# Natural Jordanian zeolite: removal of heavy metal ions from water samples using column and batch methods

**Hutaf M. Baker · Adnan M. Massadeh · Hammad A. Younes**

**Abstract** The adsorption behavior of natural Jordanian zeolites with respect to $Cd^{2+}$, $Cu^{2+}$, $Pb^{2+}$, and $Zn^{2+}$ was studied in order to consider its application to purity metal finishing drinking and waste water samples under different conditions such as zeolite particle size, ionic strength and initial metal ion concentration. In the present work, a new method was developed to remove the heavy metal by using a glass column as the one that used in column chromatography and to make a comparative between the batch experiment and column experiment by using natural Jordanian zeolite as adsorbent and some heavy metals as adsorbate. The column method was used using different metal ions concentrations ranged from 5 to 20 mg/L with average particle size of zeolite ranged between 90 and 350 μm, and ionic strength ranged from 0.01 to 0.05. Atomic absorption spectrometry was used for analysis of these heavy metal ions, the results obtained in this study indicated that zeolitic tuff is an efficient ion exchanger for removing heavy metals, in particular the fine particle sizes of zeolite at pH 6, whereas, no clear effect of low ionic strength values is noticed on the removal process. Equilibrium modeling of the removal showed that the adsorption of $Cd^{2+}$, $Cu^{2+}$, $Pb^{2+}$, and $Zn^{2+}$ were fitted to Langmuir, Freundlich and Dubinin-Kaganer-Radushkevich (DKR). The sorption energy E determined in the DKR equation (9.129, 10.000, 10.541, and 11.180 kJ/mol for $Zn^{2+}$, $Cu^{2+}$, $Cd^{2+}$ and $Pb^{2+}$ respectively) which revealed the nature of the ion-exchange mechanism.

**Keywords** Heavy metal ions · Isotherm models · Atomic absorption spectrometry · Jordanian zeolite · Column · Batch

## Introduction

Many toxic heavy metals and organic pollutants have been discharged into the environment as industrial wastes, causing serious soil and water pollution, therefore needing for advanced treatment units is important to remove these pollutants, adsorption and ion exchange are the most common technologies used in advanced wastewater treatment facilities (Baker and Khalili 2003, 2004, 2005; AL-Degs et al. 2003; Massadeh 2003). Activated carbon adsorption is considered to be

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a particularly competitive and effective process for the removal of heavy metals at trace quantities and organic pollutants, however, the use of activated carbon is not suitable in developing countries due to the high costs associated with production and regeneration of spent carbon (Ali and El-Bishtawi 1997; Baker and Abdel-Halim 2007; Baker and Khalili 2007; Baker 2008a, b). The high cost of this adsorption material, has pushed the technologists to continue investigating on alternative cheaper adsorbents. New researches regarding non-conventional adsorption materials has been mainly focused on waste material, such as carbonized coconut shell, wood, coal, and straw, organoclays, and zeolite (Farkas et al. 2005; Navia et al. 2005; Roodtaei and Tezel 2004; Baker 2008a, b).

Zeolites are hydrated aluminosilicate materials having cage-like structures with internal and external surface areas of up to several hundred square meters per gram and cation exchange capacities of up to several milliequivalents per kilogram. At least 41 types of natural zeolites are known to exist, and many others have been synthesized. Both natural and synthetic zeolites are used in industry as adsorbents, soil modifiers, ion exchangers, and molecular sieves (Rushdi et al. 1999).

Jordan is a country with limited water resources and this necessitates that much effort is put into water conservation and environmental protection. The expansion of industrial activities, including metal-based industries, requires the availability of low-cost technology and materials for wastewater treatment. However, the country has huge reserves of zeolitic tuffs, especially in the northeast where phillipsite is the dominant mineral (Ali and El-Bishtawi 1997). Zeolitic tuff deposits, rich in phillipsite, were first discovered in Jordan in 1987 in the eastern part of the country at Jebal Aritain. Since then zeolites have also been found in other locations, mainly in the basaltic areas in the northeastern region of Jordan (Rushdi et al. 1999).

The toxicity of heavy metal ions depends on the chemical form of the element that is upon its speciation. For example, the toxicity of Pb as the ion $Pb^{+2}$, and the Pb in the form of covalent molecule differ substantially (Baird 1999). If the wastewaters were discharged directly into natural waters, it will constitute a great risk for the aquatic ecosystem, whereas, the direct discharge into the sewage system may affect negatively the subsequent biological wastewater treatment (Hui et al. 2005). Cd (II), Cu (II), Pb (II) and Zn (II) are the most harmful metals to humans, for this reason these metals were selected in this study (Fzali et al. 2005; ASTDR 2005; Lazaridis et al. 2004).

In the present work, a method is proposed for wastewater treatment in Jordan by removing inorganic pollutants, Jordanian zeolite was studied for its potential use as an adsorbent for four different metal ions ($Pb^{2+}$, $Cd^{2+}$, $Cu^{2+}$ and $Zn^{2+}$) from aqueous solutions. There are many studies in literature about removing heavy metal by using zeolite by batch experiment, but no enough data about using the column experiment, the column was used to remove the heavy metal ions and a comparative between the batch experiment and column experiment was established.

The term sorption is a general expression encompassing both processes. The percent adsorption (%) was calculate as follows

$$\% \ \text{Adsorption} = \left( C_i - C_f / C_i \right) \times 100\%$$

Where $C_i$ and $C_f$ are the concentrations of the metal ion in initial and final solutions respectively (Lazaridis et al. 2004; Abd El-Rahman et al. 2006; Muhammad 2004).

## Material and methods

### Preparation of zeolite sample

Zeolitic tuff sample from Tlool al Shahbaa in Jordan kindly donated by the Jordanian Natural Resources Authority (JNRA). Zeolite samples were grounded by using a mechanically agitated sieve banks then sieved into several size fractions in the range of 90–350 μm using standard sieve series. A known quantity of sample was digested with 500 mL of concentrated $HNO_3$ and 100 mL of $H_2SO_4$ until the organic matter has been destroyed (Stylianou et al. 2007), after completion of digestion the sample was immersed in NaCl solution (25 g $dm^{-3}$) over night in order to obtain, as possible, the monoionic sodium form. The zeolite

**Fig. 1** XRD for non-treated Jordanian zeolite
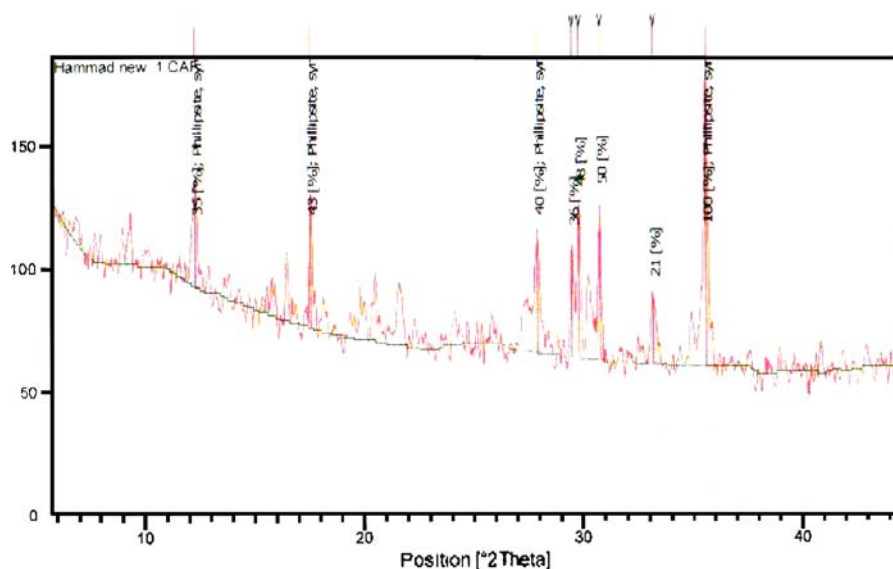


was then washed briefly with distilled water until neutral pH is obtained, dried over night in an oven at 105°C.

Identification of zeolite

X-ray diffraction (XRD, PHILIPS Type, X'pert Pro Model, Holland) analysis was done for the untreated zeolite sample to identify the mineral type, and the X-ray fluorescence (XRF, PHILIPS Type, MAGIX Model, Holland) analysis was carried out on the treated zeolite to determine their chemical compositions. The surface morphology of the treated zeolite was studied using scanning electron microscope (SEM, FEI Quanta 600 Model, Holland).

Adsorbate

Stock solutions (1,000 mg/L) of Pb (II), Cu (II), Zn (II) and Cd (II) obtained from (BHD) were prepared by dissolving an appropriate quantity of

these metal as nitrate powder in $NaClO_4$ (BHD) solution. Each stock solution of each metal ion was prepared in different ionic solution ($I$) of (0.01–0.05 M) of $NaClO_4$ separately. All the experiments were done at pH 6 by using $HClO_4$ or/and NaOH to avoid precipitation of metal ions as metal hydroxides or metal carbonate, a range of each metal ion concentrations from 5 to 20 mg/L was used.

Column adsorption studies

The experiment was carried out by using column reactor. The columns used in this experiment were filled with zeolite bed, the bottom of each column contains a plug glass wool to support the zeolite bed, distribute backwash water, and promote uniform collection of the treated water. A glass tube (0.5 × 10 cm) was packed with 0.125 g of zeolite (Analytical balance, OHAUS, As 200), the average particle size of zeolite was in range of 90<ps<125 μm. A volume of 25 mL of metal

**Table 1** Chemical compositions of treated zeolitic sample

| Oxide % | Compound | Oxide % | Compound |
|---|---|---|---|
| 47.63 | $SiO_2$ | 3.62 | TiO |
| 20.69 | $Fe_2O_3$ | 0.47 | $K_2O$ |
| 7.33 | $Al_2O_3$ | 1.00 | $Na_2O$ |
| 9.45 | MgO | 0.22 | MnO |
| 8.99 | CaO | 0.12 | $P_2O_5$ |

**Fig. 2** SEM image of treated Jordanian zeolite
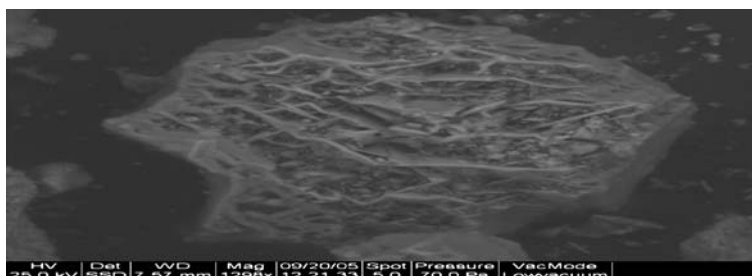


nitrate solution with a concentration in the range 5–20 ppm metal ion of $Pb^{2+}$ $Cd^{2+}$, $Cu^{2+}$ and $Zn^{2+}$ was passed through the column separately, the flow rate was (0.5 mL/min) and temperature at which experiments were carried out was $27 \pm 2°C$,

and at constant pH of 6 (pH meter, 744 Model metrohm).

The equilibrium concentration of each metal ion was established by using flame atomic absorption spectrophotometery (AAS, Unicam 929).
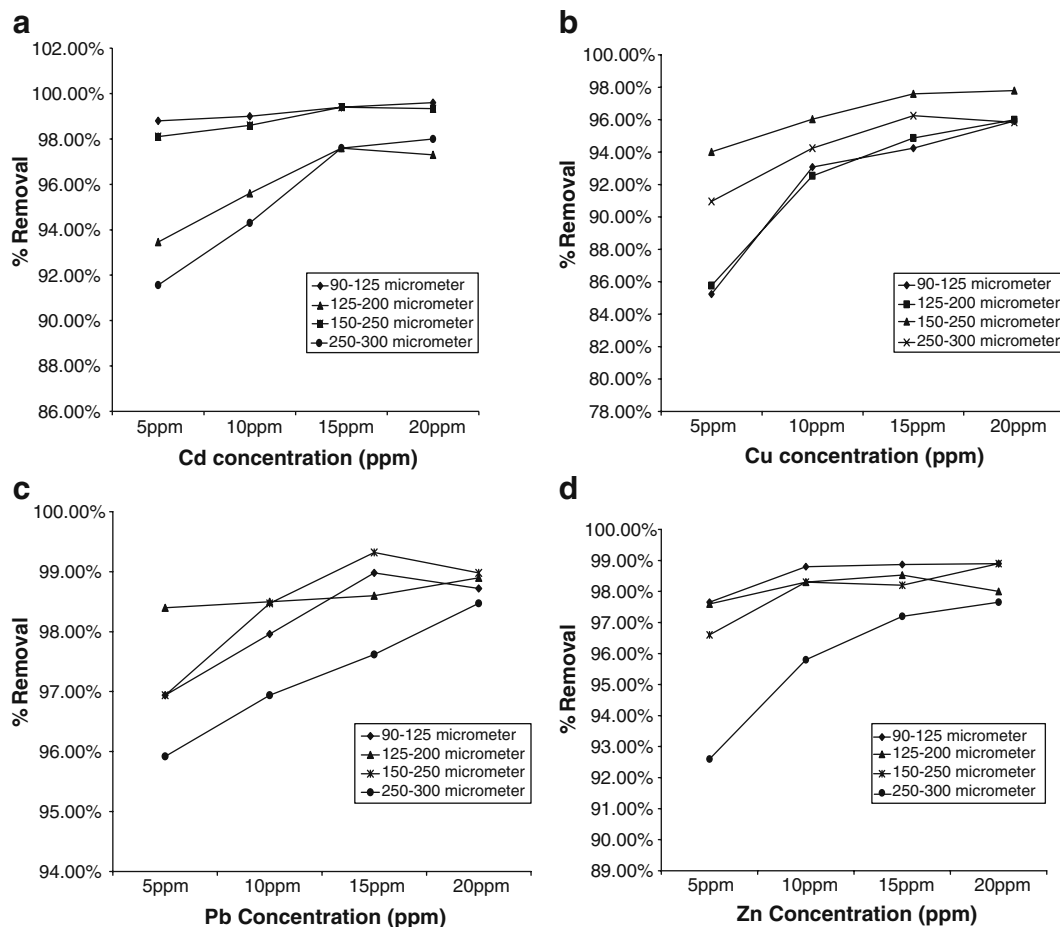


**Fig. 3** Removal of metal ions as a function of concentration at $I = 0.04$ and pH = 6 (**a** removal of $Cd^{2+}$ at different particle sizes, **b** removal of $Cu^{2+}$ at different particle sizes; **c** removal of $Pb^{2+}$ at different particle sizes; **d** removal of $Zn^{2+}$ at different particle sizes)
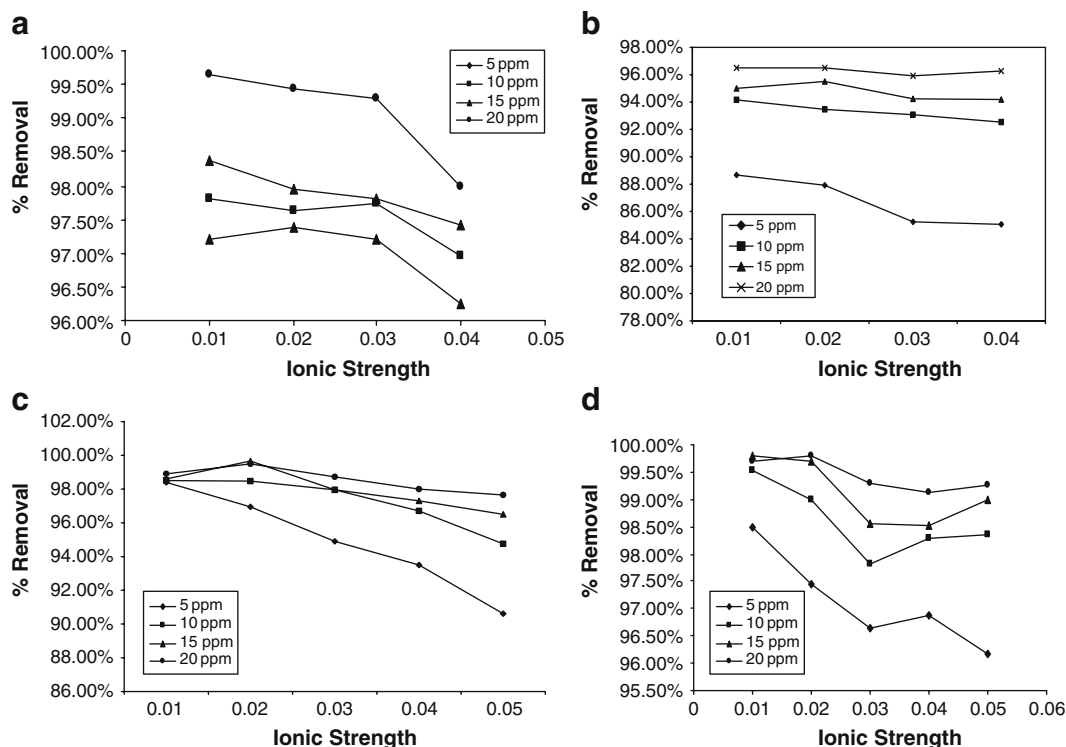
**Fig. 4** Removal of metal ions as a function of ionic strength at pH = 6, (**a** removal of $Cd^{+2}$ for different concentrations at particle size of 250–300 μm zeolite; **b** removal of $Cu^{+2}$ for different concentrations at particle size of 90–125 μm zeolite. **c** removal of $Pb^{+2}$ for different concentrations at particle size of 125–200 μm zeolite; **d** removal of $Zn^{+2}$ for different concentrations at particle size of 250–300 μm zeolite)

The fuel oxidant used was air–acetylene and the wave length used was $Cu^{2+}$ (324.7 nm), $Cd^{2+}$ (228.8 nm), $Pb^{2+}$ (283.5 nm) and $Zn^{2+}$ (213.9 nm).

### Batch adsorption studies

The ion exchange of heavy metals on natural zeolite was carried out using the batch method. Batch adsorption experiments were conducted using a 0.125 g of adsorbent with 25 ml of solutions containing heavy metal ions of desired concentrations of $Pb^{2+}$, $Cd^{2+}$, $Cu^{2+}$ and $Zn^{2+}$ at constant temperature ($25 \pm 2°C$) ionic strength (0.01) and constant pH 6, in 200 mL glass (Pyrex) bottles with screw cap. The experiments were done by using different particle size of zeolites. These solutions were shaken in a shaker water bath (GFL 1083) for 24 h, which had been found sufficient to ensure equilibration. The samples were removed from the shaker, and the zeolite was isolated by

filtration using 45 μm Whatman filter paper right away followed by centrifugation using (Sigma 2–3) centrifuge, the supernatant for each metal ion was taken and analyzed by using atomic absorption spectrophotometery.

Many variables were investigated for each examined metal ion using both column and batch experiments such as initial metal ion concentration, zeolite particle size and ionic strength to attain the required suitable correlation for this process.

## Result and discussion

### Characteristics of adsorbent

The X-ray diffraction analysis indicated that the examined raw zeolite sample is rich in phillipsite with some non-zeolitic materials as shown in Fig. 1.
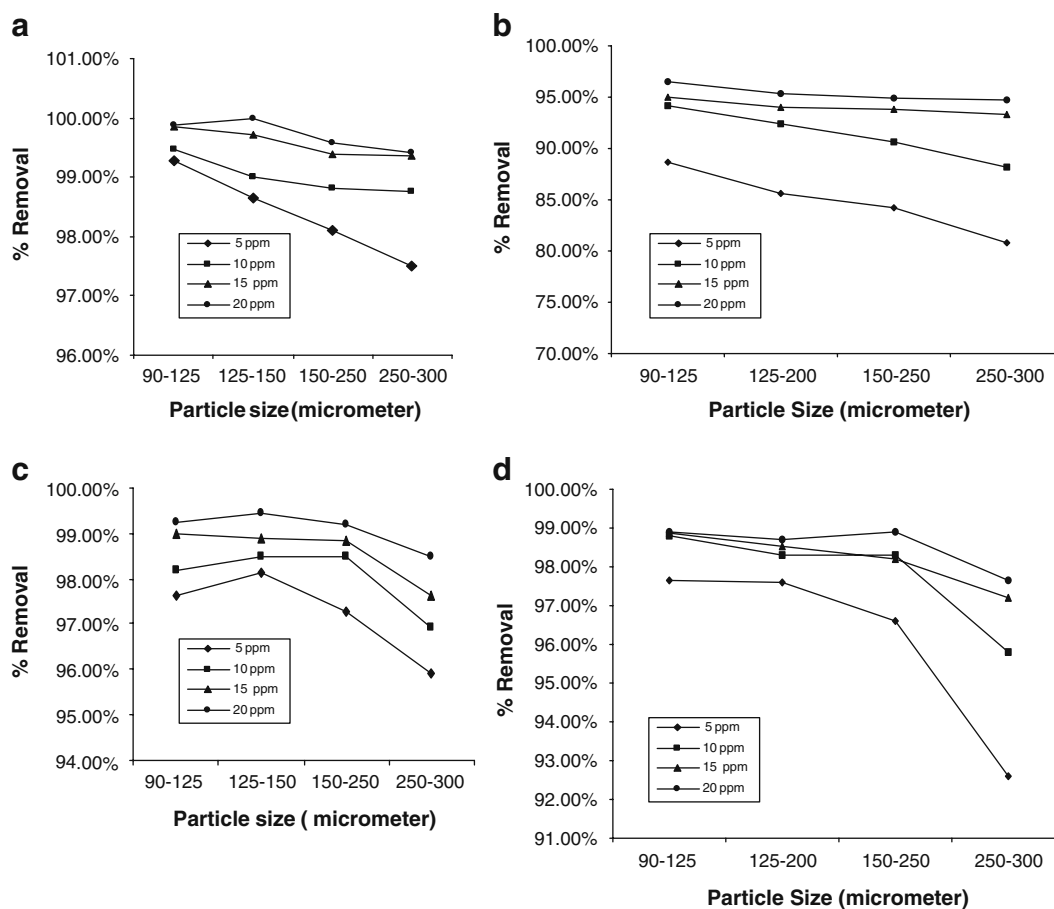
**Fig. 5** Removal of metal ions as a function of particle size at pH = 6 using column experiment (**a** removal of $Cd^{+2}$ at different concentrations, $I = 0.02$; **b** removal of $Cu^{+2}$ at different concentrations $I = 0.02$; **c** removal of $Pb^{+2}$ at different concentrations, $I = 0.01$; **d** removal of $Zn^{+2}$ at different concentrations $I = 0.04$)

The data for the chemical compositions of the sieved and treated zeolite fractions which obtained from XRF analysis are given in Table 1, from these results it can be seen that this kind of zeolite is rich with $SiO_2$, $Al_2O_3$ with % oxides compositions of 47.63 and 7.33 respectively, the moderate high $SiO_2/Al_2O_3$ ratio results in typical low anionic field that gives rise to good selectivity (Erdem et al. 2004).

Scanning electron microscope (SEM) as shown in Fig. 2 illustrates that the zeolitic sample has a large number of pores, layers and sheets which allow water to pass through it then the cation exchange may be occur, also this figure show that the surface area of the sample is very high which

means that the adsorption will be very easy and very fast.

Effect of the initial concentrations

Results obtained in this study using both column and batch technique indicated that zeolite can be removed the heavy metal ions at diffirent concentrations ranged between 5 and 20 ppm at specific ionic strength in a high percent of removal. As shown in Figs. 3a–d and 6a, the adsorption increases with increasing initial metal ion concentration and that leads to an increase in the amount of heavy metal ion adsorbed onto zeolite. This may be attributed to an increase in the driving force
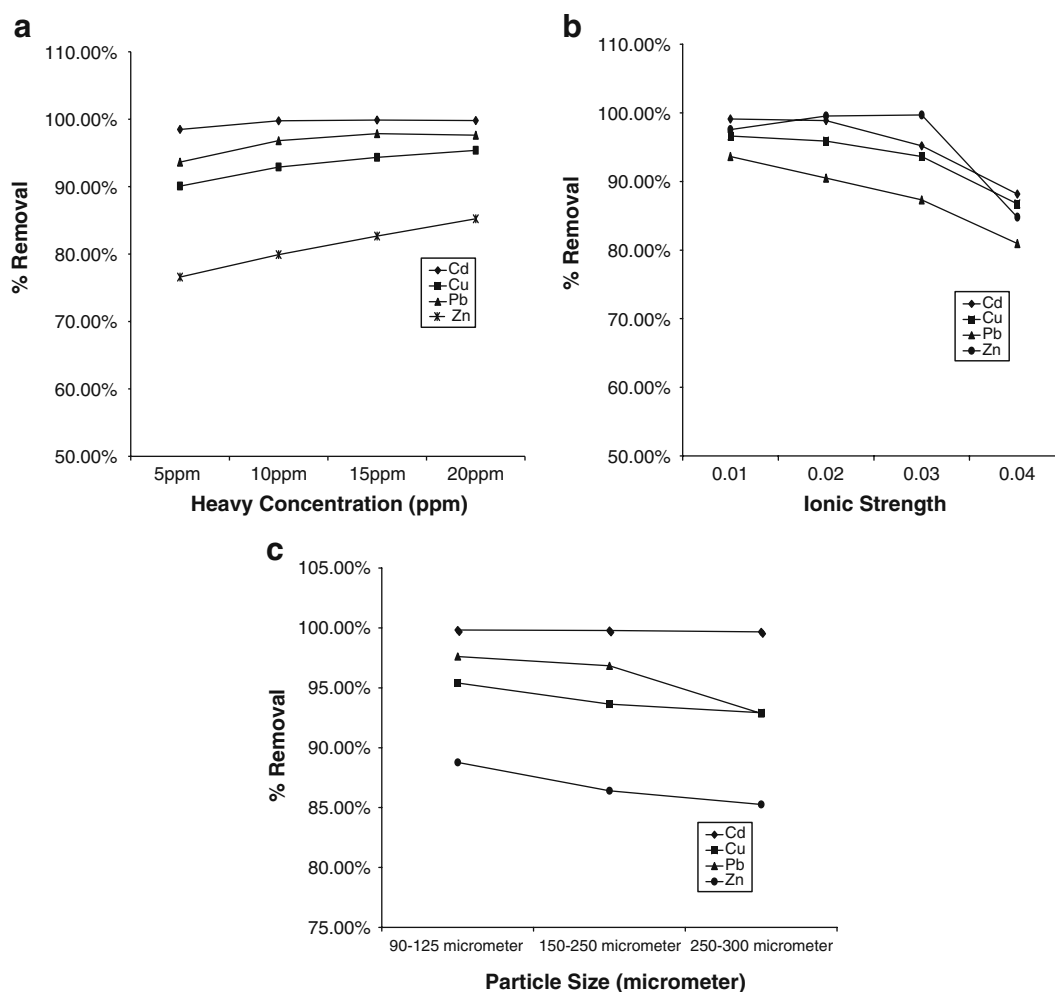
**Fig. 6** Removal of heavy metal ions using batch method, pH = 6, $I$ = 0.04 (**a** Removal of heavy metal ions as a function of concentration, at particle size of zeolite 90–125 μm; **b** removal of heavy metal ions for 20 ppm as a function of particle size; **c** removal of heavy metals for 20 ppm by zeolite at particle size 125–200 μm as a factor of ionic strength)

of the concentration gradient with the increase in the initial concentration of these heavy metals for both column and batch experiments. Also it was found that the percent removal of the desired heavy metals using column experiment is nearly higher than that of batch experiment (Weng et al. 2007).

Effect of the ionic strength

Influence of ionic strength $I$ on heavy metal ions sorption by natural zeolite was investigated to determine solution chemistry effects. Figures 4a–d

and 6b for column and batch experiments respectively illustrated the effect of different $I$ values (0.01–0.05) M of $NaClO_4$ on the selected heavy metals sorption. It can seen that the changing of the ionic strength (0.01–0.05) has little effect on the amount adsorbed because there is no competition between the metal ions and the salt ions. Competitive effects due to increasing $I$ on metal ions removal can be observed up to a $C_i$ of 20 mg $M^{2+}$/L. There are two possible ways by which increasing $I$ can influence $M^{n+}$ sorption onto zeolite: (1) decreases the solution-phase activity of $M^{n+}$ and (2) increases concentration of competing

anion ($Na^+$). With increasing $I$, there is a little disproportional decrease in $M^{n+}$ removal (Fig. 4a–d), which can be attributed to the presence of sorption sites with different affinities (Karthikeyan et al. 2002; Garcia Sanchez et al. 1999). Also the results obtained in this study indicated that zeolite can be removed the heavy metal ions at different ionic strength, the effect of the ionic strength using batch method for removal of heavy metals shows that the column method is better than the batch method as shown in Figs. 5 and 6b.

### Effect of adsorbent particle size

At diffirent particle size of zeolite at specific ionic strength. Figures 5a–d and 6c show that the removal of Cd, Cu, Pb and Zn ions as a factor of particle size of zeolite, It can be seen that as the particle size of zeolite decreases a slight increasing in the removal of these metal ions was observed. This can be explained in terms of active surface area of the adsorbent and the probability of solid-solution interaction. It was found that the removal of these metal ions using batch experiment less effcient than that of column experiment using different particle size (Garcia Sanchez et al. 1999).

From Fig. 7 which describes column method using a 90–125 μm zeolite particle size indicated that the removal of the investigated metals is a very good mean and in high percent of removal.
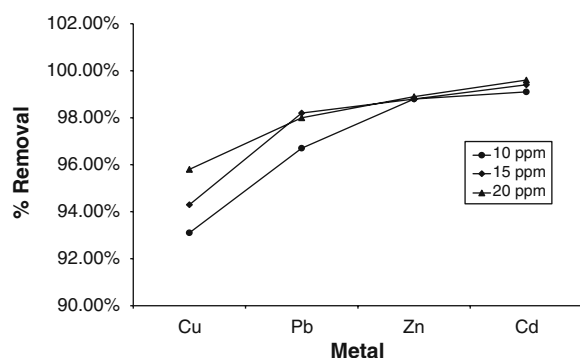


**Fig. 7** Removal of different metal ions ($Cu^{2+}$, $Pb^{2+}$, $Zn^{2+}$ and $Cd^{2+}$) with different concentrations by zeolite using column method (particle size = 90–125 μm, pH = 6, $I$ = 0.04)

### Statistical analysis of results

Analysis of Variance (ANOVA) is used to analyze the results. The results of statistical analysis indicated a significant difference between initial concentration for each investigated metal (5, 10,15 and 20 ppm) and their concentrations after using zeolite column method ($p < 0.05$), whears there was no significant effect of ionic strength and particle size on removal of Pb, Cd, Cu and Zn ions ($p > 0.05$).

### Isotherm models

The sorption data have been subjected to different sorption isotherms, namely, Langmuir, Frendlich, and Dubinin-Kaganer-Radushkevich (DKR). The equilibrium data for metal cations over the concentration range from 5 to 35 mg/L at 27°C have been correlated with the Linearized form of Langmuir isotherm (Baker 2008a, b)

$$\frac{C_e}{S_e} = \frac{1}{K_L S_m} + \frac{C_e}{S_m}$$

Where $S_e$ is the amount adsorbed on solid at equilibrium (mg/g), $C_e$ is the equilibrium liquid concentration (mg/L), $S_m$ is the adsorption capacity or adsorption maximum (mg/g), and $K_L$ is the adsorption intensity or Langmiur coefficient (L/mg).
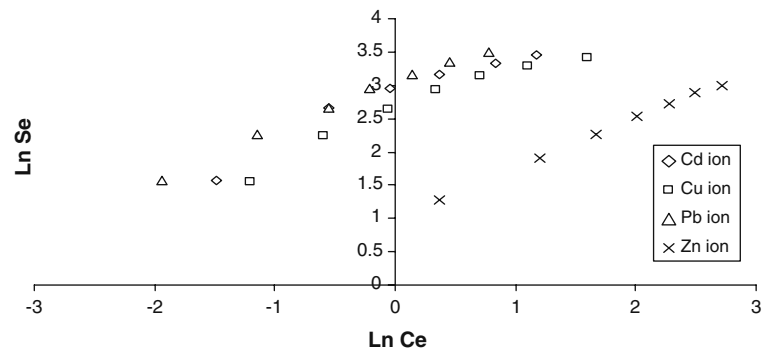
Good straight lines were obtained while plotting the lines between Ce/Se versus Ce as shown in Fig. 8a, for all metal ions $R^2$ values $> 0.97$ which clearly suggests the applicability of Langmuir adsorption model. According to $S_m$ and $K_L$ parameters the removal by natural zeolite is produced following the sequence $Zn^{2+} < Cu^{2+} < Cd^{2+} < Pb^{2+}$ as been seen can from the data that presented in Table 2.

The Freundlich adsorption isotherm is also applied to the removal of $Zn^{2+}$, $Cu^{2+}$, $Cd^{2+}$, and $Pb^{2+}$ on natural zeolite. It is one of the most widely used mathematical descriptions. This isotherm gives an expression encompassing the surface heterogeneity and the exponential distribution of active sites and their energies.
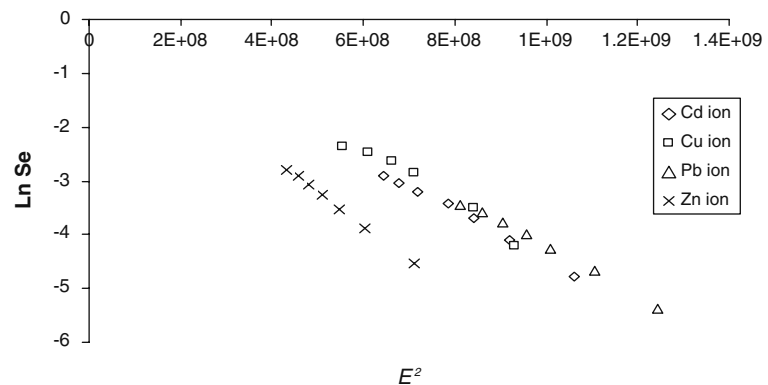
**Fig. 8** Adsorption
isotherms of Langmuir,
Freiundlich and (DKR)
which applied in the
removal of $Zn^{2+}$, $Cu^{2+}$,
$Cd^{2+}$ and $Pb^{2+}$ by natural
zeolite at 298 K
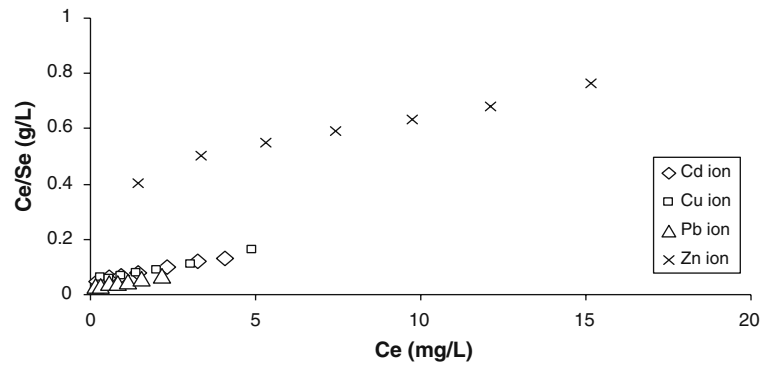


**A.** Linearized form of Langmiur isotherm



**B.** The linearized form of Freundlich isotherm



**C.** Linearized of Dubinin–Kagnar–Radushkevich isotherm

The linearized form of this model was used
to describe the nature of adsorption using the
following equation

$$\ln S_e = \ln K_F + 1/n \; \ln C_e$$

here $S_e$ and $C_e$ have the same definition as in
Langmuir isotherm, $K_F$ and $1/n$ the Freundlich
constants, respectively referred to "adsorption ca-
pacity" and "adsorption intensity". While plot-
ting the lines between $\ln S_e$ versus $\ln C_e$ yielding
a straight lines with $R^2 > 0.95$ as illustrated in
Fig. 8b, this indicated that the data were found in
good agreement as that case of the Langmiur for
all metal ions. The constants which are $K_F$, and $1/n$
were determined from the slope and the intercept
respectively as shown at Table 2, the adsorption
capacities from the $K_F$ values show the same trend

**Table 2** Constants of Langmuir, Freundlich and (DKR) models applied in the removal of $Zn^{2+}$, $Cu^{2+}$, $Cd^{2+}$ and $Pb^{2+}$ by natural zeolite at 298 K, ionic strength (0.01) and constant pH 6

| Metal ions | Langmuir | | | Freundlich | | | DKR | | |
|---|---|---|---|---|---|---|---|---|---|
| | $S_m$ (mg g$^{-1}$) | $K_L$ (L mg$^{-1}$) | $R^2$ | $n$ | $K_F$ (L g$^{-1}$) | $R^2$ | $E$ (kJ/mol) | $S_m$ (mol/g) | $R^2$ |
| $Zn^{2+}$ | 41.841 | 0.059 | 0.976 | 1.339 | 2.740 | 0.998 | 9.129 | 0.962 | 0.999 |
| $Cu^{2+}$ | 44.248 | 0.479 | 0.979 | 1.516 | 12.993 | 0.946 | 10.000 | 1.760 | 0.962 |
| $Cd^{2+}$ | 45.249 | 0.476 | 0.990 | 1.457 | 16.792 | 0.925 | 10.541 | 1.011 | 0.995 |
| $Pb^{2+}$ | 56.818 | 0.629 | 0.995 | 1.408 | 20.780 | 0.992 | 11.180 | 1.303 | 0.996 |

as in Langmiur model for these metal ions. The value $1/n$ predicts the adsorption intensity which related to the type of adsorption whether it is favored or not. It is reported that if values of $n$ are in the range 1–10 then the process of adsorption is favored, the values of $n$ which are presented in Table 2 indicted that this adsorption is favored one (Baker and Khalili 2004).

Further, the results of sorption of these four metal ions on natural zeolite surface were also analyzed using the linearized form of the Dubinin-Kaganer-Radushkevich (DKR)

$$\ln S_e = \ln S_m - \beta \varepsilon^2$$

Where $S_e$ is the amount of metal ions adsorbed per unit weight of adsorbent (mg/g), $S_m$ is the maximum sorption capacity, $\beta$ is the activity coefficient related to mean sorption energy, and $\varepsilon$ is the Polanyi potential.

The sorption energy can be calculated from the following equation:

$$E = 1 \Big/ \sqrt{-2\beta}$$

The plot of $\ln S_e$ against $\varepsilon^2$ for these metal ions removed by natural zeolite is shown in Fig. 8c, the parameters for this isotherm model are calculated from the slope and intercept and listed in Table 2. As shown in Table 2, the $E$ values are 9.129, 10.000, 10.541, and 11.180 kJ/mol for $Zn^{2+}$, $Cu^{2+}$, $Cd^{2+}$ and $Pb^{2+}$ respectively. All of these metal ions order of an ion-exchange mechanism, in which the sorption energy lies within 8–16 kJ/mol.

The sorption capacity $S_m$ for all of these metal ions follow the same trend as Langmuir and Freundlich isotherm models (Erdem et al. 2004).

Finally, according to isotherms constants the removal of these metal ions will follow this order $Zn^{2+} < Cu^{2+} < Cd^{2+} < Pb^{2+}$, this can be explain, because $pb^{2+}$ can form stable complexes with oxygen which is held by the zeolite groups, also it has a lowest hydration energy (−1,481 kJ/mol), according to other studied ions, which means weakest interaction between this ion and water molecules (Baker and Khalili 2007). The highest hydration energy is for $Zn^{2+}$ (−2,046 kJ/mol) for that it has the lowest value of removal. Copper ion has a high affinity to lose water molecules than cadmium ion (Baker and Khalili 2003, 2005), but their behavior follow the same trend which is found by (Bereket et al. 1997).

**Conclusions**

This study revealed the following points about the natural zeolite as a good resin for removal of heavy metal ions.

- By using the column experiment, zeolite has a good ability to remove heavy metal ions by adsorption process.
- The column experiment is preferable and needed less time and simple equipments compared to batch experiment.
- The removal of heavy metals increases with increasing the initial concentration because of using low concentration of metal ion from 5 to 20 ppm, and this is in good agreement with the findings of researchers in the literature (Ali and El-Bishtawi 1997; Bosso and Enzweiler 2002).
- There is a slight effect of the ionic strength on the removal of the studied metal ions due to the low concentration of the electrolyte.
- There was a slight decrease in the percentage of removal of these studied heavy metal ions with increasing the particle size.

- The Langmuir, Frendlich, and (DKR) were used to describe the sorption isotherms of single-solute systems. The sorption energy E determined in the DKR equation (9.129, 10.000, 10.541, and 11.180 kJ/mol for $Zn^{2+}$, $Cu^{2+}$, $Cd^{2+}$ and $Pb^{2+}$ respectively) which revealed the nature of the ion-exchange mechanism.
- These results show that natural zeolite can be used effectively for the removal of metal cations from wastewater.
- This naturally occurring material provides a substitute for the use of activated carbon as adsorbent due to its availability and its low cost

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