



Sorption hysteresis of Cd(II) and Pb(II) on natural zeolite and bentonite

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ABSTRACT

Sorption hysteresis in natural sorbents has important environmental implications for pollutant transport and bioavailability. We examined sorption reversibility of Cd(II) and Pb(II) on zeolite and bentonite. Sorption isotherms were derived by sorption of Cd(II) and Pb(II) from solutions containing a range of the metal concentrations corresponding to 10–100% maximum sorption capacity (SC_{max}) of the sorbents. The desorption experiments were performed immediately following the completion of sorption experiments. Sorption and desorption isotherms of Cd(II) and Pb(II) were well described by the Freundlich model. The results revealed that the desorption isotherms of Cd(II) and Pb(II) from zeolite significantly deviated from the sorption isotherms indicating irreversible or very slowly reversible sorption. For bentonite sorption/desorption isotherms were similar indicating reversible sorption. The extent of hysteresis was evaluated from sorption and desorption Freundlich parameters (K_f and n) through the apparent hysteresis index ($HI = n_{desorb}/n_{sorb}$; n is the exponent in the Freundlich equation) and differences in Freundlich K_f parameters. Higher sorption irreversibility was obtained for Pb(II) as compared to Cd(II). The amounts of Cd(II) and Pb(II) desorbed from bentonite were more than from zeolite, indicating that zeolite was a more effective sorbent for water and wastewater treatment.

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1. Introduction

Regarding acute toxicity, Cd(II) and Pb(II) together with Hg(II) form “the big three” of heavy metals with the greatest potential hazard to humans and the environment [1]. Much greater effort will be needed to reduce pollution from these elements, e.g. through immobilization of Cd(II) and Pb(II) in soil and removal of these toxic elements from contaminated water and wastewater. Utilization of low cost and efficient natural sorbents is one of the techniques, which can be used to immobilize or eliminate toxic heavy metals from soil and wastewater [2,3]. High specific surface areas, high cation exchange capacities, and low cost and ubiquitous presence in most soils, are the reasons to choose natural sorbents such as zeolite and bentonite to sorb and immobilize heavy metals in the environment [3]. Bioavailability and remobilization of heavy metals in soil and water treated with natural sorbents such as zeolite and bentonite is generally controlled by sorption–desorption reactions [3,4]. Extensive researches have been conducted on heavy metal sorption by natural sorbents. However, desorption behavior of Cd(II) and

Pb(II) from clay minerals are still poorly described and understood.

To predict the fate and transport of heavy metals in the environment pollutant transport and bioavailability models commonly rely on distribution coefficients and maximum sorption levels that are obtained from equilibrium batch sorption experiments [4,5]. However, one of the discrepancies that causes errors in predicting the potential toxicity of a metal contaminant is the often neglect of desorption, which is important in the control of metal bioavailability in the environment [4,6]. If sorption is irreversible, these models will incorrectly over predict the movement or biological fate of the metal contaminant. Thus, in order to improve remediation strategies, risk assessments, and to make better predictions about the mobility of contaminants, it is critical that the mechanism of sorption–desorption reactions as well as the reversibility or irreversibility of sorbed heavy metal cations on natural sorbents and soil constituents be quantified.

Hysteresis, or non-singularity, is a phenomenon in which the sorption and desorption isotherms do not coincide [7]. Several mechanisms have been suggested to explain hysteresis including chemical precipitation, variation of the binding mechanism with time, migration and incorporation of the solute into the soil matrix, micropore deformation and trapping [8,9,10]. Pseudo-hysteresis is related to slow desorption kinetics, non-attainment of equilibrium of the sorption before desorption was started [8] mass loss from

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vessels and sorption to non-settling colloids [9]. One possible explanation for slow desorption is that chemisorption reactions usually require a much higher activation energy in desorption direction than sorption, to break the energetically very favorable bonds of the sorbate with the surface [8,11]. The pseudo-hysteresis depends on conditions and can be eliminated, while the true hysteresis is reproducible in repeated sorption-desorption cycles [9].

Strawn et al. [12] found that sorption of Pb(II) by aluminum oxide is completely reversible within 3 days. Similar results were found by Ainsworth et al. [13] for Pb(II) sorption on iron oxides, while Shirvani et al. [14] reported that a large fraction of sorbed Cd(II) by palygorskite and sepiolite was not desorbed after 24 h. Morton et al. [15] reported that Cu(II) sorption irreversibility on montmorillonite was due to the formation of kinetically irreversible Cu(II) dimer complexes or coordination of Cu on the high-energy edge sites of the clay.

Several studies on sorption of Cd(II) and Pb(II) by zeolite and bentonite [3,16,17] as well as examples of the sorption hysteresis studies with significant irreversibility exist in the literature for various heavy metals-sorbent systems: Cd(II) sorbed to sepiolite and palygorskite [14]; Th(IV) sorbed to attapulgite [18]; Cd(II), Pb(II) and Cu(II) sorbed to soils [19]. However, no information regarding reversibility of heavy metals from zeolite and bentonite minerals is available. The objectives of the study were: (i) to quantify the hysteresis for Cd(II) and Pb(II) sorption to zeolite and bentonite and, (ii) to compare sorption irreversibility of Cd(II) and Pb(II) onto the sorbents.

2. Materials and methods

2.1. Characterization of the sorbents

The bentonite and zeolite samples used in this study were obtained from Anarak and Firuzkoh mines in central and northern Iran, respectively. The mineral samples were powdered in a mortar and sieved using a no. 270 mesh (0.05 mm) sieve. The mineralogical composition was investigated by X-ray diffraction (XRD), and the data was analyzed by the Reitveld method (program AutoQuan, GE Seifert)(data not shown). The samples were saturated with Ca²⁺ using 1 M Ca(NO₃)₂ solution. Excess salts were then rinsed from the samples with deionized water until the electrical conductivity of eluents reached about 25 μS m⁻¹. Bentonite and zeolite were stored as stock suspensions (50 g L⁻¹) in 0.01 M Ca(NO₃)₂. The sorbent concentrations in the stock suspensions were determined by evaporating aliquots of the suspensions followed by drying at 100 °C for 48 h. The specific surface area and cation exchange capacity (CEC) of the samples were measured using BET-N₂ sorption analysis and Na-acetate method, respectively [20].

2.2. Sorption procedure

Sorption experiments were conducted in a batch experiment using 15 mL polyethylene (PE) bottles at room temperature (23 ± 2 °C). Equivalents of 0.1 g sorbent sub-sample from the sorbents stock suspensions were added to 10 mL of 0.01 M Ca(NO₃)₂ solution resulting in a slurry concentration of 1% (w/w). Batches were agitated in an end over end shaker for 2 days at 6 rpm before addition of sorbate. Aliquots of Cd(II) or Pb(II) stock solution (1000 mg L⁻¹ in 0.2 vol % HNO₃ Merck, Titrisol) was added to obtain initial metal concentrations in the range of 10–100% of metal maximum sorption capacity of each sorbent. Maximum sorption capacities (SC_{max}) of sorbents were determined for Cd(II) and Pb(II) in a preliminary study. Maximum sorption capacity (SC_{max}) values of the zeolite and bentonite minerals were about 9 and 18 mg g⁻¹ for Cd(II) and 72 and 75 mg g⁻¹ for Pb(II), respectively.

The initial Cd(II) concentration ranges were 9 to 90 mg L⁻¹ for zeolite, and 18 to 180 mg L⁻¹ for bentonite suspensions. In the case of Pb(II), the initial metal ion concentration ranges were 75 to 750 mg L⁻¹ for bentonite, and 71 to 720 mg L⁻¹ for zeolite suspensions, respectively. The pH values of the solutions were adjusted to 5.0 by adding negligible predetermined volumes of 0.03 M NaOH solution. The samples were shaken again for 24 h after Pb(II) and Cd(II) was added. Preliminary experiments showed that the contact for 24 h was long enough for equilibrium to be reached. At the end of equilibrium time, the suspensions pH was measured and the samples were centrifuged for 20 min at 5000 g. Half of the supernatant volume (5 mL) was pipetted out from each tube and then acidified with 1% nitric acid. Cadmium and Pb(II) in the supernatants were measured by an AAnalyst Perkin-Elmer 200 Atomic Absorption Spectrophotometer (AAS).

Blanks were prepared without sorbents but otherwise handled identically. The amount of Cd(II) and Pb(II) sorbed on the sorbents was calculated as the difference between the metal concentration in the blanks and the concentration in the solution after equilibration. The sorption isotherms were calculated for each mineral using the Freundlich equation [21]:

$$q_e = K_{sorb} C_e^{n_{sorb}} \quad (1)$$

where q_e , C_e , K_{sorb} and n_{sorb} are the amount of sorbed Cd(II) or Pb(II) (mg g⁻¹), equilibrium liquid phase concentration (mg L⁻¹), the Freundlich bonding constant (L mg⁻¹) and sorption coefficient, respectively.

2.3. Desorption procedure

The desorption experiments were performed in sequential decant-refill technique immediately following the completion of sorption experiments. Desorption of Cd(II) and Pb(II) was studied with the clay samples initially treated with the metal loadings of 50, 75 and 100% maximum sorption capacity (SC_{max}) during the sorption study after centrifugation. Immediately after removal of the 5 ml supernatant, the same volume of Cd(II) and Pb(II) -free 0.01 M Ca(NO₃)₂ solution (with the same pH as in the sorption experiments) was added to the centrifuge tubes. The centrifuge tubes were vortexed to disperse the clay pellets, and the suspensions were mechanically shaken for 24 h. The desorption period of 24 h was chosen after a preliminary desorption kinetic experiment was conducted for 48 h. The data showed a concentration plateau after 20 h. For a more convenient operation, the desorption period was set at 24 h, the same as the sorption period.

The suspensions were then centrifuged for 20 min at 5000 g, and the supernatant was replaced again by the same volume of metal-free background electrolyte. The desorption equilibration process was repeated four successive times for each sample. The equilibrium pH and Cd(II) and Pb(II) concentrations in the supernatant solutions were measured after each desorption step as described above. Desorbed Cd(II) and Pb(II) was calculated at each desorption stage, and the amount of Cd(II) and Pb(II) still sorbed on the clay at each desorption stage was calculated as the difference between the initial sorbed amount and the desorbed amount. Desorption of Cd(II) or Pb(II) for each sorbent was described by the Freundlich relationship (equation 1) with the parameters K_{desorp} and n_{desorb} .

Non-linear regression procedure using DATAFIT software [22] was utilized for fitting Freundlich equation to sorption and desorption data. Criteria used for estimating goodness-of-fit of the Freundlich model to the data were the coefficients of determination (R^2) and standard error of estimate (SE):

$$SE = \left(\frac{\sum (q_e - q_p)^2}{n - 2} \right)^{1/2} \quad (2)$$

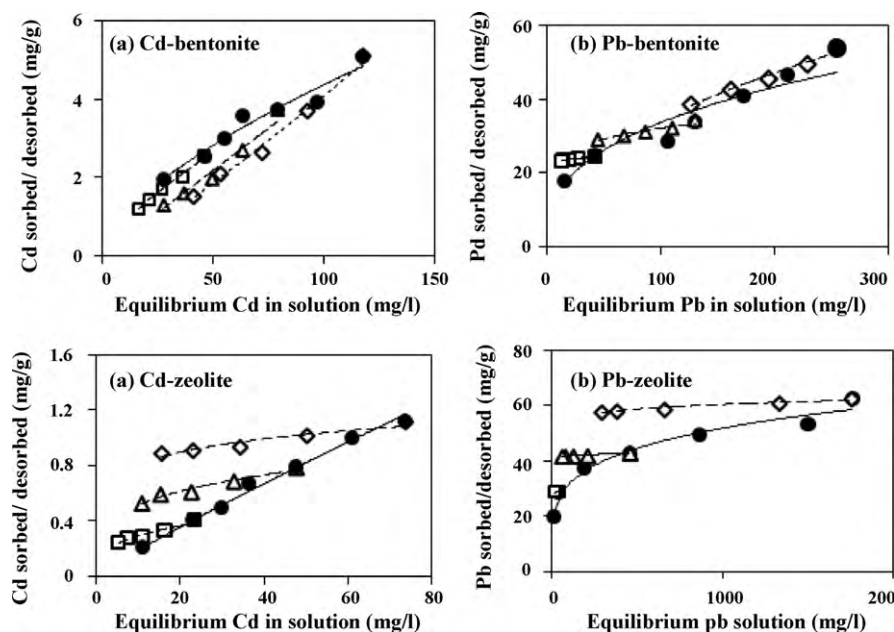


Fig. 1. Cadmium and lead sorption (●) and desorption isotherms at three initial metal loadings of 50% (□), 75% (△) and 100% (◇) of the sorbent SC_{max} . Solid and dashed lines are Freundlich model predictions of sorption and desorption, respectively (pH:5.0, contact time: 24 h, temperature: $23 \pm 2^\circ\text{C}$).

where q_e and q_p are measured and model estimated amounts of the metal sorbed, respectively, and n is the number of measurements.

Chemical species in the solutions were also predicted using Visual MINTEQ, a chemical speciation program developed to simulate equilibrium processes in aqueous systems [23].

2.4. Data analysis

The sorbed amount was calculated by mass balance equation:

$$q_e = \frac{(C_i - C_e)V}{M}, \quad (3)$$

where q_e , C_i , C_e , M and V are the sorbed amounts of the metal ions (mg g^{-1}), initial metal concentration in solution (mg L^{-1}), equilibrium metal concentration (mg L^{-1}), mass of sorbent (g), and the volume of the solute solution (L), respectively.

2.5. Hysteresis index

The sorption-desorption hysteresis was quantified for each sorbent-solute solution system using the index defined by O'Connor et al. [24] and Barriuso et al. [25]:

$$HI = \frac{n_{desorb}}{n_{sorb}} \times 100, \quad (4)$$

where HI is the hysteresis index. The lower index values indicate increased difficulty of the sorbed metal to desorb from the sorbent [26]. The n_{sorb} and n_{desorb} are the exponent of fitted Freundlich equation in the sorption and desorption branches, respectively. Theoretically, if there is no hysteresis $n_{desorb} = n_{sorb}$ and, positive hysteresis would be characterized by $n_{sorb} > n_{desorb}$ and $K_{sorb} < K_{desorb}$. In the case of negative hysteresis $n_{desorb} > n_{sorb}$ and $K_{desorb} < K_{sorb}$, respectively [24,25].

3. Results and discussion

3.1. Sorbent characteristics

According to XRD, the zeolite was composed of 82.6% clinopetilloite, 8.6% quartz, 5.3% illite and 3.5% feldspar, the bentonite 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 $91 \pm 0.5 \text{ cmol}_{(+)} \text{ kg}^{-1}$, respectively. The N_2 -surface areas of the samples were 28 ± 1 and $32 \pm 1 \text{ m}^2 \text{ g}^{-1}$ for bentonite and zeolite, respectively. It is believed that BET- N_2 determined specific surface area does not reflect the true surface area of the bentonite as demonstrated by Yukselen and Kaya [27].

3.2. Isotherms

The sorption and desorption of Cd(II) and Pb(II) by the zeolite and bentonite are characterized by their corresponding isotherms (Fig. 1). For each sorbate-sorbent system, one sorption isotherm (solid line), and three desorption isotherms (dashed lines) are shown. Sorption and desorption of Cd(II) and Pb(II) results were well described by the Freundlich model.

Fitted model parameters (K and n), coefficients of determination (R^2) and standard errors (SE) for sorption and desorption are given in Tables 1 and 2. Except for the Cd(II)-bentonite system, the fitted K values for desorption isotherms were higher than those associated

Table 1
Freundlich sorption isotherm parameters for Pb(II) and Cd(II).

	Pb(II)		Cd(II)	
	zeolite	bentonite	zeolite	bentonite
K_{sorb}	19.18 (0.31) ^a	21.46 (0.7)	0.024 (0.001)	0.237 (0.01)
n_{sorb}	0.216 (0.01)	0.36 (0.01)	0.907 (0.02)	0.633 (0.002)
R^2	0.99 ^a	0.98 ^a	0.99 ^a	0.98 ^a
SE	0.04	0.04	0.005	0.002

^a Significant at probability level < 0.001 .

^a Values in parentheses are standard errors associated with the estimated model parameters.

Table 2
Freundlich desorption isotherm parameters for Pb(II) and Cd(II).

Initial metal load (% of the SC_{max}) ^a		Pb(II)		Cd(II)	
		zeolite	bentonite	zeolite	bentonite
50	K_{desorb}	28.49 (0.510) ^b	21.47 (0.270)	0.137 (0.001)	0.17 (0.010)
	n_{desorb}	0.006 (0.001)	0.032 (0.001)	0.332 (0.002)	0.699 (0.007)
	R^2	0.99 [*]	0.99 [*]	0.99 [*]	0.99 [*]
	SE	1×10^{-5}	1×10^{-5}	7×10^{-6}	2×10^{-5}
75	K_{desorb}	40.21 (0.250)	16.70 (0.340)	0.292 (0.003)	0.044 (0.001)
	n_{desorb}	0.014 (0.001)	0.141 (0.002)	0.252 (0.011)	0.998 (0.002)
	R^2	0.99 [*]	0.98 [*]	0.99 [*]	0.99 [*]
	SE	0.0001	0.03	0.002	0.004
100	K_{desorb}	49.36 (0.60)	3.63 (0.040)	0.578 (0.012)	0.023 (0.001)
	n_{desorb}	0.044 (0.002)	0.48 (0.002)	0.147 (0.003)	1.12 (0.024)
	R^2	0.98 [*]	0.98 [*]	0.99 [*]	0.99 [*]
	SE	0.001	0.02	0.0003	0.0006

^{*} Significant at probability level < 0.001.

^a SC_{max} = maximum sorption capacity of the sorbents for Cd(II) or Pb(II).

^b Values in parentheses are standard errors associated with the estimated model parameters.

with the sorption isotherm. The opposite trend was observed for the parameter n .

3.3. Reversibility or irreversibility of sorption

3.3.1. Bentonite

The average percentage of the sorbed metals released from bentonite after four successive desorption steps, were 31% and 63% for Pb(II) and Cd(II), respectively. Since a relatively high proportion of sorbed Cd(II) was released, it indicates that the sorption of Cd(II) by bentonite was likely reversible and less specific. This suggests that ion exchange (outer-sphere complexation) is the dominant mechanism of sorption reaction between Cd(II) and bentonite [28].

As can be seen from Fig. 1a, the desorption isotherms for Cd(II) onto bentonite did not deviate strongly from the corresponding sorption isotherm indicating a reversible sorption. The amounts of desorbed Cd(II) were larger than would be predicted from the sorption isotherms. This is a case of negative hysteresis ($n_{desorb} > n_{sorb}$ and $K_{desorb} < K_{sorb}$), that is, when the sorbate is desorbed more easily than it is sorbed. Barriuso et al. [25] reported negative hysteresis for the sorption-desorption of atrazine by montmorillonite (Wyoming bentonite). They attributed this phenomenon either: (i) enhanced desorption as a result of temporarily high solid/solution ratio after centrifugation, or (ii) removal of only external water in the desorption experiments while the interlayer water is fixed [25]. In any case, this phenomenon is only observed when the sorption-desorption process is highly reversible.

In the case of Pb(II), the amount of desorbed Pb(II) was smaller than the amount that would be predicted from the sorption isotherm indicating some reactions involved in the sorption processes may be irreversible or slow reversible. Since preliminarily kinetic studies showed that both the sorption and desorption rates of Cd(II) and Pb(II) leveled within about 24 h, non-equilibrium state of the system can be ruled out as an explanation. Similar findings have been reported by Businelli et al. [28] for sorption of Pb(II) onto montmorillonite. They concluded that irreversibility of Pb(II) sorption by montmorillonite was due to the inner-sphere binding of

Pb(II) to the mineral edges and its precipitation at pH values higher than hydrolysis point of Pb(II) [28].

Based on the estimates obtained by Visual MINTEQ, the species Cd^{2+} and Pb^{2+} were the dominant species present in the equilibrium solutions and none of the systems were supersaturated with regard to Cd(II) - and Pb(II) -containing minerals. However, according to McBride [8], under-saturation state of the systems does not exclude the possibility of metal surface precipitation or co-precipitation processes. It is known that the presence of suspended colloids can trigger the nucleation of elements on the surfaces even in diluted solutions under-saturated with regard to individual minerals [8]. However, it should be considered that the precipitation reactions are often much slower than chemisorption reactions to soil constituents [7,8].

The gap between sorption and desorption isotherms was evaluated by the hysteresis index (HI). For both metal ions, the HI increased with increasing of metal loading rates on the bentonite (Table 3). This is expected, because there were only limited number of high energy sorption sites available on the sorbent, therefore the metal ions were preferentially sorbed at those high energy sorption sites first, and the sorbed metals at those sites was difficult to desorb [29]. At high initial concentrations of the metals, the limited high-energy sites (resistant fraction) were first saturated by Cd(II) or Pb(II). The rest of metal ions sorbed at the low energy sorption sites, and hence were more easily desorbed than those at high energy sorption sites. Thus, overall desorption was easier, and the hysteresis index (HI) was higher at higher metal ion loading.

3.3.2. Zeolite

The average amounts of 3 and 16% of the initially sorbed Pb(II) and Cd(II) were desorbed from zeolite after four successive desorption steps, respectively. Release of such a relatively low proportion of sorbed Cd(II) and particularly Pb(II) indicates that some reactions involved in the sorption processes may be irreversible or very slowly reversible which may be attributed to diffusion of metal ions into the zeolite channels [30] and the strong bonding to the high affinity sites (covalent bonds, inner-sphere complexation) [31].

Table 3
Hysteresis index (HI) calculated for quantification of non-singularity of Cd(II) and Pb(II) sorption and desorption isotherms.

Hysteresis index	Initial metal load (% of the SC_{max}) ^a	Pb(II)		Cd(II)	
		zeolite	bentonite	zeolite	bentonite
HI	50	2.77	8.80	36.6	110.0
HI	75	6.33	38.5	27.8	158.0
HI	100	20.0	130.0	16.2	177.0

^a SC_{max} = maximum sorption capacity of the sorbents for Cd(II) or Pb(II).

Table 4
Average distribution coefficients of the metal ions (\bar{K}_d) obtained from sorption and desorption data.

	Initial metal load (% of the SC _{max}) ^a	Pb(II)		Cd(II)	
		zeolite	bentonite	bentonite	zeolite
Sorption	-	3.2 (0.4) ^b	0.42 (0.01)	0.017 (0.002)	0.050 (0.001)
Desorption	50	15.0 (0.73)	1.40 (0.02)	0.032 (0.003)	0.065 (0.001)
	75	4.3 (0.23)	0.43 (0.001)	0.034 (0.002)	0.043 (0.002)
	100	1.2 (0.01)	0.25 (0.002)	0.036 (0.001)	0.037 (0.002)

^a SC_{max} = maximum sorption capacity of the sorbents for Cd(II) or Pb(II).

^b Values in parentheses are standard errors associated with the estimated average distribution coefficients.

Infrared spectroscopic studies by Mozgawa et al. [31] revealed that Pb(II) formed inner-sphere surface complexes with zeolite. These sorbed metal ions are relatively difficult to desorb [32].

The desorption isotherms of Cd(II) and Pb(II) onto zeolite deviated significantly from the corresponding sorption isotherms (Fig. 1c and d). The amounts of desorbed Cd(II) and Pb(II) were considerably smaller than the amount that would be predicted from sorption isotherm. This shows a normal or positive hysteresis ($n_{sorb} > n_{desorb}$ and $K_{sorb} < K_{desorb}$) and suggests that a portion of the sorbed metal ion was tightly bonded to the mineral surfaces and was not readily desorbable.

Effects of metal ion loadings on the hysteresis index are shown on Table 3. The apparent hysteresis index (*HI*) was greatly dependent on the kind of the metal ion and the initial amount of sorbed metal ions. For Pb(II)-zeolite systems, the *HI* increased with increase of the metal ion loading rates. But, in the case of Cd(II), the *HI* decreased with increasing the metal ion loading. At low Cd(II) concentrations, due to a lower gradient, fewer Cd(II) ions can penetrate into the zeolite channels, while, at high metal levels, the higher gradient of concentration may force the sorbed Cd(II) to penetrate deeper into the zeolite channels. When penetrating into the channels, the sorbed Cd(II) is less likely to be diffused from zeolite channels to equilibrium solution, so that overall desorption was more difficult at higher than at lower Cd(II) loading resulting in a lower *HI*.

3.3.3. Sorbent comparison

The relative percentage of Cd(II) or Pb(II) desorbed from bentonite was higher than from zeolite, indicating a stronger and more

specific bonding of Pb(II) and Cd(II) by zeolite compared to bentonite. Consequently, zeolite exhibited a lower *HI* as compared to bentonite. This behavior may be attributed to the differences of sorbents' characteristics and structures. Zeolite (clinoptilolite) has two channels (7.5×3.1 and $4.6 \times 3.6 \text{ \AA}$) orientated parallel to the crystallographic *c*-axis which are crossed by a channel system running parallel to the *a*-axis ($4.7 \times 2.8 \text{ \AA}$) and to the [1 0 2] plane [33]. Thus, a portion of metal ion may be entrapped into the pore channels of zeolite structure [16,30] while, bentonite has a tendency to increase in volume (swell) [34] and occupied almost the entire length of the 30 ml reactor and provided a much higher surface area for desorption.

This is in agreement with the results of Wingenfelder et al. [16] who reported natural zeolite is a suitable sorbent for removal of Pb(II) from acid mine waters and can even prevent a complete remobilization of Pb(II) in case of re-acidification.

3.3.4. Sorbate comparison

Compared to Cd(II)-sorbent systems, higher irreversibility, as reflected by low *HI* values, were obtained for Pb(II)-sorbent systems (especially Pb(II)-zeolite) (Table 3). This is usually attributed to differences in metal ion characteristics and resultant affinity for sorption sites [8,11]. The hydrated Pb(II) (5.2 \AA diameter) and Cd(II) (5.5 \AA diameter) cations have 6.1 and 7.6 water molecules in their hydration shells, respectively [35]. The hydration energy of Pb(II) is $-1425 \text{ kJ mol}^{-1}$ and that of Cd(II) is $-1755 \text{ kJ mol}^{-1}$ [35]. The lower hydration energy of Pb(II) means that it loses its hydration shell more easily than Cd(II). This could explain the stronger sorption of Pb(II) than Cd(II) [36].

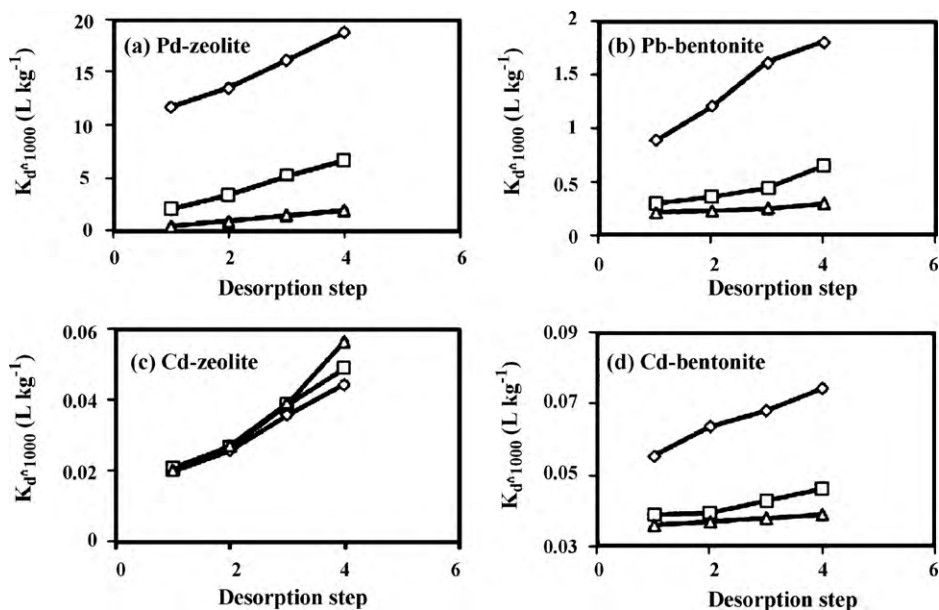


Fig. 2. Variation in distribution coefficient (K_d) with desorption step at three initial metal loadings of 50% (\diamond), 75% (\square) and 100% (\triangle) of the sorbent SC_{max}.

The Freundlich binding constants (K_{sorb}) of Pb(II) sorption onto zeolite and bentonite were greater than those of Cd(II) (Table 1), which confirms that Pb(II) was retained stronger by the sorbents. Many studies considering the sorption-desorption of Cd and Pb on soils and clay minerals have indicated that Pb was much less desorbable than Cd [11,16,37].

3.3.5. Distribution coefficient (K_d)

Heavy metals distribution between solid phase and solution is a key issue in assessing the environmental risk of heavy metals in the environment [38]. It can be characterized by the distribution coefficient (K_d) ($L\ kg^{-1}$) which is the concentration of metal ion in solid phase ($mg\ kg^{-1}$) divided by metal solute concentration ($mg\ L^{-1}$) at equilibrium

The average distribution coefficients (\bar{K}_d) calculated based on sorption and desorption isotherms are shown in Table 4. The K_d values of the target metal ions varied greatly depending on the sorbent type and the amount of initially sorbed metal ions. The measured K_d for desorption of Cd(II) and Pb(II) from both zeolite and bentonite increased with the number of desorption steps (Fig. 2), which is a further indication of hysteresis [39]. The K_d values for desorption of Cd(II) from the bentonite samples increased with the number of desorption steps less rapidly than for zeolite. The slower rate of increase in the K_d values indicates relatively less sorption-desorption hysteresis and, hence, once more indicates that the metal ions are bound less irreversible to bentonite than to zeolite surfaces.

From the environmental implication point of view, this study demonstrated that Cd(II) and Pb(II) sorbed onto bentonite were released and may be bio-available or be leached to ground water. Care should be taken with application of bentonite as a clay-liner, filter and soil-stabilizing agent. Sorption of Cd(II) and specially Pb(II) onto zeolite may be irreversible or very slowly reversible. Thus, zeolite has a high potential for immobilization of Cd(II) and Pb(II) from polluted sites.

4. Conclusion

Sorption and desorption of Cd(II) and Pb(II) results were well described by the Freundlich model. The results revealed that the desorption isotherms of Cd(II) and Pb(II) from zeolite deviated from sorption data indicating irreversible or very slowly reversible sorption, while, for bentonite sorption/desorption isotherms showed little deviation indicating reversible sorption. The amount of Cd(II) or Pb(II) desorbed from bentonite was more than that of zeolite, indicating that zeolite is a more efficient immobilizer of Pb(II) and Cd(II) from polluted soil or waste water. Irreversible sorption would be advantageous for pollutant immobilization in the remediation of already contaminated soils. The results obtained in this study may be useful in assessing remediation of soil and wastewater by natural zeolite and bentonite. Further study is needed to better understand the causes of the hysteresis in the sorption-desorption of Cd(II) and Pb(II) onto zeolite and bentonite using chemical, microscopic, and spectroscopic techniques.

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