Factors affecting adsorption characteristics of Zn^{2+} on two natural zeolites

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Abstract

Mining-related and industrial wastes are primary sources of heavy metal contamination in soils and groundwater. The limitation of such waste in drinking water needs to meet government requirements in order to safeguard human health and environment. Zinc, one of the most preponderant pollutants, is difficult to remove from wastewater rather than other heavy metals (i.e. lead, copper and cadmium). This paper investigates Zn^{2+} adsorption characteristics of two natural zeolites found in the regions of Gordes and Bigadic, in western Turkey. The results show that the Zn^{2+} adsorption behavior of both zeolites is highly dependent on the pH. Adsorption dependence on lower pH values (pH < 4) is explained by the dissolution of crystal structure and the competition of the zinc ions with the H$^+$. Between pH 4 and 6, the basic mechanism is the ion exchange process. The results also showed that decrease in grain size does not increase the adsorption capacity of zeolite from Gordes, yet it increases that of zeolite from Bigadic about 23%. The results also reveal that an increase in the initial concentration of Zn^{2+} in the system causes an increase in the adsorption capacity to a degree, then it becomes more constant at higher concentrations. With this, the removal efficiency of Gordes zeolite is two times higher than that of Bigadic zeolite. Results show that an increase in slurry concentration results in a lower uptake of Zn^{2+}. In the final part of the paper, we compared the experimental data with the Langmuir and Freundlich isotherms. The results show that there is a good fit between the experimental data and empirical isotherms.
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1. Introduction

Zinc manufacturing and other industries release large quantities of metals, mainly Cd and Zn, during production. The increasing demand for alkaline zinc manganese batteries, instead of mercury based ones, brings serious problems when those batteries are not disposed off properly [1,2]. Yet, another source of contamination can be due to the flooding of ore mines into the environment [3,4]. Since heavy metals have toxic effects on the environment and public life, many researchers suggest a cost-effective process, such as ion exchange, for removing dissolved heavy metals from wastewaters by using naturally occurring materials [5–13].

Zeolites are hydrated aluminosilicates of alkali and alkaline earth elements with unique crystal structures consisting of a three-dimensional framework of SiO$_4$ and AlO$_4$ tetrahedral [14,15]. This structure causes zeolite to have negatively charged surface. Negatively charged surface of zeolites can be used for adsorption of alkali earth metals, such as zinc. Occurrences of sedimentary zeolite are widespread in central and western Anatolia, Turkey. They are associated with clay minerals, borates, carbonates and soda minerals similar to many other parts of the world. They are also found in close association with lignite-bearing lacustrine rocks and evaporate [16].

Because zeolite has high adsorption capacity for pollutants, Jacobs and Förstner [17] proposed the possible use of natural and modified zeolites for capping contaminated sediments with active barrier systems. Czurda and Haus [18] emphasized that not only clay minerals, but also natural zeolites and fly ash zeolites can be used in reactive walls to protect the plume flow. Besides, utilization of bentonite–zeolite mixtures as a clay liner has been of interest for the last few years. Researchers investigated the advantages of bentonite-embedded zeolites for possible use as a clay liner instead of liners made of bentonite–sand mixtures [14,15,19]. The motivation for using the former rather

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than the sand–bentonite mixture is the high cation exchange capacity (CEC) of zeolites.

Studies on the removal efficiency of zeolites for zinc are very limited in the literature. Previous studies mostly contain comparisons of the adsorption characteristics of zeolite against some heavy metals, including zinc. For example, Kang and Wada [20] showed that zeolite had a higher selectivity for ammonium than for zinc. Zamzow and Murphy [3] investigated the removal capacity of a wide variety of zeolite minerals for cadmium, copper and zinc and revealed that zinc had the lowest adsorbed ions, among others, by all types of zeolites. Later, Colella et al. [21] obtained the same results that phillipsite and chabazite had limited adsorption capacity for zinc as compared to copper. Recently, Trgo and Peric [22] recommended the use of zeolite tuff as an ion exchanger in the technological processes of water with low Zn ion concentrations.

The objective of this study is to investigate the efficiency of two natural zeolites from Turkey, which consist mainly of clinoptilolite, in the removal of zinc ions from aqueous solutions. The effects of grain size, initial solution pH, initial metal ion concentration and slurry concentration on adsorption characteristics of zeolites were examined in detail. The experimental data was compared with Langmuir and Freundlich isotherms.

2. Materials and methods

2.1. Materials

The two natural zeolites used in this experimentation were obtained from Bigadic and Gordes locations, in western Turkey. The first was obtained from Bigadic reserves and Gordes zeolite was provided from Incal Co., Izmir, Turkey. They were crushed into small pieces from rock forms and then powdered in a mortar. The pulverized amounts were then passed through the corresponding sieves to determine the grain size effect. Sieving was conducted between nos. 50 and 70 (300–212 μm), between nos. 70 and 140 (212–106 μm), between nos. 140 and 270 (106–53 μm) to obtain coarser, mid-coarser and finer zeolites, respectively. No attempt was made to activate the materials. They were dried for 1 week at 60 °C in an oven before starting the experiments. The mineralogical composition of both materials consists mainly of clinoptilolite. The associated minerals for Gordes and Bigadic zeolites are k-feldspar and quartz, respectively. The cation exchange capacity and specific surface area were obtained by the Na-method [23] and spot test, respectively [24]. The cation exchange capacity of Gordes and Bigadic zeolites were 69.3 and 57.2 meq/100 g, while specific surface areas were 95 and 54 m^2/g, respectively. The chemical compo-

sitions were determined by inductively coupled plasma-atomic emission spectroscopy (ICP-ES). The results are presented in Table 1.

2.2. Methods

The solution preparation method was same as the previous study conducted on natural and Na-enriched bentonites [13]. The chemical used in the batch experiments was a chloride solution of zinc (ZnCl$_2$). A volume of 100 cm^3 of zinc solutions with various amounts of natural materials was placed in an Erlenmeyer flask to start the experiments. The initial metal ion concentration used in the tests ranged between 2.5 and 20 mg/l. Samples were weighted between 0.1 and 1 g to get the slurry concentrations in the range of 1.0–10.0 g materials per liter. Before adding the zeolites into the solutions, the pH values were adjusted by adding NaOH and HCl solutions. Samples were agitated with a speed of 100 rpm at a room temperature and suspension pH values were recorded. After separating the supernatant liquid from the samples by centrifugation, the metal ion concentration of the supernatant was determined by using UNICAM atomic adsorption spectrophotometry.

2.3. Determining the amount of zinc ion removal, q_e

The interaction between the zinc ion and zeolite can be given by the equilibrium:

$$mZn^{2+}_{(s)} + 2M^{m+}_{(z)} \rightarrow mZn^{2+}_{(z)} + 2M^{m+}_{(s)} \tag{1}$$
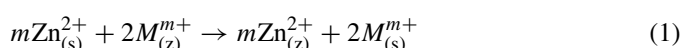
where m is the valence of exchangeable cations M (Na, K, Ca and Mg) and subscripts (s) and (z) denote solution and zeolite phases, respectively.

The amount of zinc ion adsorption onto the zeolite can be calculated by:

$$q_e = \frac{(C_i - C_e)}{S} \tag{2}$$

where q_e is the zinc ion adsorbed onto the zeolite (mg/g), C_i the initial metal ion concentration (mg/l), C_e the final metal ion concentration in the solution (mg/l) and S is the slurry concentration (g/l).

During the contact time of 2 days, the amount of the zinc ions adsorbed by the two zeolites was determined and plotted in Fig. 1. Fig. 1 indicates that the uptake of zinc was very fast in the first 6 h, then the exchange equilibrium was established within 2 days for both materials.

Table 1
Chemical compositions of starting materials (on weight basis)

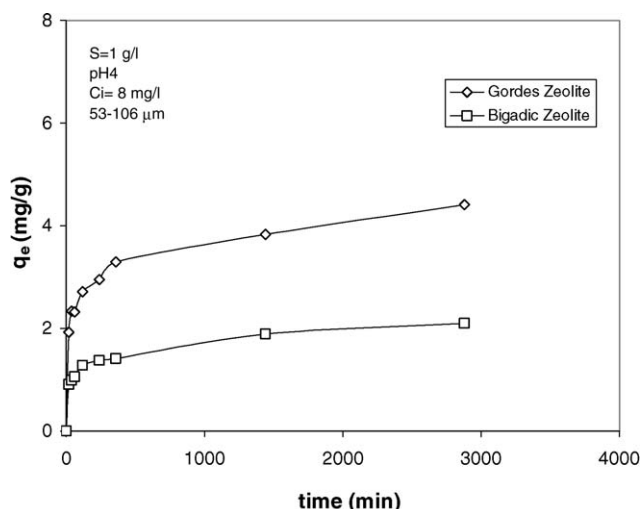| Materials	SiO$_2$ (wt.%)	Al$_2$O$_3$ (wt.%)	Fe$_2$O$_3$ (wt.%)	MgO (wt.%)	CaO (wt.%)	Na$_2$O (wt.%)	K$_2$O (wt.%)
Bigadic zeolite	65.85	11.22	1.09	1.07	2.94	0.49	3.05
Gordes zeolite	63.74	11.80	1.66	1.18	1.86	0.51	2.46

Fig. 1. Adsorption characteristics of materials during 2 days.

3. Results and discussions

3.1. Grain size effect

The adsorption characteristics of zeolites with respect to grain sizes are given in Table 2. Table 2 indicates that decreasing the grain size results in two different adsorption capacities: (i) decrease in grain size of Bigadic zeolite causes an increase in adsorption capacity and (ii) grain size has little influence on adsorption capacity of Gordes zeolite. Increase in adsorption capacity of Bigadic zeolite may be attributed to increase in the specific surface area. However, one would expect that the same would hold true for Gordes zeolite. Thus, it appears that the increase in specific surface area is not the only mechanism that causes an increase in the adsorption capacity. Also note that even 23% increase in adsorption capacity of Bigadic zeolite is almost half that of Gordes zeolite. The two-fold difference between the adsorption capacity of Gordes and Bigadic zeolites can be explained as participation of ion exchange accompanied with external or/and internal surface adsorption. Despite main mineral is clinoptilolite for both zeolites, associated minerals may lead this difference in the adsorption capacity between Gordes and Bigadic zeolites. Therefore, increase in adsorption capacities with decrease in grain size (increase in specific surface area) of Bigadic zeolite is not significant when compared with that of Gordes.

The finding of this study is not unique, there are studies reporting that decrease in grain size leads to an increase in adsorption capacity [25], whereas Leyva-Ramos et al. [26] reports that decreasing the grain size does not increase the adsorption capacity. It appears that the effect of decrease in grain size on adsorption capacity hinges on an increase of the internal surface area. This is because increase in external surface area has little influence upon the internal surface area. In porous materials, the contribution of the external surface area to the total surface area is limited, and therefore, size reduction has a negligible effect on increasing the total surface area. It is evident from the results of this study that an increase in external surface area has little effect on the internal surface area, thus, it has little effect on the adsorption capacity.

3.2. pH Effect

After determining the effect of grain size on Zn^{2+} removal, the smallest grain size fraction (53–106 μm) was chosen for the remaining parts of the batch adsorption experiments. In order to determine the pH effect on adsorption capacity of materials, solutions were prepared at different pH levels ranging from 3 to 8. Fig. 2 shows the change in Zn^{2+} uptake by the zeolites at different initial solution pH levels. As can be seen from Fig. 2, adsorption capacity of both materials increased when the initial pH of the solution was increased from 3 to 4 (region I). In the second region, from pH 4 to 6, the adsorption performance of Gordes zeolite remained almost unchanged, while that of Bigadic increased. Above pH 6, like the Bigadic zeolite, the Gordes zeolite had a tendency to increase and reached the highest value at pH 8.

These results are in agreement with the results previously reported [27,28]. Also, it is revealed that clinoptilolite still had negative surface charge even at very acidic conditions (i.e. pH 2) which enables it to have a great advantage for organic and inorganic cationic contaminants [31]. From Fig. 2, the lowest Zn^{2+} adsorption rates were obtained at pH 3 and it may have been due to the increase in firstly, the competition for adsorption sites by H^+, secondly, the existence of particular zinc hydroxyl species and dissolution of Al^{3+} ions from the aluminosilicate layers [22,29].
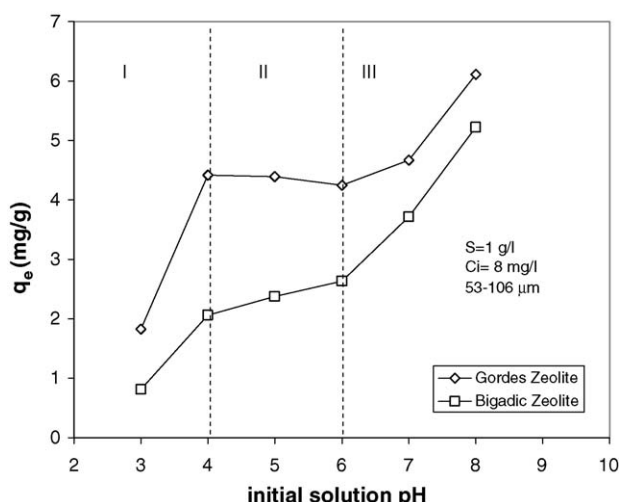
Table 2
Effect of grain size fractions on heavy metal uptake[a]

Size (μm)	Metal adsorbed, q_e (mg/g)		Increase in adsorption (%)	
	Bigadic zeolite	Gordes zeolite	Bigadic zeolite	Gordes zeolite
300–212	1.715	4.056	–	–
212–106	1.973	4.141	15	2.1
106–53	2.110	4.406	23	8.6

[a] Initial pH 4.0, $S = 1$ g/l, Ci ≈ 8 mg/l.

Fig. 2. Changes in the adsorbed amount of Zn^{2+} between pH 3 and 8.
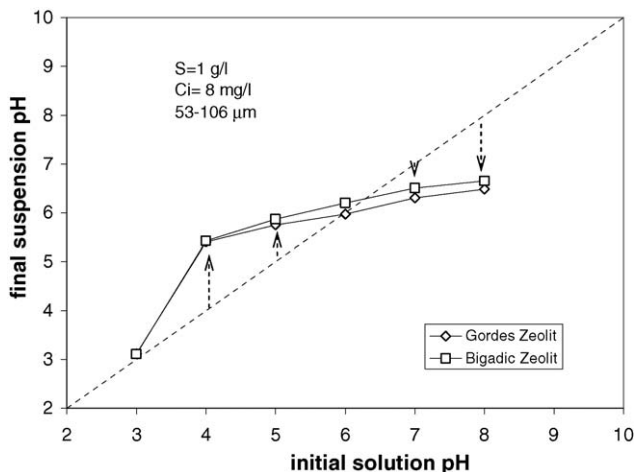
Fig. 3. Change in initial pH after the experiments.

Fig. 4. Relationship between initial metal ion concentration and Zn^{2+} removal.

The mechanism that governs the adsorption characteristics of zeolites at pH ranges between 4 and 6 are adsorption and ion exchange. The rapid increase at pH 4 can be attributed to the replacement of exchangeable cations present at the exchangeable sites, i.e. Na^+, K^+, Ca^{2+}, Mg^{2+} with Zn^{2+} cations in the aqueous solution. On the other hand, the adsorption did not show considerable change between pH 4 and 6 and one of the possible explanations is that the resorption of exchangeable cations to the zeolite surface may have been occurred as a result of shaking.

In addition to the ion exchange, the formation of zinc species with OH^- plays an important role in the increase of heavy metal removal above pH 6 (region III). Depending on the pH and metal concentration, zinc may form complexes with OH^-, for example $Zn(OH)_2$, $Zn(OH)_3^-$ and $Zn(OH)_4^{2-}$, at higher pH values (pH > 6), and as a result, zinc hydroxyl species may participate in the adsorption and precipitate onto the zeolite structure [22,27,28,30].

Measurement of the final pH values of the suspensions, after a contact time of 2 days, supports the statements made above. Fig. 3 shows the suspension pH values at the end of the experiments. The path of the final pH values of both zeolites showed almost the same trend for all initial solution pH levels. From pH 3 to 8, an abrupt change followed by a gradual increase in the final pH indicates a tendency of neutralizing the initial solution pH. Ersoy and Celik [31] obtained similar results from the elektrokinetic measurements that clinoptilolite suspensions exhibited buffer pH around pH 9. In acidic conditions, balancing of pH is due to either the exchanging process of alkaline ions from the mineral with H^+ or binding the protons on the Lewis basic sites. However, removal of protons from the surface Bronsted acidic sites and zeolitic water that coordinate exchangeable cations cause reduction in the final solution pH in the alkaline region [22].

3.3. Initial metal concentration effect

For the rest of the experiments, pH 4 was used in order to evaluate the effect of initial metal ion concentration on adsorption characteristics of the zeolites. Fig. 4 represents the change
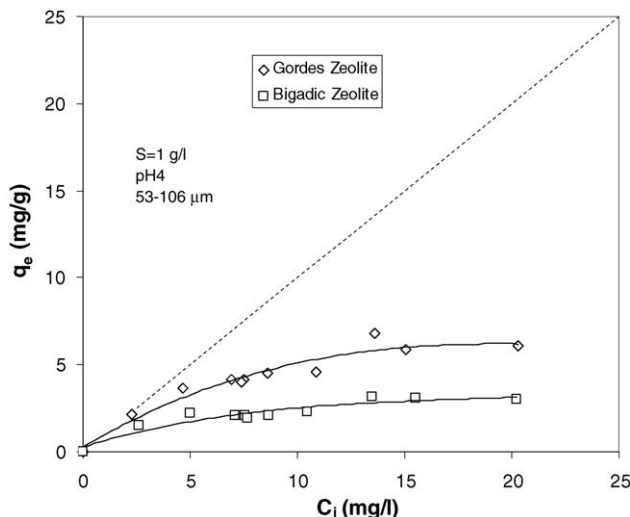
in adsorption behavior of both materials under different metal ion concentrations. As can be seen from Fig. 4, increasing the metal ion concentration led to an increase in the Zn^{2+} uptake by the materials to a certain point, then a plateau was seen for both zeolites which indicated unavailability of further adsorption of heavy metals onto the zeolite on account of zinc saturated surfaces. As it is seen from Fig. 4, the maximum adsorption capacity of Gordes and Bigadic zeolite is 6 and 3 mg/g, respectively.

The difference in the uptake of Zn^{2+} may be due to the difference in the mineralogical compositions and associated cations in the exchangeable sites [20,32,33]. Also, having almost twice the specific surface area of Bigadic zeolite can make Gordes zeolite more sorption capability for zinc. The lower selectivity of Zn^{2+} as compared to other heavy metals, such as Pb^{2+}, Cd^{2+}, Cu^{2+} by zeolites was demonstrated by some researchers [32–35]. Sheta et al. [33] investigated the adsorption characteristics of natural zeolite and bentonite via zinc and iron and concluded that heavy metal uptake substantially depends on the mineralogical compositions of materials and kinds of heavy metal used in the tests.

3.4. Slurry concentration effect

In the literature, only limited data exists regarding the effect of slurry concentration on heavy metal removal by the zeolites [25,36]. Thus, we attempted to determine the effect of slurry concentration on uptake of Zn^{2+} on zeolite; initial metal ion concentrations were taken as 20 mg/l for zeolites and other situations, such as pH, grain size and temperature were kept constant. Fig. 5 expresses the effect of slurry concentration for Zn^{2+} removal from the aqueous solutions and the final pH of the solutions. The solid lines with opened symbols indicate the change in zinc adsorption by the slurry concentration; the dashed lines with closed symbols denote to the final solution pH.

From Fig. 5, the amount of adsorbed zinc onto the zeolites decreases with an increase in the slurry concentration. Raising the concentration from 1 to 10 g/l reduces the zinc removal 68 and 49% for Gordes and Bigadic zeolite, respectively. The rea-
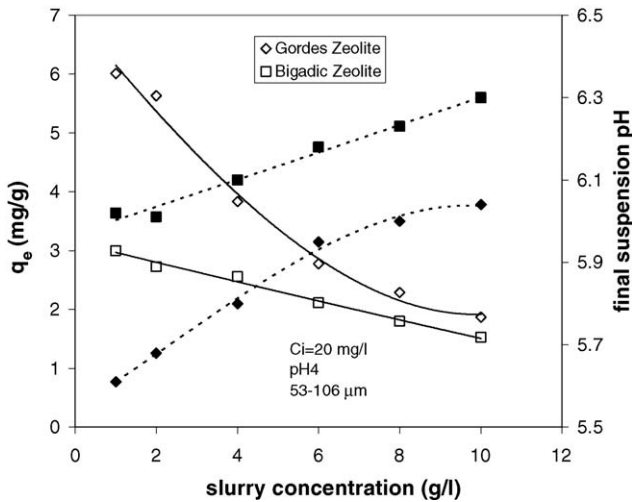
Fig. 5. Change in adsorption amount of zinc under various zeolite concentrations.

son for decrease in the zinc removal was due to the increasing interface area when the suspension was diluted [37].

Also, the symmetrical change in final pH of the solution with respect to slurry concentration can be seen in Fig. 5 with the dashed lines. For both zeolites, the rise in the final pH can be attributed to the increase in the concentrations of alkaline ions released from zeolite exchangeable sites [25].

3.5. Comparison of adsorption isotherms

Adsorption isotherms for zinc ion removal by zeolites in terms of Langmuir and Freundlich models were expressed mathematically. The obtained experimental data here are expectedly well fitted with the linearized form of Langmuir and Freundlich models:

$$\frac{C_e}{q_e} = \left(\frac{1}{K_L}\right) + \left(\frac{a}{K_L}\right) C_e \qquad (3)$$

$$\log q_e = \log K_F + n \log C_e \qquad (4)$$

The empirical constants K_L and a for Langmuir model are related to the adsorption maximum (l/g) and bonding strength (l/mg), respectively, whereas K_F (mg/g) and n (g/l) are the constants for Freundlich model. In addition to the experimental data, the linearized form of Langmuir and Freundlich isotherms using Eqs. (3) and (4) for zinc ion removal by zeolites can be seen in Fig. 6.

As it is seen from the Fig. 6, the experimental data for both materials fit well with the linearized Langmuir and Freundlich isotherms. The values of K_L, a, K_F and n obtained from both models are presented in Table 3.

The comparison of the experimental values with the values of q_e obtained by both models is shown in Fig. 7. As is seen from this figure, Freundlich isotherms were well fitted with the experimental data rather than Langmuir isotherms. Cincotti et al. [38] found similar adsorption values for the zeolites which had 20 and 50 wt.% clinoptilolite content and their results again fit well with the Langmuir isotherms. Also, some other studies showed
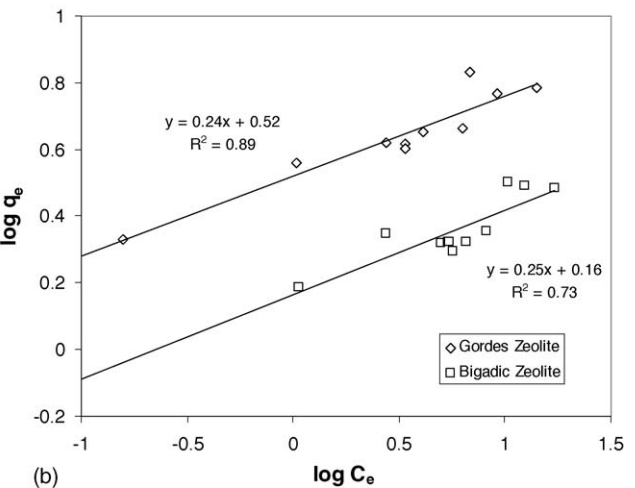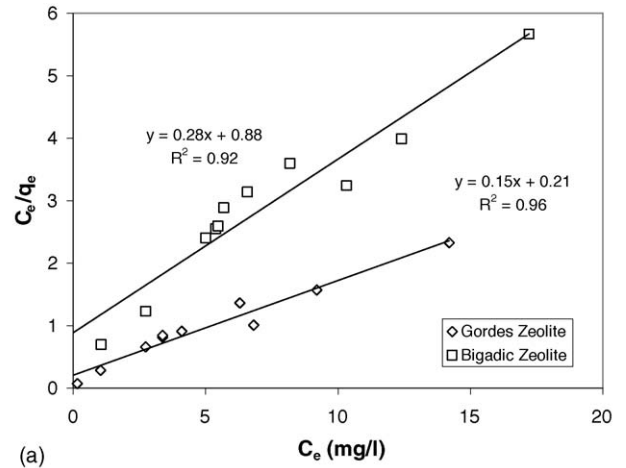

Fig. 6. Linearized (a) Langmuir and (b) Freundlich isotherms for Zn^{2+} removal by zeolites.

that Langmuir and Freundlich isotherms correspond well with the experimental results of other heavy metals [25,33,35,39].

The obtained results are in the range of cited values in the literature. For example, Ouki and Kavannagh [27] and Panayotova and Velikov [34] found that clinoptilolite had a maximum adsorption capacity for zinc of 2.7 and 2.3 mg/g, respectively. Elsewhere, Sheta et al. [33] reported that the adsorption performance against zinc was as much as 2.9 and 1.9 mg/g for two clinoptilolite, whereas Trgo and Peric [22] showed higher adsorption rates when compared to the findings from the literature (12 mg/g). The lower adsorption rates for zeolites with

Table 3
The parameters for Langmuir and Freundlich isotherms

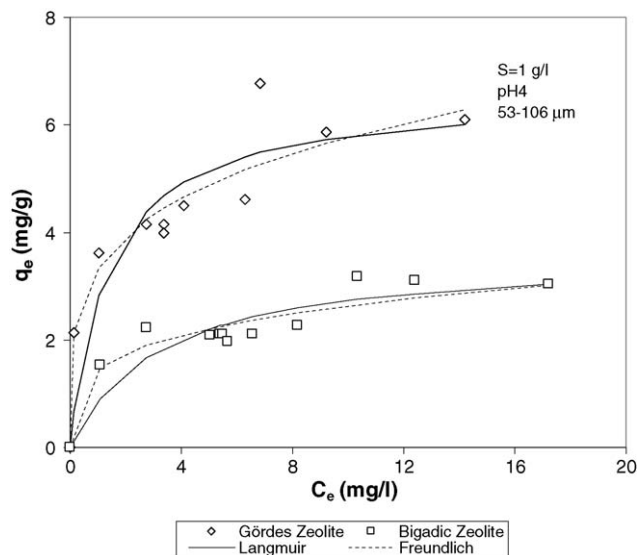| Isotherm parameters	Gordes zeolite	Bigadic zeolite
Langmuir		
K_L (l/g)	4.773	1.132
a (l/mg)	0.723	0.315
Freundlich		
K_F (mg/g)	3.321	1.461
n (g/l)	0.24	0.255

Fig. 7. Comparison of the experimental results with the q_e values obtained by Langmuir and Freundlich isotherms.

respect to bentonites may be due to the difficulty in the penetration of hydrated zinc ions into the zeolite channels.

4. Conclusions

The adsorption characteristics of two Turkish zeolites were examined for Zn^{2+} at different grain size fractions, pH values, initial metal ion concentrations and slurry concentrations. The obtained results can be summarized as follows:

- The adsorption capacity of Gordes zeolite is almost twice that of Bigadic in all cases (i.e. grain size, pH, metal concentration and slurry concentration). Although the main minerals are the same for both zeolites (clinoptilolite), existence of different associated minerals may cause this difference.
- The effect of grain size fraction is not as pronounced for the Gordes as for the Bigadic.
- pH experiments showed that the governing factors affecting the adsorption characteristics of all materials are competition of the H^+ ions with Zn^{2+} ions (under pH 4), ion exchange (pH 4–6), participation of zinc hydroxyl species in the adsorption and precipitation onto the zeolite structure (pH 6–8).
- The adsorption characteristics of zeolites for zinc ions were very limited when compared with natural and Na-enriched bentonites [13]. Previous investigation on bentonites showed that the maximum adsorption capacity of Na-enriched bentonite and natural bentonite was 54 and 24 mg/g, respectively. Considering the zeolites, it was 6 and 3 mg/g for Gordes and Bigadic. The lower adsorption rates for zeolites with respect to bentonites may be due to the difficulty in the penetration of hydrated zinc ions into the zeolite channels. Hence, adsorption may take place at the zeolite surfaces.
- The general adsorption behavior of zeolites in the name of initial metal ion concentration and slurry concentration were same as the natural and Na-enriched bentonites studied before [13].

- The experimental results were a good fit with the Langmuir and Freundlich isotherms. It is seen that Freundlich isotherms have a better correspondence with the experimental findings rather than with Langmuir.

Acknowledgments

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