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## HEAVY METAL REMOVAL WITH MEXICAN CLINOPTILOLITE: MULTI-COMPONENT IONIC EXCHANGE

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**Abstract**—This paper describes the interactions of Pb(II), Cd(II), and Cr(VI) competing for ion-exchange sites in naturally occurring clinoptilolite. Dissolved Pb and Cd were effectively removed within 18 h in batch reactors, with higher removal efficiencies (>95%) in the acidic pH range. The presence of Cr(VI), which can interact with these metals to form anionic complexes, significantly diminished the Pb and Cd removal efficiencies. A decrease in the efficiency of clinoptilolite to remove Pb was also observed in the high ( $\geq 10$ ) pH range. This was attributed to the formation of anionic hydroxo-complexes with little affinity for cationic ion exchange sites. Pb outcompeted Cd for ion exchange sites in a flow-through column packed with clinoptilolite (contact time = 10 s). The preferential removal of Pb in column, but not in batch reactors, reflects that competitive retention can be affected by contact time because diffusion kinetics may influence the removal efficiency to a greater extent than equilibrium partitioning. Phenol, which was tested as a representative organic co-contaminant, slightly hindered heavy metal removal in batch reactors. This was attributed to the formation of organometallic complexes that cannot penetrate the zeolite exchange channels. Altogether, these results show that natural zeolites hold great potential to remove cationic heavy metal species from industrial wastewater. Nevertheless, process efficiency can be hindered by the presence of ligands that form complexes with reduced accessibility and/or affinity for ion exchange. © 2000 Elsevier Science Ltd. All rights reserved

*Key words*—cadmium, chromium, lead, phenol, pH, zeolite, clinoptilolite

### INTRODUCTION

Heavy metals such as lead, cadmium and chromium, are toxic priority pollutants that commonly interfere with the beneficial use of wastewater for irrigation and industrial applications. They are also common groundwater contaminants at industrial and military installations. Numerous processes exist for removing dissolved heavy metals, including ion exchange, precipitation, phytoextraction, ultrafiltration, reverse osmosis, and electro dialysis (Applegate, 1984; Geselbracht, 1996; Schnoor, 1997; Sengupta and Clifford, 1986). Nevertheless, many of these approaches can be marginally cost-effective or difficult to implement in developing countries. Therefore, the need exists for a treatment strategy that is simple, robust, and that addresses local resources and constraints. In this regard, naturally occurring zeolites hold great

potential for use as packing material in subsurface reactive barriers intercepting ground water plumes, and for fixed bed reactors designed to remove heavy metals from industrial wastewater (Bowman *et al.*, 1995; Steimle, 1995).

Zeolites are hydrated aluminosilicate minerals with a cage-like structure that offers large internal and external surface areas for ion exchange (i.e., in the range of several hundred square meters per gram) (Ming and Mumpton, 1989). They possess a net negative structural charge due to isomorphous substitution of cations in the mineral lattice. Hence they have a strong affinity for transition metal cations, but only little affinity for anions and non-polar organic molecules (Bowman *et al.*, 1995).

Clinoptilolite is the most abundant natural zeolite, and has the chemical formula  $\text{Na}_{0.1}\text{K}_{8.57}\text{Ba}_{0.04}(\text{Al}_{9.31}\text{Si}_{26.83}\text{O}_{72}) \cdot 19.56\text{H}_2\text{O}$  (Galli *et al.*, 1983). Its characteristic tabular morphology shows an open reticular structure of easy access, formed by open channels of 8–10 membered rings (Mondale *et al.*, 1995). Exchangeable ions such as Na(I), K(I), Ca(II)

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and Mg(II) commonly occupy these channels (Ackley and Yang, 1991). Clinoptilolite has been shown to selectively remove cesium and strontium ions from radioactive wastewater (Lukac and Foldesova, 1994), and its use for removing other dissolved heavy metal cations is receiving increasing attention.

Considerable research has been conducted to characterize the chemical, surface, and ion exchange properties of clinoptilolite (e.g., Ackley and Yang, 1991; Carland and Aplan, 1995; Mondale *et al.*, 1995; Semmens and Martin, 1988; Zamzow and Murphy, 1992). Nevertheless, our incomplete understanding of multicomponent ion exchange processes preclude us from taking full advantage of clinoptilolite properties for tertiary treatment. A better understanding of how water chemistry affects heavy metal removal kinetics and equilibrium partitioning is needed to optimize the design of clinoptilolite-based ion exchange reactors.

This paper addresses the interactions of lead, cadmium, and chromium competing for ion exchange sites in natural clinoptilolite. The presence of phenol as organic co-contaminant and the effect of pH on the performance of multi-component ionic exchange were also investigated.

## METHODOLOGY

### *Zeolite source and conditioning*

Etla zeolite samples were collected from a Mexican tuff in a deposit near Oaxaca city in Southeast Mexico (17°14' N, 97°13' W), the biggest and most well known of its kind in this country (Mumpton, 1973). This mineral has been commercially available for construction ornament purposes only. X-ray diffraction analysis showed that this material was 70% clinoptilolite, and the remainder consisted of mordenite, muscovite and quartz (Vaca-Mier *et al.*, 1997). For batch studies, the zeolite was crushed to mesh +40, -80, (0.8294 g zeolite/mL). A +30, -40 mesh was used for packing the fixed bed reactors to obtain a particle/column diameter ratio of 25 and avoid hydrodynamic wall effects (Smith and Weber, 1988). The zeolite was converted to homoionic sodium form (to increase its cation exchange capacity) using the procedure described by Carland and Aplan (1995). Approximately 30 g of washed zeolite and 200 mL of NaCl 1 M solution were heated to 120°C at 2 atm for 2 h. After a cool-down period, the samples were filtered and washed three times with distilled water. This procedure was repeated twice.

### *Batch experiments*

Completely mixed batch reactors were used to study heavy metal removal by a natural (homoionic) zeolite. Cd, Cr, Pb, and phenol were tested alone or in pairs to study their competition for ion exchange sites. For each combination, the initial pH was adjusted with nitric acid 0.1 N or with sodium hydroxide 0.1 N to six different initial values (i.e., pH 4, 6, 7, 8, 10 and 12).

Hermetic flasks (50 mL) were filled in triplicate with 1.5 g of homoionic zeolite and a heavy metal solution containing lead nitrate, cadmium nitrate, and/or potassium dichromate. The concentration of each metal was 30 meq/L for single-metal solutions, and 15 meq/L for binary solutions. These concentrations were selected to preclude exceeding the 2 meq/g maximum cationic exchange capacity (CEC) of

the zeolite. The CEC was determined quantifying all the exchangeable ions present in the leachate after the homoionizing procedure. The eluant volume was measured and analyzed for its calcium, potassium, magnesium, and iron ion content. These ions were measured at 1.43 mg Ca<sup>2+</sup>, 0.66 mg K<sup>+</sup>, less than 0.01 mg Fe<sup>2+</sup> and less than 0.01 mg<sup>2+</sup>/g of zeolite. Phenol was added at 30 mg/L to appropriate reactors. Heavy-metal solutions were prepared with deionized water and element standards (Titrisol™ Merck standards for heavy metals and Phenol F. Titrisol™ Merck for phenol). All reactors were agitated for 18 h at 30 rpm to exceed the minimum Biot number (>100) recommended to eliminate mass transfer effects caused by the liquid and obtain data that reflects intraparticle mass transfer resistance (Hand *et al.*, 1984). Final metal concentrations were measured in the equilibrium solution after separating the zeolite through Whatman paper filtration.

### *Fixed-bed reactors experiments*

Fixed-bed reactors (FBRs) were used to investigate the effect of contaminant mixture on the breakthrough characteristics of Cd, Cr and Pb. The reactors consisted of glass columns (1.0 cm internal diameter, 12 cm bed depth) packed with (+30, -40 mesh) sodium homoionic zeolite (Weber and Smith, 1987). The hydraulic load was 0.5 m<sup>3</sup>/m<sup>2</sup>-min and the bed porosity was 40%. The empty bed contact time was 10 s (effective contact time = 4 s). Influent total heavy metal (30 meq/L) concentrations were the same as those used for batch studies. The influent pH was adjusted with nitric acid to 4.5, and there was no change in pH as the solution passed through the column. A Gilson F-3 peristaltic pump was used to feed the influent solution in an upflow mode. Three replicate columns were prepared for each initial condition.

### *Analytical procedures*

Total heavy metal concentrations were measured with a Varian Spectra 100 and atomic absorption spectrophotometer. Phenol was analyzed with a Varian 3500 gas chromatograph equipped with a DB-1 capillary column (30 m length, 0.53 mm I.D.) and a FID detector. The limits of detection were 0.09 mg/L (0.0009 meq/L) for Pb, 0.03 mg/L (0.0009 meq/L) for Cd, 0.06 mg/L (0.003 meq/L) for Cr, and 0.01 mg/L for phenol.

## RESULTS

### *Batch experiments*

Figure 1 summarizes the results for single-metal removal assays. Lead was completely removed from solution within 18 h at circum-neutral or acidic pH, but its removal efficiency decreased in the basic pH range (e.g., 77% for pH 12). Cadmium exhibited a similar behavior. More than 90% of the added Cd was removed across the pH scale from 4 to 10, but only 50% was removed at pH 12. The clinoptilolite zeolite did not exhibit a high affinity for chromium or phenol. The maximum average removal efficiency was 12% for Cr at pH 7, and 35% for phenol, at pH 8. No changes in pH were observed during these experiments.

Considering the Pb-Cd binary solutions, clinoptilolite exhibited a slightly higher affinity for lead in acid and circum-neutral media, although this difference was not statistically significant (Fig. 2). Increas-

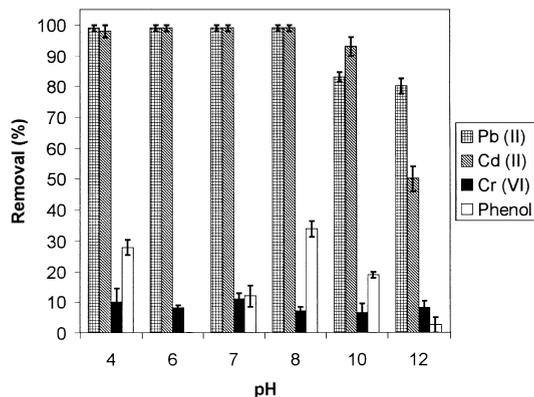


Fig. 1. Effect of pH on total metal and phenol removal by homoionic zeolite. Compounds were fed separately and agitated for 18 h at 30 rpm and 25°C. Error bars represent  $\pm 1$  standard deviation from the mean of triplicate reactors.

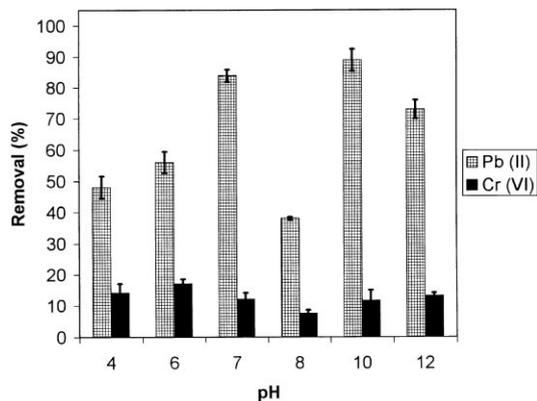


Fig. 3. Effect of pH on total Pb(II) and Cr(VI) removal from binary solution by homoionic zeolite. Compounds were fed separately and agitated for 18 h at 30 rpm and 25°C. Error bars represent  $\pm 1$  standard deviation from the mean of triplicate reactors.

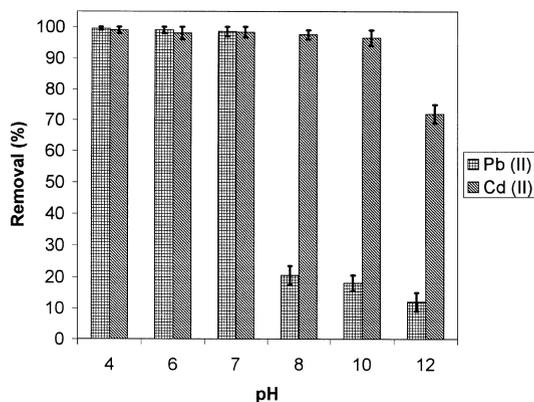


Fig. 2. Effect of pH on total Cd(II) and Pb(II) removal from binary solution by homoionic zeolite. Compounds were fed separately and agitated for 18 h at 30 rpm and 25°C. Error bars represent  $\pm 1$  standard deviation from the mean of triplicate reactors.

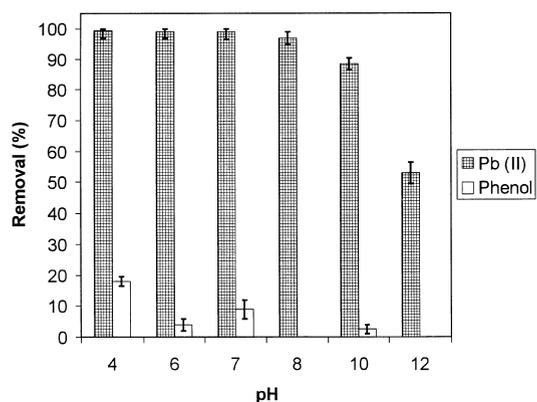


Fig. 4. Effect of pH on total Pb(II) and phenol removal from binary solution by homoionic zeolite. Compounds were fed separately and agitated for 18 h at 30 rpm and 25°C. Error bars represent  $\pm 1$  standard deviation from the mean of triplicate reactors.

ing the pH to the basic range significantly decreased the removal efficiency for Pb and reversed the relative affinity of clinoptilolite for these metals. For example, at pH 12, the average removal efficiency was 69% for Cd and less than 25% for Pb.

For Pb–Cr binary solutions, Pb removal was irregular and did not exhibit a clear pattern as a function of pH (Fig. 3). Interestingly, the presence of Cr(VI) decreased the Pb removal efficiency in the acidic pH range to as low as 50% for pH 4. Similar to single-metal solutions, the zeolite did not remove more than 20% of the added Cr(VI) at any pH.

Relatively high Pb removal efficiencies were also observed in binary solutions with phenol (Fig. 4). More than 97% of the added Pb was removed at pH values between 4 and 8. However, the average removal efficiency decreased in the basic pH range, down to 55% for pH 12. Phenol removal efficiency was low ( $\sim 18\%$ ) and negligible removal was observed at pH 8, and 12.

Cadmium was removed at nearly 100% efficiency from binary solutions containing chromium, except

at the highest tested pH value (pH 12) where the average removal efficiency decreased to 68% (Fig. 5). In contrast, only small amounts of Cr(VI) were removed ( $< 10\%$ ) regardless of pH.

Cadmium was effectively removed from binary solutions with phenol ( $>95\%$ ), except at pH 12 where the average removal efficiency decreased to 72% (Fig. 6). Similar to other assays, phenol was poorly removed. Its removal efficiency was consistently below 20%.

In summary, Pb and Cd removal was generally very high in all combinations tested, especially in the acidic pH range. On the other hand, the zeolite exhibited a low affinity for Cr and phenol, which were never removed at greater than 35% efficiency.

#### Multicomponent ion exchange in the fix-bed reactors

Lead outcompeted cadmium for ion exchange sites in the FBRs. This is reflected by the retarded breakthrough of lead relative to cadmium (Fig. 7).

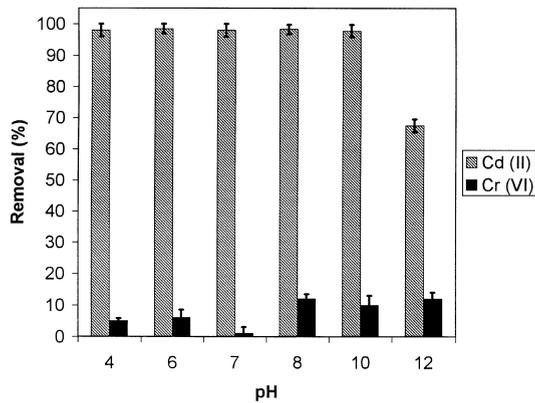


Fig. 5. Effect of pH on total Cd(II) and Cr(VI) removal from binary solution by homoionic zeolite. Compounds were fed separately and agitated for 18 h at 30 rpm and 25°C. Error bars represent  $\pm 1$  standard deviation from the mean of triplicate reactors.

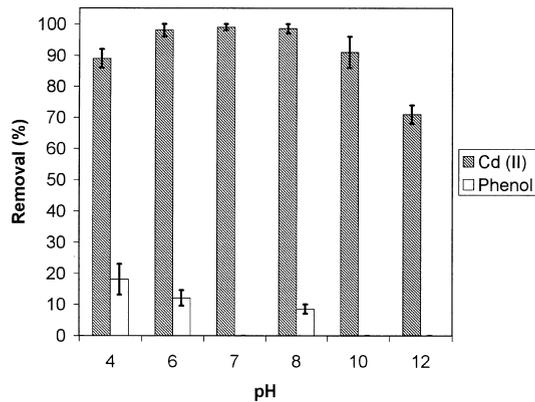


Fig. 6. Effect of pH on total Cd(II) and phenol removal from binary solution by homoionic zeolite. Compounds were fed separately and agitated for 18 h at 30 rpm and 25°C. Error bars represent  $\pm 1$  standard deviation from the mean of triplicate reactors.

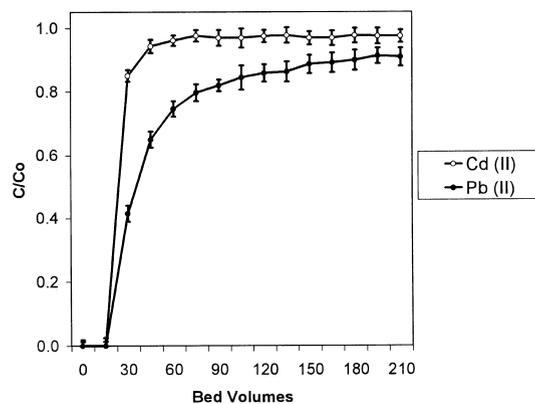


Fig. 7. Total Pb(II) and Cd(II) breakthrough from an FBR fed with binary solution. The influent concentration was 15 meq/L for each metal, the influent pH was 4.5, and empty bed contact time was 10 s. Error bars represent  $\pm 1$  standard deviation from the mean of triplicate reactors.

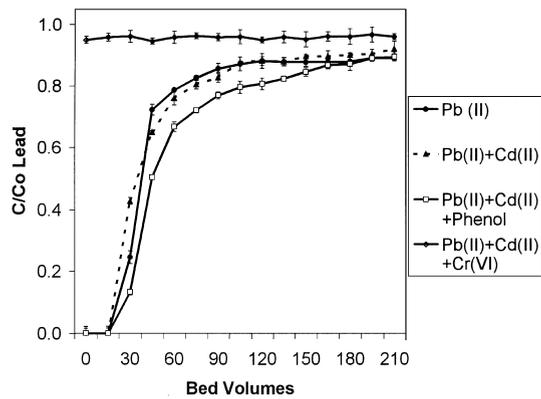


Fig. 8. Total Pb(II) breakthrough from an FBR fed with binary solution. The influent lead concentration was 30 meq/L when fed alone, 15 meq/L for the tertiary metal solution. The empty bed contact time was 10 s, and the influent pH was 4.5. Error bars represent  $\pm 1$  standard deviation from the mean of triplicate reactors.

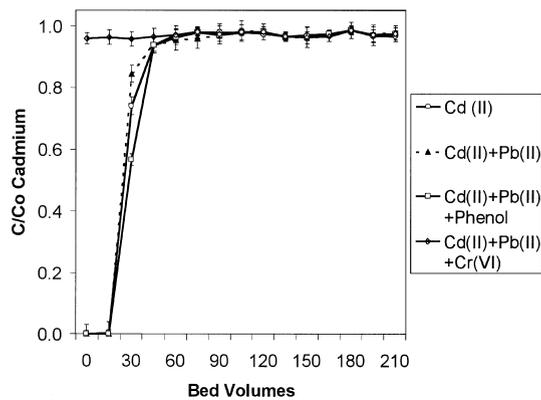


Fig. 9. Total Cd(II) breakthrough from an FBR fed with binary solution. The influent lead concentration was 30 meq/L when fed alone, 15 meq/L for the tertiary metal solution. The empty bed contact time was 10 s, and the influent pH was 4.5. Error bars represent  $\pm 1$  standard deviation from the mean of triplicate reactors.

When Pb was first detected in the effluent, the effluent Cd concentration was already 85% of its influent value.

Figure 8 depicts the effect of other co-contaminants on Pb breakthrough from clinoptilolite-packed FBRs. The Pb breakthrough curves are nearly identical for the solution containing Pb alone as for the binary solution containing Pb and Cd. Thus, the presence of Cd alone had no discernable effect on Pb removal. However, the presence of Cd and Cr adversely affected Pb removal. In this case, the total amount of Pb removed decreased from 17.8 meq (1845 mg) when fed alone to 2.3 meq (238 mg) when fed with Cd and Cr. A similar adverse effect was observed for Cd in tertiary metal solutions (Fig. 9). While 9.5 meq (984 mg) were removed when Cd was fed alone, only 1.8 meq (187 mg) were removed when fed with Pb and Cr. Whether the decrease in removal efficiency was due to occlusion of ion exchange sites by other species or to the formation of anionic

Table 1. Speciation of different metals in water<sup>a,b</sup>

pH	Dominant species (>90%) (Second dominant species (<10%))			
	Cd	Pb	Cr(III) [25°C]	Cr(VI)
<6	Cd <sup>2+</sup> [CdHCO <sub>3</sub> <sup>+</sup> ]	Pb <sup>2+</sup> [PbHCO <sub>3</sub> <sup>+</sup> ]	Cr <sup>3+</sup> [Cr <sub>3</sub> (OH) <sub>4</sub> <sup>5+</sup> ]	HCrO <sub>4</sub> <sup>-</sup> Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup>
7	Cd <sup>2+</sup> [CdHCO <sub>3</sub> <sup>+</sup> ]	Pb <sup>2+</sup> [PbCO <sub>3</sub> ]	Cr(OH) <sub>2</sub> <sup>+</sup> Cr <sub>3</sub> (OH) <sub>4</sub> <sup>5+</sup>	CrO <sub>4</sub> <sup>2-</sup>
8	Cd <sup>2+</sup> [CdOH <sup>+</sup> ]	PbCO <sub>3</sub> [PbOH <sup>+</sup> ]	Cr(OH) <sub>2</sub> <sup>+</sup> [Cr <sub>3</sub> (OH) <sub>4</sub> <sup>5+</sup> ]	CrO <sub>4</sub> <sup>2-</sup>
10	Cd(OH) <sub>2</sub> [CdOH <sup>+</sup> ]	Pb(OH) <sub>2</sub> [PbOH <sup>+</sup> ]	Cr(OH) <sub>4</sub> <sup>-</sup> [Cr(OH) <sub>5</sub> <sup>0</sup> ]	CrO <sub>4</sub> <sup>2-</sup>
12	Cd(OH) <sub>2</sub>	[Pb(OH) <sub>6</sub> ] <sup>4-</sup>	Cr(OH) <sub>4</sub> <sup>-</sup> [Cr(OH) <sub>5</sub> <sup>0</sup> ]	CrO <sub>4</sub> <sup>2-</sup>

<sup>a</sup>Sources: Baes and Mesmer, 1976; Cotton and Wilkinson, 1974; Long and Angino, 1977.

<sup>b</sup>For Cr(VI) and pH < 6, HCrO<sub>4</sub><sup>-</sup> prevails at concentrations < 10 mm total Cr, and Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> prevails at concentrations > 10 mm total Cr. H<sub>2</sub>CrO<sub>4</sub><sup>0</sup> prevails at pH < 0.9.

complexes between Cr(VI) and Pb or Cd was not determined.

## DISCUSSION

The pH of the solution had a pronounced effect on the removal efficiency of the tested compounds. This is primarily due to the effect that pH has on metal speciation. Removal by ion exchange with natural zeolites is more effective when the metal species are cationic. Thus, lead is best removed at pH  $\cong$  8, when the prevailing species are Pb<sup>2+</sup> and Pb(HCO<sub>3</sub>)<sup>+</sup> (Table 1). As the pH increases above 10 units, anionic hydroxo complexes with little affinity for zeolite surfaces can form and reduce the removal efficiency. Similarly, Cd is best removed at pH < 10, when cationic species such as Cd<sup>2+</sup>, Cd(HCO<sub>3</sub>)<sup>+</sup>, and Cd(OH)<sup>+</sup> prevail. Hexavalent chromium, on the other hand, is predominantly present as anionic species because it has a tendency to establish double ring metal-oxygen generating a pi-link between the oxygen and the metal (Huheey, 1981). This favors the formation of [Cr<sub>2</sub>O<sub>7</sub>]<sup>2-</sup> and [CrO<sub>4</sub>]<sup>2-</sup> that have little affinity for negatively charged ion exchange sites in clinoptilolite. Therefore, Cr(VI) was not effectively removed. In contrast, clinoptilolite can effectively remove dissolved Cr(III), which prevails as cationic species such as Cr<sup>3+</sup> and Cr(OH)<sub>2</sub><sup>+</sup> (Table 1) (Vaca-Mier *et al.*, 1997). This suggests that Cr(VI) could be effectively removed by zeolites if it is previously reduced to its trivalent form.

The pH of the solution can also affect the removal efficiency by affecting the integrity of the zeolite. For example, clinoptilolite is known to partially degrade and lose its ion exchange capacity in alkaline media. In fact, X-ray diffraction analysis showed that clinoptilolite crystals are destroyed at pH > 10 (Vaca-Mier, 1999).

Clinoptilolite has been reported to have more affinity for lead among the studied metals (Semmens and Martin, 1988). While this is generally true, this work shows that this preference can change at higher pH values, as observed for the binary Pb-Cd solution (Fig. 2). In this case, the decrease in Pb uptake at pH > 10 may be explained by the formation of anionic hydroxocomplexes which have little affinity for

cationic ion exchange sites in clinoptilolite (e.g., [Pb(OH)<sub>6</sub>]<sup>2-</sup>) (Table 1). Cd, on the other hand, is less prone to form such anionic hydroxocomplexes (Morel and Hering, 1993) and was removed more effectively than Pb at high pH values.

A comparison of Figs 1 and 3 shows that Cr generally inhibited Pb removal, although the reason for this phenomenon is unclear. In the basic pH range, Cr(VI) is found as divalent chromate anion, [CrO<sub>4</sub>]<sup>2-</sup>, which has electrostatic affinity for cationic Pb species. An insoluble lead chromate (PbCrO<sub>4</sub>) can precipitate at pH between 8 and 12 (Long and Angino, 1977), which would initially enhance Pb removal. Nevertheless, this precipitate could block some ion exchange channels and eventually offset the overall Pb removal efficiency. Similarly, dichromate [Cr<sub>2</sub>O<sub>7</sub>]<sup>2-</sup> forms in the acidic pH range (i.e., 2HCrO<sub>4</sub><sup>-</sup>  $\leftrightarrow$  [Cr<sub>2</sub>O<sub>7</sub>]<sup>2-</sup> + H<sub>2</sub>O). This anion also can combine with cationic Pb species to form an insoluble lead chromate (PbCr<sub>2</sub>O<sub>7</sub>). It is therefore hypothesized that at pH < 7, dichromate formation occurred, which also decreased the lead removal efficiency by precipitating and occluding ion exchange channels.

Phenol has been reported to form organometallic complexes with cationic metals (e.g., 2C<sub>6</sub>H<sub>6</sub>O + Cd  $\leftrightarrow$  (C<sub>6</sub>H<sub>6</sub>O)<sub>2</sub>Cd) (Cotton and Wilkinson, 1974). These complexes are generally too large to penetrate ion exchange channels in zeolite (Breck, 1974; Coppens, 1997). Thus, the slight decrease in Pb and Cd removal efficiency in batch reactors amended with 30 mg/L phenol (Fig. 1 vs. Figs 4 and 6) was probably due to the formation and molecular sieving of organometallic complexes. Although such complexes were not analyzed in this work, these results show that organic matter can affect heavy metal removal by zeolites and underscore the need for a better understanding of the role of organic ligands on metal speciation and fate.

Regarding the fate of free phenol, it should be pointed out that phenol has an anionic character at high pH values (pK<sub>a</sub> = 10) and should not be removed by cationic exchange. Nevertheless, some of the impurities of the natural zeolite (mordenite and clays) and cations such as Ca(II) and Mg(II) persist after the homionization procedure (Semmens and Martin, 1988). This may allow for some sorption of phenol.

The affinity of clinoptilolite for different heavy metals in a flow-through treatment system is not necessarily reflected in equilibrium partitioning (batch) experiments. One needs to consider also potential mass transfer limitations. When the contact time is relatively short, some metal species that diffuse faster from the bulk liquid to an ion exchange site may be removed to a greater extent than metals with more favorable equilibrium partitioning if the latter diffuse slower. It is important to point out that these batch reactor studies used a relatively large equilibration period (18 h) compared to the contact time in FBRs (10 s). Such differences in contact time cause a discrepancy in relative removal efficiencies. For example, the competition for exchange sites between Cd and Pb in binary solution fed to the FBR was favorable to Pb (Fig. 7). Yet, no preferential removal of Pb was observed in batch reactors fed a similar binary solution (Fig. 2).

### CONCLUSIONS

- The removal of Pb and Cd with clinoptilolite natural zeolite holds great potential for simple and binary solutions. However, when other substances that form anionic complexes are present (e.g., Cr(VI)), the efficiency of the process could be significantly diminished.
- Although not quantified in this work, the precipitation of metallic species, and the formation of anionic hydroxocomplexes are important potential reactions in the basic pH range. These reactions could decrease the efficiency of ionic exchange in the separation of metals with zeolite.
- The presence of organic compounds (e.g., phenol) could hinder metal removal efficiencies. Based on the literature, it was hypothesized that this effect can be due to the formation of organometallic complexes that cannot penetrate the zeolite exchange channels.
- Batch ion exchange studies with clinoptilolite may appropriately reflect equilibrium partitioning relationships. However, the design of full-scale systems must consider shorter contact times and mass transfer limitations. Therefore, FBRs that simulate the hydrodynamic characteristics of full-scale systems are recommended to conduct treatability studies.

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