

Journal of Environmental Science and Health, Part A: Toxic/Hazardous Substances and Environmental Engineering

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/lesa20>

Adsorption of some heavy metals by natural zeolites : XPS and batch studies

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Published online: 15 Dec 2008.

To cite this article: G. Yuan , H. Seyama , M. Soma , B.K.G. Theng & A. Tanaka (1999) Adsorption of some heavy metals by natural zeolites : XPS and batch studies, Journal of Environmental Science and Health, Part A: Toxic/Hazardous Substances and Environmental Engineering, 34:3, 625-648, DOI: [10.1080/10934529909376856](https://doi.org/10.1080/10934529909376856)

To link to this article: <http://dx.doi.org/10.1080/10934529909376856>

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ADSORPTION OF SOME HEAVY METALS BY NATURAL ZEOLITES : XPS AND BATCH STUDIES

Key Words: X-ray photoelectron spectroscopy, zeolite, adsorption, Pb, Cd

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ABSTRACT

The adsorption of some heavy metal ions by mordenite and clinoptilolite has been investigated using batch techniques and X-ray photoelectron spectroscopy (XPS). At 10^{-5} M of Pb, Cu, Cd, and Zn, and in the presence of 10^{-3} M Ca as a competing cation, the preferential sequence of adsorption was $\text{Pb} > \text{Cu} > \text{Cd} > \text{Zn}$ for mordenite, and $\text{Pb} > \text{Cu} > \text{Zn} > \text{Cd}$ for clinoptilolite. The adsorption capacities and removal efficiencies of the zeolites for the two highly toxic heavy metals, Cd and Pb, were also determined at a low-to-medium concentration range (10^{-6} to 10^{-3} M), and at a zeolite:solution ratio of 50:30 (mg:mL), in competition with 10^{-3} M of Ca. Below 10^{-4} M, both mordenite and clinoptilolite removed Pb from the solution almost completely. As Pb concentration increased, removal efficiency decreased. However,

the zeolite samples (particularly mordenite) were not effective in reducing Cd concentrations to the legal $\mu\text{g/L}$ level. Solution pHs and the photoelectron binding energies of adsorbed $\text{Pb}(4f_{7/2})$ and $\text{Cd}(3d_{5/2})$ gave no evidence of precipitation of Pb and Cd as hydroxides or carbonates during adsorption. Up to one-third of the cation exchange capacity (CEC) of mordenite, and half that of clinoptilolite, were used for Pb adsorption. A much smaller fraction of the CEC was used in Cd adsorption. XPS showed that Na ion was the principal cation involved in the exchange adsorption of Pb and Cd. As such, clinoptilolite with 676 mmol/kg of exchangeable Na adsorbed more Pb and Cd than mordenite with only 326 mmol/kg of exchangeable Na. Comparing surface (XPS) with bulk (average) concentrations of adsorbed Pb and Cd showed that Pb was evenly distributed within zeolite particles but Cd accumulated on particle surfaces. This may be because the hydration energy of Cd ion is larger than that of Pb ion.

INTRODUCTION

Zeolites are hydrated aluminosilicates of alkali and alkaline earth cations with a three-dimensional crystal structure and a large cation exchange capacity (CEC) of 1000-3000 mmoles(+)/kg (Ming and Dixon, 1987). In their natural state, the exchangeable ions are predominantly sodium, calcium, and potassium. These, together with their large CEC, wide availability, and low cost make natural and synthetic zeolites potentially useful for pollution control. In particular, adsorption onto zeolites is an attractive alternative to chemical precipitation for removing heavy

metals from solutions and waste waters (Blanchard et al., 1984; Kesraoul-Oukl et al., 1993, 1994; Malliou et al., 1994; Lin and Hsi, 1995; Singer and Berkgaut, 1995; Pansini, 1996; Curkovic et al., 1997; Ali et al., 1997). It remains to be seen, however, whether laboratory-scale findings can be extrapolated to field situations.

Selectivity sequences for a range of heavy metal cations have been determined from ion-exchange isotherms (Breck, 1974; Tsitsishvili et al., 1992), but in many studies the concentrations of heavy metals used were unrealistically high (≥ 1000 mg/L) (Blanchard et al., 1984; Kesraoul-Oukl et al., 1993; Curkovic et al., 1997), far exceeding those found in most municipal and industrial effluents. As selectivity can vary with concentration (Dyer, 1995), selectivity sequences determined at concentrations of relevance to environmental control will provide a better measure of the effectiveness of zeolites in removing heavy metals from waste waters.

Further, waste waters may contain significant amounts of Ca and other cations. In many cases, competition of these cations with heavy metal ions for adsorption sites on the zeolites has been ignored. Typical examples are systems of zeolites and heavy metal ions, containing no competing cation (Kesraoul-Oukl et al., 1993; Malliou et al., 1994; Curkovic et al., 1997; Ali et al., 1997) or only with Na as the competing ion (Pansini, 1996), for which zeolites have a low affinity.

The adsorption by zeolites of heavy metals from solution has conventionally been investigated using the batch method. Solid-state surface analytical techniques, such as X-ray photoelectron spectroscopy (XPS), have so far not been exploited.

The present study is an attempt to assess (I) the preference of two common natural zeolites (mordenite and clinoptilolite) for adsorbing Cd, Pb, Cu, and Zn ions at low solution concentration (10^{-5} M); (ii) the adsorption capacity of mordenite and clinoptilolite for Cd and Pb at low-to-moderate concentrations (10^{-6} to 10^{-3} M) in the presence of Ca ion; (iii) the distribution of adsorbed Pb and Cd on the surface and in the bulk phase of the zeolites.

MATERIALS AND METHODS

Granular samples of mordenite and clinoptilolite were obtained from Shiroishi (Miyagi Prefecture) and Nishiaizu (Fukushima Prefecture), Japan, respectively. The samples were ground and passed through a 150-mesh sieve. Because zeolites, in practice, are not further treated (e.g. by acid washing or sodium saturation), the materials were used as received.

The mineralogy of the zeolite samples was analysed by X-ray diffractometry (XRD). The XRD data were then compared with those of reference mordenite and clinoptilolite (JCPDS, 1980).

The pH of the zeolites, suspended in Milli-Q water, was measured at a water:solid (mL:g) ratio of 4, using a combination electrode.

The cation exchange capacity and the composition of the exchangeable cations of the zeolites were determined by the ammonium acetate method. Briefly, the samples were repeatedly (4x) washed with 1 M NH_4OAc at pH 7. The excess ammonium was removed by three washings with isopropanol, and the adsorbed

ammonium was displaced by four extractions with 1 M KCl. The Ca, Mg, K, and Na ions in the combined NH_4OAc washings were determined by atomic absorption. The amount of ammonium displaced by K ion was taken to represent the CEC.

We first assessed the reaction time for the adsorption of Pb, Cd, Cu and Zn on mordenite and clinoptilolite and then determined the preference sequences for the metal ions. To this end, constant amounts of mordenite and clinoptilolite (50 mg) were mixed with five 30-mL solutions containing 1.1×10^{-5} M of Pb, Cd, Cu, and Zn (nitrate salts), and 1.0×10^{-3} M $\text{Ca}(\text{NO}_3)_2$ as the background electrolyte. The pH of the solutions had been adjusted to 5.0. After shaking for 1, 4, 7, 16, and 24 hours, the suspensions were centrifuged. After measuring their pH, the supernatants were acidified by addition of HNO_3 , and the concentration of Pb, Cd, Cu, and Zn determined by inductively coupled plasma atomic emission spectrometry (ICP-AES). The amount of metal adsorbed was derived from the difference between the amount initially added and that remaining in the supernatants.

Adsorption of two highly toxic metals, Cd and Pb, was then determined separately as follows. Seven 30-mL Cd or Pb solutions adjusted to pH 5.0 and containing 1.00×10^{-3} M of $\text{Ca}(\text{NO}_3)_2$ were added to centrifuge tubes into which 50 mg of mordenite or clinoptilolite had been placed. The concentration of Cd ranged from 1.04×10^{-6} to 1.03×10^{-3} M and of Pb from 4.57×10^{-6} to 1.00×10^{-3} M. Thus, the composition of the suspension simulates that in which zeolites would be used to treat waste waters. After shaking for 7 h, the tubes were centrifuged and the pH of the supernatants was measured. After acidifying with nitric acid, the concentration

of Cd and Pb in the supernatants was determined by ICP-AES. The Cd and Pb adsorbed was calculated as before. The residues in the tubes with the highest initial Cd or Pb concentration (10^{-3} M) were washed three times with acetone to remove entrained Cd or Pb, air-dried, and stored for subsequent X-ray photoelectron spectroscopy (XPS) analysis.

XPS provides information on the chemical composition of surface and near-surface (to a depth < 10 nm) layers of zeolite particles. For simplicity the term "surface" is used below. XPS was carried out on mordenite and clinoptilolite before and after adsorption of Cd and Pb using a Vacuum Generators ESCALAB 5 instrument. The samples were mounted onto stainless steel sample holders of 10-mm diameter by double-sided adhesive tape and analyzed using Mg- K_{α} and Al- K_{α} radiations. Wide-scan spectra of the samples were first obtained. For each detectable element in the spectra, a narrow-scan spectrum was also taken, the signals of which were accumulated. The resultant enhancement in the signal/noise ratio allowed the position of each narrow-scan peak to be determined accurately. The binding energies (BEs) of ejected photoelectrons were determined from the corresponding peak positions and calibrated against the $4f_{7/2}$ line (at 84.0 eV) of gold deposited on the zeolite samples under vacuum. The uncertainty in BE values is typically ± 0.2 eV.

Atomic ratios of Al, O, C, Ca, Mg, K, Na, Fe, Pb, and Cd, relative to Si, were calculated from the peak areas of Al(2p), O(1s), C(1s), Ca(2p), Mg(KLL Auger), K(2p), Na(KLL Auger), Fe(2p), Pb(4f), Cd(3d), and Si(2s) lines, respectively, using experimentally determined atomic sensitivity factors (Seyama and Soma, 1988).

RESULTS

Table 1 lists the d spacings for the mordenite and clinoptilolite samples together with the closely matching values for the corresponding reference minerals. A small amount of quartz might be present in the mordenite sample, as indicated by d values of 0.4257 and 0.3336 nm. Similarly, quartz (d = 0.3321 nm) and feldspars (d = 0.3179 nm) might exist as impurities in the clinoptilolite sample.

The pH in water of mordenite and clinoptilolite was 7.4 and 9.4, and the CEC was 1.79×10^3 and 1.88×10^3 mmol(+)/kg, respectively. Exchangeable cations (mmol/kg) in mordenite were Ca (310), Mg (76), K (377), Na (326); and Ca(226), Mg(9), K(504), Na(676) in clinoptilolite. Although the CECs did not differ greatly, clinoptilolite contained more exchangeable sodium than mordenite.

Fig. 1 shows the competitive adsorption of Pb, Cd, Cu, and Zn cations by mordenite and clinoptilolite as a function of time. The concentrations of Pb, Cd, Cu and Zn did not change appreciably after 7 h of contact with the zeolites, suggesting that at the end of this period adsorption by the fine-ground (<150 mesh) zeolites was practically complete. For the same initial concentration of Pb, Cd, Cu, and Zn (10^{-5} M), a lower C_t/C_0 concentration ratio (Fig.1) was indicative of a higher preference for that metal. On this basis, the following preference sequences applied:

mordenite	$\text{Pb} \gg \text{Cu} > \text{Cd} > \text{Zn}$
clinoptilolite	$\text{Pb} > \text{Cu} > \text{Zn} > \text{Cd}$

That is, both mordenite and clinoptilolite preferred Pb to Cu, Cd, and Zn and, therefore, could selectively remove Pb from solution. Further, even though the Ca

TABLE 1
Lattice Spacings (nm) of Zeolites - Samples VS. References (JCPDS, 1980)

Mordenite						Clinoptilolite			
Sample	Ref	Sample	Ref	Sample	Ref	Sample	Ref	Sample	Ref
1.362	1.37	0.3336	0.331	0.2047	0.2047	0.9014	0.899	0.3119	0.3122
0.9059	0.910	0.3216	0.322	0.2013	0.2019	0.7944	0.791	0.3073	0.3074
0.6579	0.661	0.3093	0.310	0.1992	0.1998	0.6814	0.676	0.2969	0.2976
0.6364	0.638	0.2938	0.2946	0.1951	0.1953	0.6603	0.664	0.2796	0.2794
0.6065	0.610	0.2889	0.2896		0.1936	0.5948	0.593	0.2730	0.2733
0.5792	0.579	0.2734	0.2743			0.5264	0.523		
0.5041	0.503	0.2696	0.2700			0.5119	0.512		
0.4869	0.487		0.2639			0.4659	0.4654		
0.4518	0.453	0.2561	0.2560			0.4353	0.4346		
0.4257		0.2515	0.2522			0.3970	0.3971		
0.4141	0.414	0.2458	0.2465			0.3894	0.3910		
0.3994	0.400	0.2426	0.2437			0.3758	0.3835		
0.3835	0.384		0.2343			0.3554	0.3549		
0.3754	0.376		0.2299			0.3478			
0.3637	0.362	0.2280	0.2275			0.3411	0.3418		
	0.356	0.2229	0.2228				0.3383		
0.3470	0.348	0.2159	0.2162			0.3321			
0.3392	0.339	0.2124	0.2123			0.3179	0.3165		

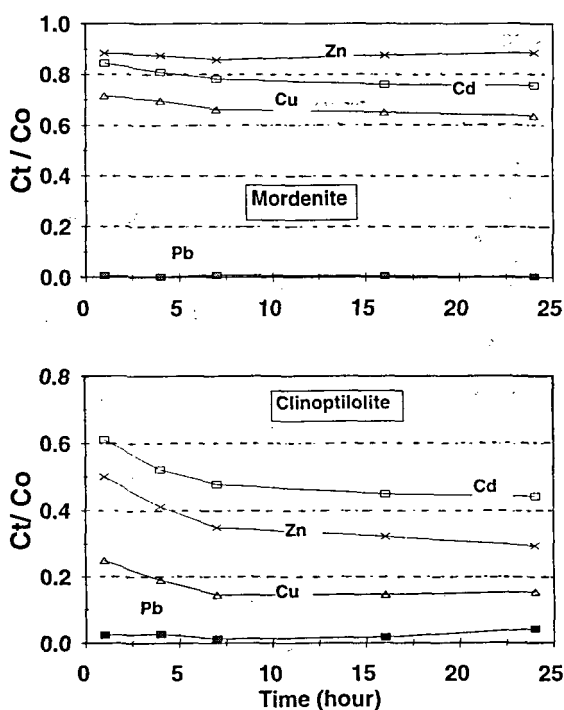


FIGURE 1

Pb, Cu, Zn, and Cd adsorption on zeolites with time (C_t = concentration after t-hour reaction, C_o = initial concentration).

concentration (10^{-3} M) was much higher than that of Pb (10^{-5} M) Ca did not appear to compete with Pb for adsorption on the zeolites, as indicated by the low C_t/C_o values in Fig. 1.

Fig. 2 shows that as the initial concentration of Pb and Cd increased, the amount of Pb and Cd adsorbed also increased. However, the percentages of Pb and Cd removed by the zeolites decreased (Fig.3). At the same initial concentration, clinoptilolite adsorbed more Cd, and therefore was more effective in removing Cd than mordenite. Both zeolites adsorbed much more Pb than Cd. For example, at the

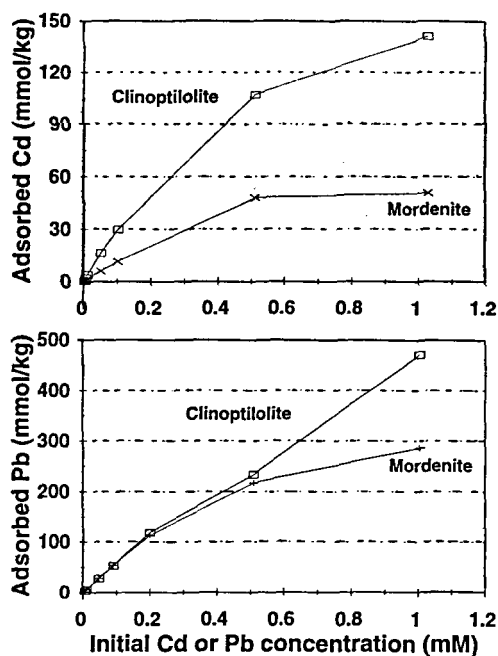


FIGURE 2
Adsorption capacities of zeolites for Cd and Pb.

highest initial concentration (1 mM) and a zeolite:solution ratio of 50mg to 30mL used, mordenite adsorbed 285 mmol/kg of Pb but only 51 mmol/kg of Cd; the corresponding values for clinoptilolite were 468 mmol/kg and 142 mmol/kg.

Lead and Cd are likely to exist as divalent cations (as explained in Discussion section). Table 2 gives the percentage of CEC occupied by Pb or Cd on the assumption that both cations are adsorbed as a divalent species by cation exchange. That is, the charge percentage of exchange is $2 \times 100 \times \text{adsorbed Pb or Cd (mmol/kg)} / \text{CEC (mmol(+) / kg)}$. For comparison, the charge percentages of initially added Pb or Cd /zeolite CEC are also shown. The charge percentages of adsorbed Pb/CEC increased with the initial concentration. At the highest initial concentration,

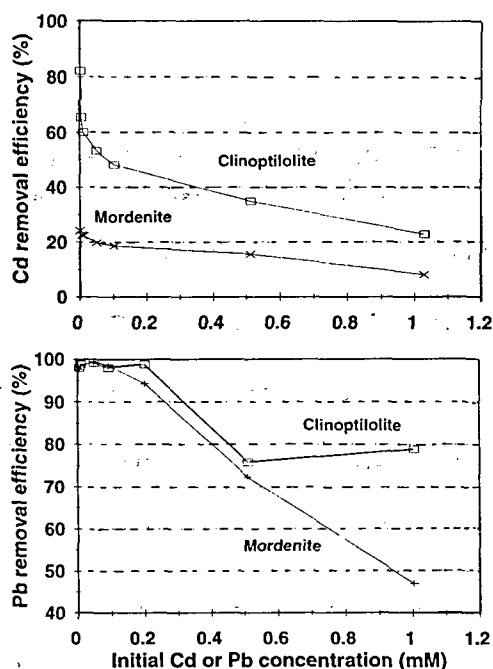


FIGURE 3
Removal efficiencies of zeolites for Cd and Pb.

one-third of mordenite CEC and half of clinoptilolite CEC still were used for Pb adsorption.

Fig. 4 shows the XPS spectra of mordenite before and after Pb and Cd adsorption, and Fig. 5 gives the spectra for clinoptilolite. The reduction of Na (KLL Auger) peak, and the appearance of the Pb(4f) or Cd(3d) peaks, after adsorption of Pb and Cd, are clearly visible, even in the wide-scan spectra. The binding energies of adsorbed Pb(4f_{7/2}) were 140.0 eV for mordenite and 139.9 eV for clinoptilolite, while those of adsorbed Cd(3d_{5/2}) were 406.3 eV and 406.0 eV, respectively.

Table 3 gives the element/Si atomic ratios for mordenite and clinoptilolite before and after adsorption of Pb or Cd. Since the Al/Si ratio did not change

TABLE 2
Charge Percentages of Zeolite CEC Exchanged by Pb or Cd (in the presence of 10^{-3} M of Ca as a Competing Cation)

Mineral	Initial Pb or Cd		Initially added		Adsorbed Pb or Cd	
	concentration (M)		Pb or Cd (% CEC)		(% CEC)	
	Pb	Cd	Pb	Cd	Pb	Cd
Mordenite	4.57×10^{-6}	1.04×10^{-6}	0.31	0.07	0.29	0.02
	9.75×10^{-6}	5.52×10^{-6}	0.65	0.37	0.64	0.08
	4.77×10^{-5}	1.11×10^{-5}	3.2	0.74	3.2	0.17
	9.14×10^{-5}	5.12×10^{-5}	6.1	3.4	6.0	0.67
	2.00×10^{-4}	1.03×10^{-4}	13	6.9	13	1.3
	5.10×10^{-4}	5.13×10^{-4}	34	35	24	5.4
	1.00×10^{-3}	1.03×10^{-3}	67	69	32	5.7
Clinoptilolite	4.57×10^{-6}	1.04×10^{-6}	0.29	0.07	0.28	0.05
	9.75×10^{-6}	5.52×10^{-6}	0.62	0.35	0.61	0.23
	4.77×10^{-5}	1.11×10^{-5}	3.1	0.71	3.0	0.42
	9.14×10^{-5}	5.12×10^{-5}	5.8	3.3	5.7	1.7
	2.00×10^{-4}	1.03×10^{-4}	13	6.6	13	3.2
	5.10×10^{-4}	5.13×10^{-4}	33	33	25	11
	1.00×10^{-3}	1.03×10^{-3}	64	66	50	15

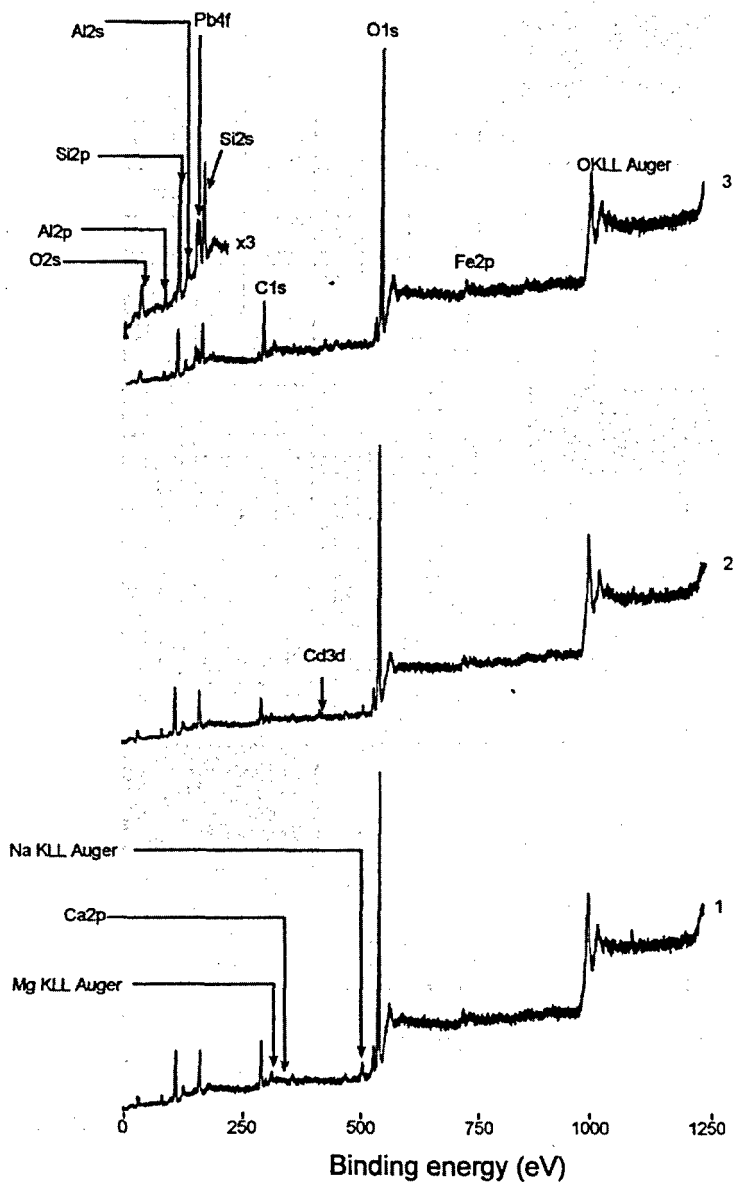


FIGURE 4

XPS wide-scan spectra of mordenite before and after Pb and Cd adsorption (1 = mordenite, 2 = after Cd adsorption, 3 = after Pb adsorption).

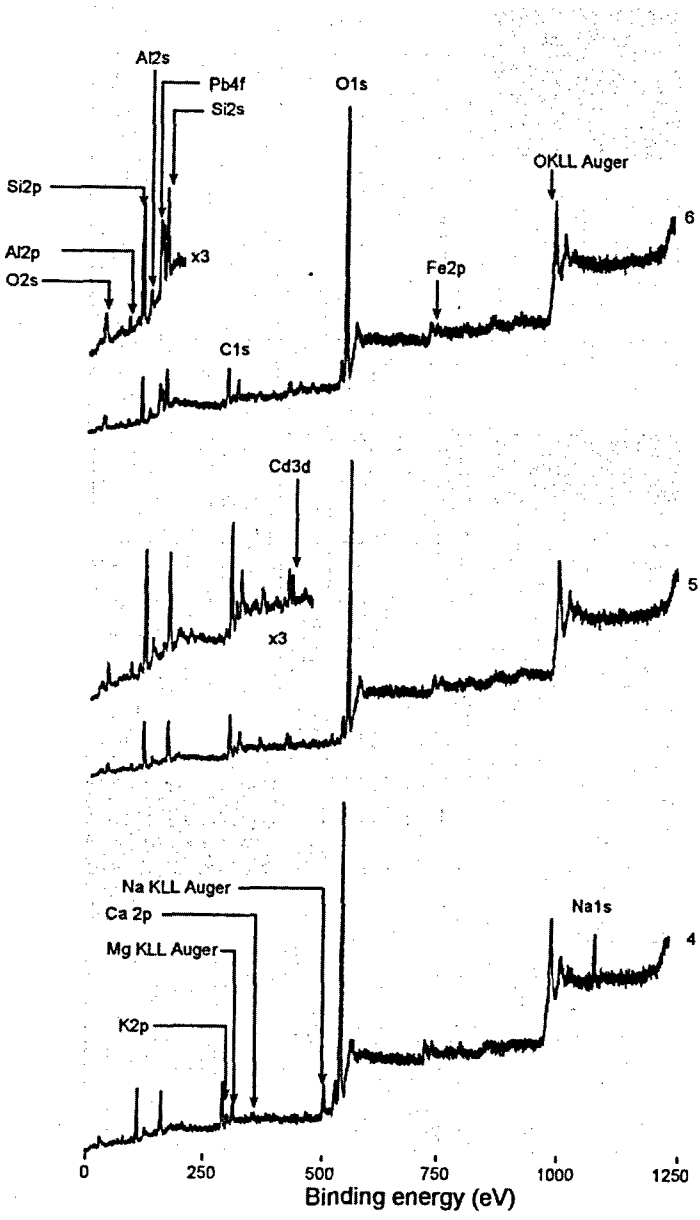


FIGURE 5
XPS wide-scan spectra of clinoptilolite before and after Pb and Cd adsorption (4 = clinoptilolite, 5 = after Cd adsorption, 6 = after Pb adsorption).

TABLE 3
Surface Composition (Atomic Ratios) of Zeolites Determined by XPS Before and After Pb or Cd Adsorption

Mineral / adsorbed ion	O/Si	Al/Si	Fe/Si	Pb/Si	Cd/Si	Ca/Si	Mg/Si	K/Si	Na/Si
Mordenite	3.80	0.30	0.03			0.02	0.04	0.03	0.08
Mordenite / Pb	4.08	0.31	0.04	0.037		0.02	0.03	0.02	0.01
Mordenite / Cd	3.98	0.31	0.04		0.012	0.03	0.02	0.03	0.04
Clinoptilolite	3.87	0.24	0.06			0.03	0.06	0.04	0.16
Clinoptilolite / Pb	3.98	0.25	0.07	0.055		0.02	0.06	0.04	0.01
Clinoptilolite / Cd	3.84	0.25	0.05		0.025	0.04	0.06	0.05	0.03

appreciably, the zeolite structure appeared to be stable during the adsorption process. On this basis, atomic ratios can be used to indicate the changes in composition of zeolite surfaces following adsorption. From the atomic ratios and atomic weights, elemental contents (weight %) on zeolite-particle surfaces can be calculated, assuming the contribution of H to elemental contents is negligible.

Fig.6 compares the concentration of adsorbed Pb and Cd in the bulk phase, calculated from the amount of Pb and Cd adsorbed, with that on the surface of zeolites particles, derived from XPS. To eliminate the potential dilution effect by carbon contaminants, the surface concentration of Pb and Cd was expressed on a C-free basis.

DISCUSSION

Although natural zeolites show different selectivity sequences for a range of metals, there is general agreement that clinoptilolite has a strong affinity for Pb (Blanchard et al., 1984; Malliou et al., 1994; Curkovic et al., 1997; Semmens and Martin, 1988; Semmens and Seyfarth, 1978; Zamzow et al., 1990). The reason why a zeolite may be selective for a particular cation can only be broadly defined (Dyer, 1995) because selectivity is influenced by many factors including framework topology (channel configuration and dimensions), ion size and shape, charge density in the channels and cages, ion valency, and electrolyte composition and concentration in the aqueous phase (Barrer, 1978; Ming and Mumpton, 1989).

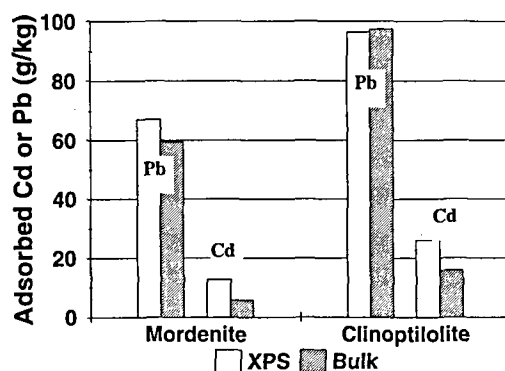


FIGURE 6

Comparison of surface (XPS) and bulk (average) concentrations of adsorbed Pb and Cd.

Caution should be exercised in comparing the adsorption capacities for Pb and Cd, obtained in this study, with the corresponding values in the literature. This is because the zeolites and the experimental conditions used are not identical. The data in Fig.2 refer to the adsorption of Pb and Cd in competition with Ca, and under the specified experimental conditions. Inclusion of competing cations in the solution of heavy metal salts simulates waste water more closely than would otherwise have been the case. However, under these conditions it is unrealistic to expect a large percentage of the zeolite exchange complex to be occupied by heavy metal ions despite the high zeolite:solution ratio used here. Even in the presence of Na, a cation with a low affinity for zeolites, there is competition with Pb and Cd for adsorption sites (Pansini, 1996). Our results (Fig. 2 and Table 2) indicate that both mordenite and clinoptilolite have a high preference for Pb and hence are potentially useful for recovering Pb ions from solution and waste waters. However, it would not be easy to reduce Cd concentration to $\mu\text{g/L}$ levels.

Removal efficiency has been used to indicate the effectiveness of zeolites to remove added heavy metals from solutions (Kesraoul-Oukl et al, 1993; Curkovic et al., 1997). Being dependent on the initial metal concentration and the zeolite:solution ratio, efficiency may decrease as the metal concentration increases and the zeolite:solution ratio decreases. The differential adsorption percentages between Pb and Cd, and between low and high initial concentrations (Table 2) merit attention. For Cd, only a small percentage of the CECs of the zeolites, particularly mordenite, is involved in adsorption. For Pb, at the lower range of the initial concentrations ($\leq 2 \times 10^{-4}$ M), added Pb is almost completely adsorbed by the zeolites. High Pb and Cd removal efficiencies (>90%) over a wide range of initial concentrations (up to hundreds of mg/L) were reported for clinoptilolite (Kesraoul-Oukl et al., 1993; Curkovic et al., 1997). Here we obtain much lower Cd removal efficiencies even at lower concentration ranges (Fig. 3). This would indicate that the presence of competing cations (in this case Ca ion) in the system affects Cd adsorption. Pb removal efficiency is high at low initial concentrations (Fig. 3), but decreases as the concentration increases. This suggests that at low Pb concentrations Ca does not effectively compete with Pb for adsorption on the zeolites, but does so at high concentrations, particularly in the case of mordenite. This observation has an important implication for the removal by zeolites of heavy metal cations from waste waters which commonly contain significant amounts of Ca, Na, and other cations. Our investigation indicates that the adsorption capacity and removal efficiency of zeolites for heavy metals in waste waters cannot be reasonably estimated unless the competing effect of Ca and other cations is taken into account.

Precipitation of Pb and Cd as hydroxides is negligible in this instance although the pH of the mordenite and clinoptilolite samples in Milli-Q water is 7.4 and 9.4 respectively. The addition of the zeolites, particularly clinoptilolite, to Pb or Cd solution raises the pH of the solution from an initial value of 5.0 to a final value of up to 5.3 (mordenite/Cd), 5.8 (mordenite/Pb), 5.9 (clinoptilolite/Cd), and 6.0 (clinoptilolite /Pb). Since these pH values are well below the hydrolysis products of Pb ion ($pK_1 = 7.8$) and Cd ion ($pK_1 = 10.2$) (Baes and Mesmer, 1976), Pb and Cd are likely to adsorb as divalent cations rather than as the corresponding hydroxides or carbonates.

The magnitude of the binding energy (BE) of adsorbed Pb and Cd provides additional evidence for this conclusion. The BE of the Pb($4f_{7/2}$) line for mordenite (140.0 eV) and clinoptilolite (139.9 eV) was much higher than that for Pb(OH)₂ (137.95), PbO (137.25), and PbCO₃ (138.3) (Wagner, 1990), but close to the BE of Pb ($4f_{7/2}$) in Pb (SO₄)₂ (139.4). The BE of adsorbed Cd ($3d_{5/2}$) on mordenite and clinoptilolite was 406.3 and 406.0 eV, respectively, higher than that of Cd ($3d_{5/2}$) in Cd (OH)₂ (405.1), CdCO₃ (405.1) (Wagner, 1990), and CdO (404.2) (Seyama and Soma, 1988), but similar to the value for CdF₂ (406.0) and exchangeable Cd in montmorillonite (406.4) (Seyama and Soma, 1988).

Adsorption of Pb and Cd as divalent cations at an initial concentration of 10^{-3} M would amount to 569 and 101 mmol(+)/kg in mordenite, and 936 and 283 mmol(+)/kg in clinoptilolite. If exchangeable Na ions are the first to be replaced by Pb or Cd, only a part of the exchangeable Na ions in mordenite (326 mmol/kg), and

in clinoptilolite (676 mmol/kg) would be replaced by Cd. In contrast, other exchangeable cations, besides Na, would be replaced by Pb.

The changes in (Ca, Mg, K, Na) / Si ratios (Table 3) clearly show that Na is the principal exchangeable cation involved in the adsorption of Pb and Cd with Ca as a competitive ion. This accords with previous macroscopic studies showing that Na is the most effective exchangeable ion for heavy metal removal (Blanchard et al., 1984; Zamzow and Murphy, 1992). Similarly, the high content in exchangeable Na of clinoptilolite (676 mmol/kg) relative to mordenite (326 mmol/kg) lies behind the greater capacity of clinoptilolite for adsorbing Cd and Pb as compared with mordenite.

The fact that less Cd than Pb is adsorbed at similar initial concentrations (Fig.2) suggests a smaller number of sites which are accessible to Cd than to Pb in both zeolites. The higher adsorption capacity of the zeolites for Pb than Cd could not be explained in terms of the charge characteristics of the metal ions in that both Pb ($pK_1 = 7.8$) and Cd ($pK_1 = 10.2$) are likely to exist as divalent ions at the solution pH (<6.0) used in this study. Neither could it be explained in terms of the ionic radii of Cd and Pb, and the free dimensions of channels in the zeolite structure. The hydrated radii of Cd is 0.426 nm, and of Pb is 0.401 nm (Nightingale, 1959), making their respective diameters larger than the channel dimensions in mordenite (0.29 x 0.57 and 0.7 x 0.67 nm) and in clinoptilolite (0.41 x 0.47, 0.40 x 0.55, and 0.44 x 0.72 nm) (Tsitsishvili et al., 1992). On this basis, fully hydrated Pb and Cd ions would be precluded from entering the zeolite channels. For adsorption to take place on channel surfaces inside zeolite particles, at least some of the waters of hydration

must be stripped from the solvated ions. Semmens and Seyfarth (1978) listed the free energies of hydration as -357.8 kcal/g ion for Pb, and -430.5 kcal/g ion for Cd. In order to satisfy its hydration requirement, Cd would prefer the aqueous phase whereas Pb would rather associate with the zeolite phase. Thus, all things being equal, more Pb than Cd will be adsorbed.

In line with this presupposition, the data in Fig. 6 indicate that adsorbed Cd accumulates on external zeolite surfaces, whereas adsorbed Pb tends to be evenly distributed within the zeolite particles. Because of the smaller hydration energy relative to Cd, Pb ions can more readily lose part of their water of hydration. The partially hydrated Pb ions are apparently small enough to enter the zeolite channels, giving rise to a relatively even distribution of adsorbed Pb.

CONCLUSIONS

This study shows that both mordenite and clinoptilolite have a high selectivity for Pb. At concentrations of relevance to environmental control the preferential adsorption of heavy metal ions decreases in the order $Pb > Cu > Cd > Zn$ for mordenite, and $Pb > Cu > Zn > Cd$ for clinoptilolite.

Up to one-third of the CEC in mordenite and half that in clinoptilolite could be used for Pb adsorption at initial Pb concentrations of 10^{-6} - 10^{-3} M, and in the presence of 10^{-3} M of Ca as a competing cation. The corresponding figures for Cd are much lower. The efficiency of mordenite and clinoptilolite in removing Pb and Cd from solution is lower than that reported in the literature. This might be because

Ca competes with Pb and Cd ions for adsorption sites on the zeolites. Although this competitive effect of Ca is well documented for soil systems (Alloway, 1995), it has been ignored in many studies on heavy metal adsorption by zeolites.

Among the exchangeable cations Na contributes most to the adsorption of Pb and Cd. Since clinoptilolite has more exchangeable Na than mordenite, the former mineral can adsorb more Pb and Cd ions than the latter.

XPS has proved to be a useful tool in probing the concentration and bonding state of adsorbed Pb and Cd on zeolite surfaces. Adsorbed Pb is more or less evenly distributed within zeolite particles, whereas adsorbed Cd accumulates on particle surfaces.

ACKNOWLEDGMENTS

G. Yuan thanks the Science and Technology Agency of Japan for a fellowship during which tenure this work was carried out. The assistance of emeritus professor H. Minato in obtaining the mordenite and clinoptilolite samples, and the suggestions and comments of Dr. H.J. Percival on the manuscript are gratefully acknowledged.

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Received: July 16, 1998