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Kinetic and isothermal studies of cadmium sorption onto bentonite and zeolite

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A b s t r a c t. This study deals with the use of natural bentonite and zeolite for the removal of Cd(II) from aqueous solutions. Batch sorption experiments were carried out to investigate the sorption of Cd(II) to the sorbents with particular focus on sorption kinetics, the pH dependence of sorption, sorption capacity and isotherms. Percent removal of Cd(II) by the minerals increased with increasing pH, contact time and sorbent dose. Bentonite had a higher percent removal of Cd(II) in all chemical conditions compared to zeolite. Our data showed that the Koble-Corrigan models had a better fit ($r^2 \geq 0.99$) as compared to the Langmuir model. Maximum sorption capacity calculated from the Langmuir model was 17.6 and 9.4 mg g^{-1} for bentonite and zeolite, respectively. Pseudo-second order kinetic model provided a perfect fit for the kinetic data of Cd(II) sorption onto both minerals. Based on the sorption and kinetic information obtained for Cd(II) removal by these minerals, it may be concluded that Iranian zeolite and especially bentonite are effective sorbents for Cd(II).

K e y w o r d s: Cd(II), sorption, isotherm, kinetics, zeolite, bentonite

INTRODUCTION

The release of heavy metal cations into the environment is a potential threat to water and soil quality as well as to plant, animal and human health (Stępniewska *et al.,* 2005; Wingenfelder *et al*., 2005). A vast amount of literature exists which documents the adverse health effects from acute and chronic exposure to Cd(II) in both humans and animals (Wagner, 1993). The primary adverse health effects which have been observed are lung cancer and kidney damage (Wagner, 1993).

A number of technologies for the removal of heavy metal ions from the environment have been developed over the years (Ansari Mahabadi *et al*., 2007). The conventional methods for heavy metals removal from the environment include oxidation-reduction, precipitation and ion exchange/sorption. Among all the methods, ion exchange/sorption is highly effective, easy to adapt and economical (Bhattacharya e*t al*., 2006).

Many mechanisms have been reported for metal ion sorption, such as cation exchange, surface complexation, surface induced precipitation, surface co-precipitation, colloid formation at surfaces and diffusion onto particle micropores (Bhattacharya *et al*., 2006; Christl and Kretzschmar, 1999).

Abundance of bentonite and zeolite and their low cost make them strong candidates as sorbents for the removal of heavy metals from various effluents, such as industrial and processing waters and wastewaters, or extracts resulting from the treatment of contaminated soils by soil washing (Abollino *et al*., 2003). Because of high specific surface area and CEC, these minerals also play a significant role in determining the availability and transport of metal species in soil and waters (Kaya and Ören, 2005; Wingenfelder *et al*., 2005).

Studies conducted recently showed that bentonite (Kaya and Ören, 2005; Ouhadi *et al*., 2006) and zeolite (Wingenfelder *et al*., 2005) can retain a significant amount of heavy metals from aqueous solutions, however, factors such as pH, nature of minerals, sorbent dose, initial metal ion concentration, metal ion properties and ionic strength can influence the sorption of metal ions by these minerals (Abollino *et al*., 2003).

Large deposits of bentonite and zeolite minerals have been recently found in several locations in Iran and mining of the mineral deposits have already been started. These minerals have been selected as the candidates for removal of heavy metals from industrial wastewater in Iran. However, information about the chemical behaviour of the Iranian bentonite, as compared to zeolite, is very limited. Therefore,

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this study is an attempt to explore the potential use of these minerals in the field of environmental clean-up and remediation.

The aim of this study was, therefore, to investigate the sorption of Cd(II) to natural zeolite and bentonite with particular focus on sorption kinetics, the pH dependence of sorption, sorption capacity and isotherms.

MATERIALS AND METHODS

The bentonite and zeolite powder samples used in this study originated from Anarak and Firouzkoh mines in central and northern Iran, respectively. The samples were then saturated with Na using 1 M $NaNO_3$ solution. The mineralogical composition of the mineral materials was investigated by means of X-ray diffraction (XRD) and the data were analysed by the Reitveld method (program AutoQuan, GE Seifert). Total elemental analysis was per- formed by fluorescence spectroscopy using a Spectro X-Lab 2000 X-Ray instrument (Table 1). The specific surface area and cation exchange capacity of the samples were measured using BET-N_2 sorption analysis and Na-acetate method described by Rhoades (1986), respectively.

T a b l e 1. Chemical properties of zeolite and bentonite samples

Characteristics (wt %)	Bentonite	Zeolite
SiO_2	59.6	61.5
Al_2O_3	12.5	8.00
TiO_2	0.11	0.12
Fe_2O_3	1.69	0.91
MgO	0.71	0.70
CaO	1.18	2.39
Na_2O	1.44	1.06
K_2O	0.54	1.14

All sorption experiments were conducted in batch experiments in 0.01M $Ca(NO_3)_2$ at pH 6.5, at sorbents concentrations of 1 % and at ambient temperature (25±2°C).

Predetermined amounts of clay mineral stock suspensions (0.3 g) were transferred into a centrifuge tube containing 30 ml of background electrolyte. Batches were shaken for 2 days before Cd(II) addition. For each mineral, a predetermined amount of metal from the Cd(II) stock solution (1000 mg l^{-1} in 0.2 vol. % HNO_3 Merck, Titrisol) was added to give the final concentration of 100 mg l^{-1} of Cd(II). The pH values of the solutions were adjusted by adding predetermined volumes of 0.01M NaOH solution. The suspensions were shaken for periods ranging from 0.5 to 24 h with a rotary shaker at a speed of 150 r.p.m. The tubes were then centrifuged at 2000 g for 20 min, the supernatant was filtered, and Cd(II) concentration was determined in the extract by an AAnalyst Perkin-Elmer 200 Atomic Absorption Spectrophotometer (AAS) at the wavelength of 228.8 nm.

To investigate the effect of initial solution pH on sorption, 0.3 g samples of bentonite or zeolite stock suspensions with adjusted initial pH were mixed with 30 ml Cd(II) solution (100 mg l^{-1}) in 50 ml centrifuge tubes and the initial pH of the suspensions were adjusted to values ranging from 4-9 using HNO_3 or NaOH. The suspensions were shaken for 12 h, then centrifuged for 20 min at 2000 g, filtered, and analysed for Cd(II) concentration.

The effect of sorbent dose on sorption of Cd(II) onto the sorbents was also conducted. The initial solution pH, the initial concentration of the metal ions and the shaking time were fixed at 6.5, 100 mg l^{-1} and 12 h, respectively, while the sorbent dose was varied from 0.2-2 g 30 ml^{-1}.

After 30 ml 0.01 M of $Ca(NO_3)_2$ was transferred into 50 ml centrifuge tubes, predetermined amounts (0.3 g) of zeolite or bentonite stock suspensions were added to obtain sorbent concentration of 10 g l^{-1}.Then a predetermined amount of metal from the Cd(II) stock solutions was added to give a final concentration ranging between 10 and 500 mg l^{-1} of Cd(II). Initial pH of the solution was adjusted to 6.5±0.1 by predetermined amount of 0.01 M HNO_3 or NaOH solution. The tubes were then shaken for 24 h and the same procedures (measuring pH, centrifuging and metal analysis) were performed as above.

The amount of Cd(II) sorbed on each solid phase was calculated from the difference between the initially added and finally measured Cd(II) concentrations.

The sorption kinetics was tested with the pseudo-second order equation (Ho and McKay, 2002). It can be represented as follows:

$$Q_t = \frac{Q_e^2 k_1 t}{1+Q_e k_1 t}, \quad (1)$$

where: Qe and Q_t are the amount of Cd(II) sorbed (mg g^{-1}) at equilibrium and any time t, respectively, and k_1 is the pseudo-second order rate constant (g $mg^{-1}min^{-1}$). The $k_1Q_e^2$ is the initial sorption rate (h) (mg g^{-1} min^{-1}) as $t \rightarrow 0$.

The sorption isotherms were tested for fit to the Langmuir (Langmuir, 1918) and Koble-Corrigan (Koble and Corrigan, 1952) models:

$$Q_e = \frac{Q_{\max} C_e K_L}{1+K_L C_e}, \quad (2)$$

$$Q_e = \frac{A C_e^{\beta}}{1+B C_e^{\beta}}, \quad (3)$$

where: Q_e is the amount of adsorbed Cd(II) per unit mineral mass (mg g^{-1}), C_e is the equilibrium concentration of the Cd(II) ion in solution (mg L^{-1}), $Q_{\max}$ and K_L are the Langmuir constant related to the sorption maximum and energy

of sorption, respectively, A, B and β are the Koble-Corrigan parameters, respectively. This model is valid when $\beta \geq 1$. The values in the models were found by non-linear curve fitting analysis method, using Data-fit software (trial version).

RESULTS AND DISCUSSION

According to XRD, the zeolite was composed of 82.6% clinopetilolite, 8.6%. quartz, 5.3% illite and 3.5% feldspar. The bentonite used in this study was composed of 86.5% montmorillonite, 9.5% quartz, 2.5% illite and 1.5% calcite. The CEC of bentonite and zeolite were 76±0.5 and 91±0.5 $cmol^c\ kg^{-1}$, respectively. The N_2-surface areas of the samples were 28±1 and 32 ± 1 $m^2\ g^{-1}$ for bentonite and zeolite, respectively.

Figure 1 shows the effect of shaking time on the removal of Cd(II) from the solutions by bentonite and zeolite. Two distinct phases in sorption of Cd(II) by these minerals may be recognized: (I) a sharp relatively linear phase in which instantaneous extremely fast sorption takes place, and (II) a quasi-stationary state phase where very small amount of sorption occurred. In phase I, bentonite and zeolite sorbed 35 and 14% of Cd(II) at 30 min, respectively. In phase II, a quasi-stationary state was observed after 120 min of contact, in which the amount of metal ions sorbed was practically constant. This phenomenon may be attributed to the instantaneous utilisation of the most readily available sorption sites on both sorbent surfaces at the initial contact time. However, as the coverage increases, the number of available surface sites for sorption comes down, and the rate decreases till it reaches equilibrium (Zhang and Hou, 2008). The quick sorption of Cd(II) on both sorbents suggests that chemical sorption rather than physical sorption contributes to Cd(II) sorption on these minerals surfaces (Bhattacharya *et al*., 2006). Similar results have been reported by Mohapatra and Anand (2007) and Álvarez-Ayuso and García-Sánchez (2007) who investigated Cd(II) removal from aqueous solution by chromite and palygorskite, respectively.

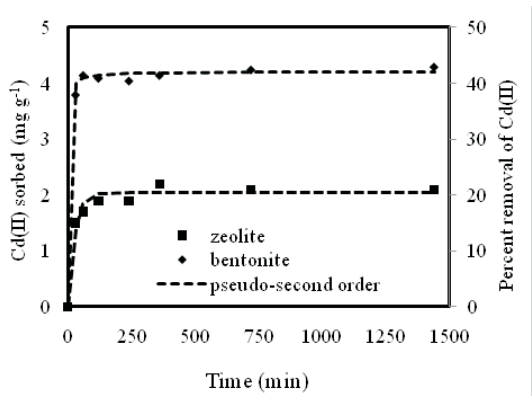

Fig. 1. Effect of contact time on the removal of Cd(II) by bentonite and zeolite. The initial concentration of Cd(II) was 100 mg l^{-1}, the slurry concentration was 1%, the agitation speed was 150 r.p.m., and the initial pH was 6.8.

To analyse the sorption rate of Cd(II) on bentonite and zeolite, the pseudo-second order model (Ho and McKay, 2002) was used to simulate the sorption kinetics.

Table 2 lists the calculated parameters and constants obtained from the pseudo-second order kinetic models. The correlation coefficients for the pseudo-second order kinetic model obtained were greater than 0.99 for bentonite and zeolite, indicating a perfect fit of data with this kinetic model (Fig. 1). Good correlations of experimental data with the pseudo-second order kinetic model have been reported for the sorption of Cd(II) on bentonite (Purna Chandra Rao *et al.,* 2006), montmorillonite (Sen Gupta and Bhattacharyya, 2008), zeolite (Purna Chandra Rao *et al*., 2006), and palygorskite (Shirvani *et al*., 2006). The rate constant k_1 values were 0.07 and 0.03 g $mg^{-1}min^{-1}$for bentonite and zeolite, respectively.

The calculated Q_e values also agreed very well with the experimental data. These indicate that the sorption system studied conforms to the second-order kinetic model, therefore, the rate limiting step may be chemical sorption or chemisorption involving valence forces through sharing or exchange of electrons between Cd(II) and both sorbents as covalent forces, and ion exchange (Ho and McKay, 2002).

The initial sorption rate, h, has been widely used for the evaluation of sorption rates (Ho and McKay, 2002; Shirvani *et al*., 2006). In the present study the values of h decreased as follows: 1.39 mg g^{-1} min^{-1} (bentonite) > 0.155 mg g^{-1} min^{-1} (zeolite), indicating that bentonite can sorb Cd(II) more rapidly than zeolite from aqueous solutions. According to the pseudo-second order kinetic model (Ho and McKay, 2002), the rate of the sorption reaction decreased non-linearly with time. For example, the instantaneous rates at 50 and 90% of Cd(II) sorption (SR_{50} and SR_{90}, respectively) can be calculated from pseudo-second order rate equation as follows:

T a b l e 2. Kinetic parameters for sorption of Cd(II) onto zeolite and bentonite

Parameters	Bentonite	Zeolite
$Q_{e\ exp.}$ (mg g^{-1})	4.2	2.2
	Pseudo-second order	
Q_e (mg g^{-1})	4.2	2.1
k_1 (g mg^{-1} min^{-1})	0.07	0.03
h (mg g^{-1} min^{-1})	1.39	0.155
SR_{50} (mg g^{-1} min)	0.35	0.038
SR_{90} (mg g^{-1} min)	1.39 10^{-2}	1.55 10^{-3}
$t_{1/2}$ (min^{-1})	3	12.9
*R^2	0.998	0.999
SE	0.07	0.08

*All determination coefficients are significant at probability level ≤0.001.

$$SR_{50} = k_1[Q_e - (0.5Q_e)]^2 = \frac{k_1 Q_e^2}{4} = \frac{h}{4}, \quad (4)$$

$$SR_{90} = k_1[Q_e - (0.9Q_e)]^2 = \frac{k_1 Q_e^2}{100} = \frac{h}{100}. \quad (5)$$

Therefore, SR_{50} and SR_{90} values are one-fourth and one-hundredth of the initial sorption rate, h, respectively (Table 2). Comparisons based on h values can be extended onto the entire experimental duration. Based on the pseudo-second order kinetic model, $t_{1/2}$ or the time at which the sorbed Cd(II) quantity is the half value of Q_e depends on the sorption capacity of the sorbent and inversely relates to the initial sorption rate (Shirvani *et al.*, 2006):

$$t_{1/2} = \frac{1}{k1Q_e^2} = \frac{Q_e}{h}. \quad (6)$$

The $t_{1/2}$ values for the sorbents followed the order: zeolite > bentonite (Table 2). The kinetic results indicated that after 24 h of contact time the sorbed amounts of cadmium on bentonite were higher than on zeolite. Moreover, this mineral showed high k_1 and low $t_{1/2}$ values confirming its affinity towards cadmium and its effectiveness in the removal of the metal.

The pH of the aqueous solution is an important variable which controls the sorption of the metal at the clay-water interfaces (Kaya and Ören, 2005). The effects of initial solution pH on the removal of Cd(II) by zeolite and bentonite are shown in Fig. 2. It can be seen that the sorption of Cd(II) onto both sorbents is markedly pH-dependent. Between pH 4 and pH 6, the sorption efficiency increased from 10 to 28% and from 35 to 57% for zeolite and bentonite, respectively. In the second section (pH 6-9) sorption efficiency of zeolite remained constant, but it increased for bentonite slightly, up to 62%.

In order to interpret the effect of pH on sorption behaviour of Cd(II) ions onto zeolite and bentonite, a knowledge of Cd(II) speciation and final (equilibrium) pH is essential. Species activities were estimated using the Visual MINTEQ speciation program (Gustafsson, 2006).

In pH range less than 6.5, the predominant Cd(II) species is Cd^{2+}, accounting for 90% of total Cd(II) in solution, and other species such as $Cd(OH)^+$, $Cd(OH)_2$ are present only in very small amounts. Therefore, lower sorption of the metal ions at initial pH, 4, is probably due to the presence of excess H^+ ions competing with the Cd^{2+} species for the sorption sites (Kaya and Ören, 2005). It is also possible that hydroxyl functional groups at the clay surface interact with water in an acidic medium forming some aqueous complexes (Sen Gupta and Bhattacharyya, 2008) as follows:

$$\equiv SO^- + H_2O \xleftrightarrow{H^+} SOH_2^+ + OH^-. \quad (7)$$

This surface charge interacts repulsively with approaching metal ions and prevents them from reaching the surface and thus the sorption was low at low pH. With increasing initial pH from 4 to 6 mineral surfaces become negatively charged, favouring Cd(II) species sorption (Sen Gupta and Bhattacharyya, 2008).

$$\equiv SOH + OH^- \Leftrightarrow \equiv SO^- + H_2O, \quad (8)$$

$$\equiv 2SO^- + Cd^{2+} \Leftrightarrow \equiv (SO^-)_2 \ldots Cd^{2+} + H^+. \quad (9)$$

Changes of initial pH during the sorption process are shown in Fig. 3. Initial acidic pH values changed to the near-neutral values after 12 h of contact time for both minerals and initial concentrations (dotted lines).

This is possibly due to the buffering capacity of these minerals which is mainly given by exchange of H^+ and binding of the protons on the Lewis basic sites according to the following reaction (Trgo and Perić, 2003):

$$\equiv SOH + H^+ \Leftrightarrow \equiv SOH_2^+. \quad (10)$$

This reaction is favoured at lower pH values (Trgo and Perić, 2003). The decrease of solutions pH with initial alkaline pH is due to adsorbing of OH^- to functional groups of the sorbents according to the following reaction (Trgo and Perić, 2003):

$$\equiv SOH + OH^- \Leftrightarrow \equiv S\text{-}OH(OH^-) \Leftrightarrow \equiv SO^- + H_2O. \quad (11)$$

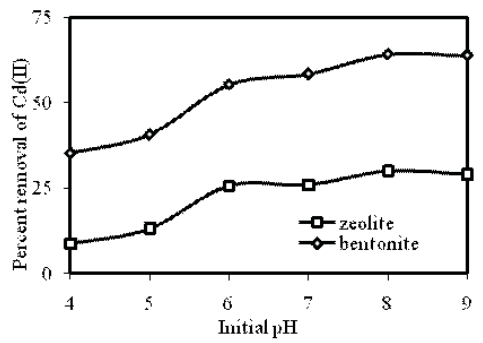

Fig. 2. Effect of initial pH on the removal of Cd(II) by bentonite and zeolite. The initial concentration of Cd(II) was 100 mg l^{-1}, the slurry concentration was 1% and the contact time was 12 h.

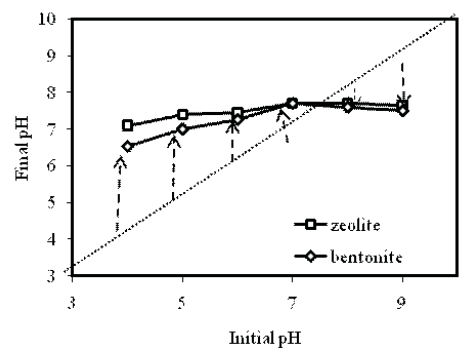

Fig. 3. pH changes during the experiment.

It is also possible that the protons from the zeolitic water that coordinate exchangeable cation (Na^+) are removed (Trgo and Perić, 2003):

$$[Na_x H_2 O]^{m+} + OH^- \Leftrightarrow [Na_{(x-1)} H_2 O(OH)]^{(m-1)} + H_2 O. \quad (12)$$

The final pHs of solution after Pb(II) sorption were 6.5-7.0 for zeolite and 7.0-7.3 for bentonite when the initial adjusted pH values were in the range of 4-9.

According to Visual MINTEQ simulation at pH≥7, the system is supersaturated with respect to the $Cd(OH)_2$ solid phase, therefore, precipitation of $Cd(OH)_2$ is probable. Formation of $CdCO_3$ also cannot be ruled out. Thus, these processes may be responsible for the removal of Cd(II) from solutions at higher pHs.

To identify the mechanism of sorption processes, some researchers proposed monitoring of solution pH at equilibrium as a function of different metal concentrations (Zhu *et al.*, 2008). Figure 4 shows the effects of equilibrium metal concentrations on final pH of suspensions. Final pH of solution decreases gradually with increasing initial concentration of Cd(II). At low metal concentration, decreasing of final solution pH with an increase in initial metal concentration may be regarded as an indication of cation exchange as the dominant mechanism of Cd(II) sorption, as follows (Zhu *et al.*, 2008):

$$\equiv XH + Cd^{2+} \Leftrightarrow \equiv XCd^+ + H^+, \quad (13)$$

$$\equiv S\text{-}ONa + H_2O + Cd^{2+} \Leftrightarrow \equiv S\text{-}OCdOH + Na^+ + H^+, \quad (14)$$

Surface complexation should be the dominant mechanism at higher concentrations of Cd(II) solutions, which was confirmed by an evident change in the pH of the final solution (Zhu *et al.*, 2008):

$$\equiv SOH + Cd^{2+} \Leftrightarrow \equiv SOCd^+ + H^+, \quad (15)$$

$$2\equiv SOH + Cd^{2+} \Leftrightarrow (\equiv SO)_2 Cd + 2H^+. \quad (16)$$

However, surface precipitation should be considered as another mechanism at higher concentrations of Cd(II) solutions, which was confirmed by release of hydronium ions:

$$Cd^{2+} + 2H_2O\text{-}Cd(OH)_{2(s)} + 2H^+. \quad (17)$$

The amount of sorbent is an important parameter because this determines the sorption capacity of a sorbent for a given initial concentration of the sorbate. The effects of bentonite and zeolite doses on the removal of Cd(II) from the solution are shown in Fig. 5. As we had expected, an increase in the percent removal of Cd(II) with an increase in the dose of both sorbents was observed. This is simply because of an increase in the number of sorbent sites as the result of an increase in the number of mineral particles in the suspension (Kaya and Ören, 2005).

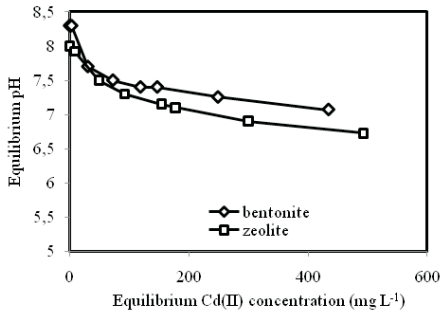

Fig. 4. Effect of equilibrium metal concentration on final pH of suspensions.

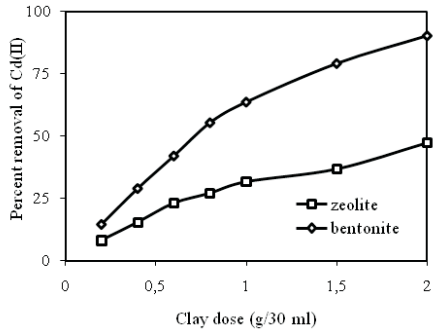

Fig. 5. Effect of sorbent concentration on Cd(II) sorption. The initial concentration of Cd(II) was 100 mg l^{-1}, the initial pH was 6.5 and the contact time was 12 h.

Sorption isotherms have been extensively used to study the sorption capacity and the chemical affinity of a mineral for various elements.

The isotherm constants, sum of square error (SE) and correlation coefficient (R^2) based on the actual deviation between the experimental points and predicted values are given in Table 3. The Langmuir sorption affinity, K_L is larger for bentonite (0.005) compared to zeolite (0.004). Maximum experimental sorption capacity of Cd(II) for bentonite (17.6 mg g^{-1}) was approximately 2 times higher than that for zeolite (9.4 mg g^{-1}). The lower sorption rate for zeolite as compared to bentonite may be due to difficulty in the penetration of hydrated Cd(II) ions into zeolite channels (Kaya and. Ören, 2005).

Higher K_L and Q_{max} values obtained for sorption of Cd(II) ions onto bentonite indicates a higher Cd(II) sorption capacity and intensity for bentonite as compared to zeolite.

According to Giles *et al.* (1947), we obtained isotherms with a convex shape and a constant sorption maximum, equivalent to *H* isotherms, where the sorption affinity increases with decreasing concentration.

In order to determine whether the sorption process by the sorbents is conforming to the Langmuir adsorption model, the isotherm shape can be classified by a term *RL*, a dimensionless constant separation factor which is defined as below (Hall *et al.*, 1966):

T a b l e 3. Langmuir and Koble-Corrigan isotherms constants for sorption Cd(II) onto zeolite and bentonite

Parameters	Bentonite	Zeolite
	Langmuir	
Q_{max} (mg g^{-1})	17.60	9.40
K_L(l mg^{-1})	0.005	0.004
R^2	0.97	0.92
SE	0.65	0.70
	Koble-Corrigan	
A (mg^{1-b} g^{-1} l^b)	4.3 10^{-2}	4.8 10^{-5}
B (l^b mg^{-b})	2.8 10^{-3}	8 10^{-6}
β	1.17	2.44
*R^2	0.98	0.98
SE	0.69	0.50

Explanations as in Table 2.

$$RL = \frac{1}{1+K_L C_i}. \quad (18)$$

The parameter *RL* is a measure of the favourability of the sorption process as follows: $RL > 1$, unfavourable; $RL = 1$, linear; $RL = 0$, irreversible; $0 < RL < 1$ favourable, respectively. The *RL* values for Cd(II) sorption were from 0.3-0.9 and 0.33-0.96 for bentonite and zeolite, respectively. They are in the range of 0-1, which indicates favourable sorption (Hall e*t al*., 1966).

The values of the Koble-Corrigan constant *A* were 4.3 10^{-2} and 4.8 10^{-5} for bentonite and zeolite respectively. This constant is an indicator of sorption capacity and affinity of the sorbent. The greater Koble-Corrigan constants (*A* and *B*) values for bentonite as compared to zeolite once more indicate a higher Cd(II) sorption capacity, affinity and intensity for bentonite compared to zeolite sorption.

On the basis of standard errors of estimate (*SE*) and determination coefficient (R^2), the Koble-Corrigan model correctly simulates the sorption behaviour of Cd(II) onto zeolite and bentonite (Fig. 6). The coefficient of correlation was high ($R^2 \geq 0.99$) and the *SE* value (0.5) was low for sorption of Cd(II) on zeolite. The Langmuir model provided a good fit with experimental and predicted values for Cd(II) sorption by bentonite ($R^2 \geq 0.98$ and $SE \leq 0.65$).

Bentonite removed greater amounts of Cd(II) from the solution as compared to zeolite in simillar chemical conditions. Similar sorption behaviour was reported for sorption of Zn on Turkish zeolite and bentonite (Kaya and Ören, 2005).

This may be attributed to larger real surface area of bentonite, and possibly different active functional groups. The fact that the greater CEC did not result in greater metal sorption by the zeolite suggests that both exchangeable and high affinity sites contributed to Cd(II) sorption.

It is reported (Kaya and Ören, 2005; Wingenfelder *et al.*, 2005) that zeolite channels with small diameters (5 10^{-9} m) could have hindered diffusion of hydrated Cd(II) ions (4.26 10^{-9} m) into their channels. Pore clogging or structural damage may also have occurred for zeolite particles during grinding process. This has been shown to decrease zeolite sorption capacity (Inglezakis *et al*., 1999).

Comparison of maximum monolayer sorption capacities of Cd(II) for some minerals is also given in Table 4. Many researchers tested the sorption capacity of some natural minerals, but the obtained results are often difficult to compare. The values were reported in the form of monolayer sorption capacity. The experimental data of the present study show that natural zeolite and bentonite used in this study exhibit a reasonable sorption capacity for Cd(II) and, therefore, may be useful for removal of Cd(II) from polluted environmental sites.

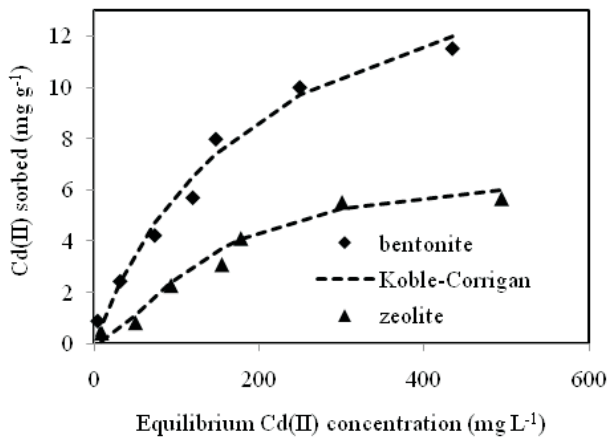

Fig. 6. Koble-Corrigan isotherm for sorption of Cd(II) on bentonite and zeolite.

T a b l e 4. Comparison of maximum monolayer sorption capacities of Cd(II) on different clays

Sorbent	Q_{max} (mg g^{-1})	References
Palygorskite	1	(Shirvani *et al*., 2006)
Kaolinite	6.8	(Sen Gupta and Bhattacharyya, 2008)
Palygorskite	3.15	(Álvarez-Ayuso and García-Sánchez, 2007)
Montmorillonite	5.2	(Abollino *et al.*, 2003)
Zeolite	9.3	This study
Bentonite	17.8	This study

CONCLUSIONS

1. Commercial Iranian bentonite and zeolite minerals have good potential for the removal of Cd(II) from aqueous systems.

2. Bentonite was more effective in the removal of Cd(II) as compared to zeolite.

3. The amount of Cd(II) sorbed by bentonite and zeolite increased with increasing solution pH, sorbent dose and contact time.

4. Cadmium sorption on bentonite and zeolite conforms well to Langmuir and Koble-Corrigan isotherms, with Koble-Corrigan being the best.

5. Cadmium sorption kinetics on bentonite and zeolite were very well described with a second-order rate reaction.

6. The sorption of Cd(II) ions by zeolite and bentonite is complex and probably involves several mechanisms.

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