorption phenomena in a simple approach. The slope of
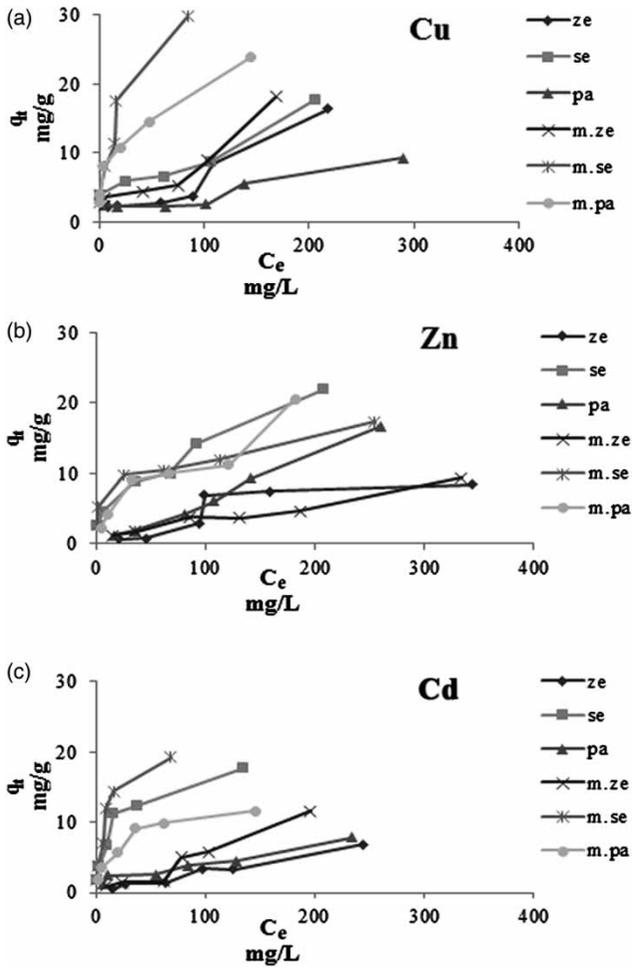
Figure 5 │ Effects of Cu (a), Zn (b), and Cd (c) concentrations on their sorption by selected minerals.
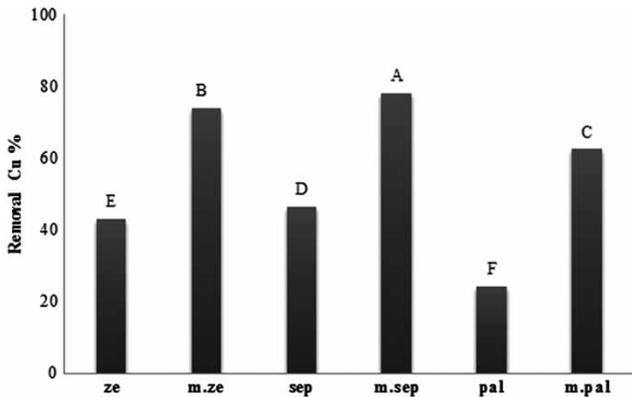

Figure 6 │ Evaluation of various minerals sorption in the removal of copper in concentration of 140 mg L^{-1}. Ze: Zeolite, Se: Sepiolite, Pa: Palygorskite, m: modified (average of common letters is not significant at the level of 0.05 Duncan).

Figure 7 │ Evaluation of various minerals sorption in the removal of zinc in concentration of 140 mg L^{-1} (average of common letters is not significant at the level of 0.05 Duncan).

Figure 8 │ Evaluation of various minerals sorption in the removal of cadmium in concentration of 140 mg L^{-1} (average of common letters is not significant at the level of 0.05 Duncan).

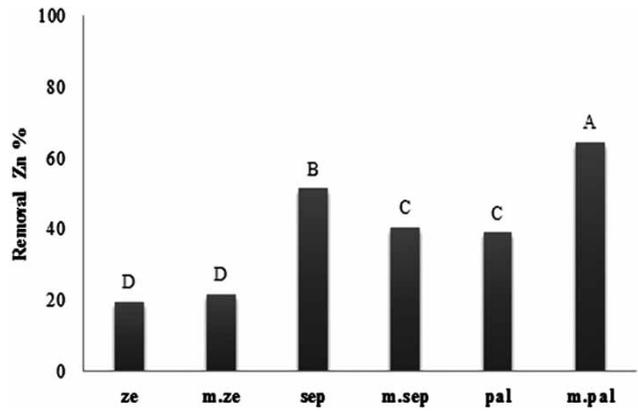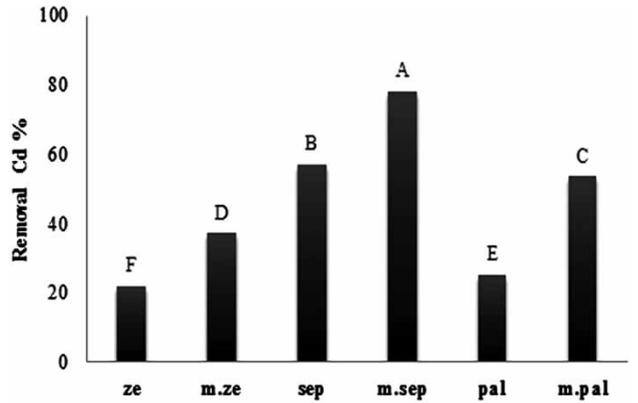isotherm gives information about the affinity between sorbent and solute (Ayuso & Sanchez 2007). The results indicated that the Freundlich model effectively and much better described sorption of Cu, Zn, and Cd on natural and Fe (III) modified sorbents (with an average R^2 = 0.89) than Langmuir model (R^2 = 0.85). Shirvani *et al.* (2006) also showed that the sorption of Cd ions onto sepiolite was better described by the Freundlich model. Kragović *et al.* (2012) studied the sorption of lead onto natural and modified zeolites and found that Freundlich was more appropriate for modelling the equilibrium sorption of sorbents at low metal concentrations. The Freundlich model parameters and the statistical fits of equilibrium data to this equation are given in Table 2.

The K$_F$ is related to multilayer sorption capacity and n is the intensity of sorption, which varies with the heterogeneity of the sorbent surfaces. A relatively $n < <1$, indicates that the more heterogeneity of sorbent surface and sorption intensity is favorable over the whole initial concentration, while $n > 1$ means that intensity sorption is only desirable

Table 2 | Freundlich isotherm parameters for Cu, Zn and Cd sorption for studied minerals

Mineral		Freundlich model $q_e = K_F C_e^n$			
	Metal	n	K_F	R_2	SE
Zeolite	Cu	1.202	0.025	0.712	1.708
	Zn	0.625	0.240	0.826	2.031
	Cd	0.958	0.034	0.936	0.462
Modified zeolite	Cu	0.353	1.443	0.570	1.421
	Zn	0.816	0.07	0.956	0.730
	Cd	1.145	0.027	0.824	0.983
Sepiolite	Cu	0.532	0.926	0.804	2.696
	Zn	0.516	1.355	0.949	1.426
	Cd	0.349	3.343	0.940	1.655
Modified sepiolite	Cu	0.419	4.606	0.947	2.349
	Zn	0.283	3.429	0.896	1.286
	Cd	0.380	4.107	0.915	2.40
Palygorskite	Cu	0.757	0.121	0.484	1.464
	Zn	1.110	0.035	0.979	0.512
	Cd	0.583	0.301	0.852	0.826
Modified palygorskite	Cu	0.354	3.968	0.975	1.220
	Zn	0.821	0.356	0.906	4.855
	Cd	0.342	2.259	0.97	1.002

at high initial concentrations (Eren et al. 2010; Sevim et al. 2011). The n coefficient (Table 2) showed that Zn is better sorbed by zeolite ($n = 0.62$) compared to other metals. The value of $n > 1$ for copper indicates a more unfavorable adsorption of this metal by zeolite in comparison with zinc and cadmium. The n value for copper in modified zeolite decreased; that is why a better adsorption for modified zeolite comparing to natural zeolite was found. The value of $n > 1$ for cadmium ($n = 1.14$) shows an unfavorable adsorption by modified zeolite. The least value of n coefficient for sepiolite related to cadmium ($n = 0.34$) was observed. The value of this coefficient for modified sepiolite in Zn adsorption was 0.28, which is lower than other metals and it shows better adsorption of Zn by modified sepiolite than the natural form of this mineral. The n coefficient for palygorskite related to cadmium is the lowest value that represents the ideal sorption of Cd by palygorskite, while n coefficient for zinc was the highest ($n = 1.11$). Palygorskite modification process caused n coefficient for zinc to be reduced; thus, more favorable sorption of Zn by modified palygorskite occurred compared to natural mineral. Generally speaking, natural and modified sepiolite still tends to adsorb three metals under study.

K_F factor is a measure of the adsorption rate of metals by clay minerals. The results showed that the modification process increased the K_F factor for Cu sorption by zeolite that resulted in more adsorption of copper by the mineral. The

K_F values of 0.92, 1.13, and 3.34 mg g^{-1} for copper, zinc and cadmium show better adsorption of this metal by sepiolite. K_F value for cadmium by sepiolite is 3.34 mg g^{-1}, which shows more adsorption of this metal by sepiolite (Table 2).

The K_F for modified sepiolite increased and metals sorption by this mineral was also much better. The highest K_F value was investigated for cadmium by palygorskite (0.301 mg g^{-1}) that confirms a better adsorption of cadmium by palygorskite compared to other metals. Modification of palygorskite increased the K_F coefficient and adsorption for copper and cadmium more than zinc.

In general, comparison of K_F for minerals showed that sepiolite has more efficient adsorption positions for heavy metals compared to the natural minerals. Besides, modified minerals adsorbed copper with more intensity than other metals. Eren et al. (2010) also concluded that the modified sepiolite by iron chloride adsorbed Cu rather than other heavy metals and the adsorbed data fitted well with both Freundlich and Langmuir models.

Comparison of metals adsorption by clay minerals

Langmuir and Freundlich equations did not show high coefficients (R^2) in describing sorption data for the studied metals by zeolite. That is why a comparison among means of metal sorption was made for natural and modified clay minerals. Looking at Figure 9, natural minerals of sepiolite and zeolite sorbed greater amounts of copper compared to other metals. Besides, Zn and Cd sorption at concentration of 140 mg L^{-1} by sepiolite is more than the other two minerals.

Modified forms of sepiolite, zeolites, and palygorskite showed the ordered rates of sorption of copper, respectively. In the modified forms, the highest and lowest sorption of Zn were observed for palygorskite and sepiolite, respectively.
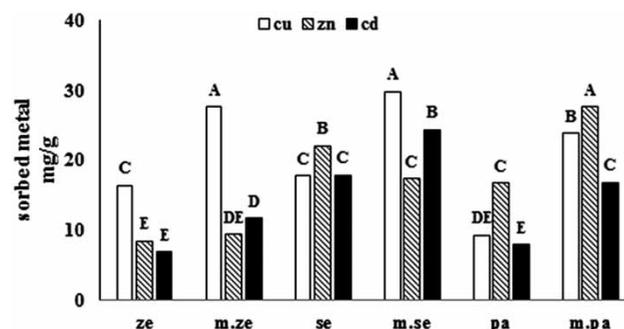

Figure 9 | Average sorption of the three metals Cu, Zn and Cd in concentration of 140 mg L^{-1} by the studied minerals. Ze: Zeolite, Se: Sepiolite, Pa: Palygorskite, m: modified (average of common letters is not significant at the level of 0.05 Duncan).

Cadmium was sorbed by modified sepiolite more than the other two modified minerals. In general, the sequence of metal sorption on minerals was as Cu > Zn > Cd. Such sorption selectivity sequences can be explained by metal characteristics including electronegativity, ionic ratio, hydrolysis constant and hardness (Vidal *et al.* 2009; Sdiri *et al.* 2012). Formation of precipitation phases on the clay surfaces is suggested as one of the main reasons for greater sorption of Cu than Zn, Cd and Ni on zeolites (Majdan *et al.* 2003; Hui *et al.* 2005).

CONCLUSION

Palygorskite mineral surface modification with iron chloride, which is performed for the first time in the present study, increased capability of this mineral to sorb heavy metals. Palygorskite modification process increased sorption of Cu by 38.14%, Zn by 25.53%, and Cd by 28.39%. The sequence of metal sorption on studied minerals was as Cu > Zn > Cd. Modified sepiolite and palygorskite showed more sorption of copper than the other two elements, respectively. In the case of Zn and Cd, modified sepiolite, sepiolite and palygorskite minerals, showed the highest sorptions, respectively. Modification increased the ability of minerals to sorb Cu, Zn and Cd.

Freundlich and Langmuir models were used to describe sorption of Cu, Zn and Cd, but Freundlich model showed the best fitting on sorption data. Comparison of isothermal coefficients for minerals showed that modified sepiolite has the best ability to sorb copper; however, modified palygorskite also sorbs cadmium well. Besides, the modification of palygorskite mineral reduced the *n* coefficient for Zn and increased the sorption of this metal. The results showed that modification of clay minerals with iron chloride increases the sorption of heavy metals from aqueous solutions.

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