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Removal of Heavy Metals from Aqueous Solution Using Novel Nanoengineered Sorbents: Self-Assembled Carbamoylphosphonic Acids on Mesoporous Silica

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ABSTRACT

Self-assembled monolayers of carbamoylphosphonic acids (acetamide phosphonic acid and propionamide phosphonic acid) on mesoporous silica supports were studied as potential absorbents for heavy and transition metal ions in aqueous wastes. The adsorption capacity, selectivity, and kinetics of the materials in sequestering metal ions, including Cd^{2+}, Co^{2+}, Cu^{2+}, Cr^{3+}, Pb^{2+}, Ni^{2+}, Zn^{2+}, and Mn^{2+}, were measured in batch experiments with excess sodium ion. The solution pH ranged from 2.2 to 5.5. The kinetics study shows that the adsorption reached equilibrium in seconds, indicating that there is little resistance to

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mass transfer, intraparticle diffusion, and surface chemical reaction. The competitive adsorption study found the phosphonic acid-SAMMS to have an affinity for divalent metal ions in decreasing order of $Pb^{2+} > Cu^{2+} > Mn^{2+} > Cd^{2+} > Zn^{2+} > Co^{2+} > Ni^{2+}$. The measured Cd^{2+} adsorption isotherm was of the Langmuirian type and had a saturation binding capacity of 0.32 mmol/g.

Key Words: Self-assembled monolayers on mesoporous silica; MCM-41; Carbamoylphosphonic acid; Kinetics; Equilibrium; Adsorption.

INTRODUCTION

Separation of hazardous heavy and transition metal ions (e.g., Cd^{2+}, Co^{2+}, Cu^{2+}, Cr^{3+}, Pb^{2+}, Ni^{2+}, Zn^{2+}, and Mn^{2+}) from aqueous solutions represents a significant portion of industrial waste treatment applications, including hydrometallurgical processing, electroplating operations, electrochemical metal refining, and production of textiles, paint, and dyes.[1] Typically, researchers have based the development of effective sorbent materials on the properties of functional ligands (e.g., acid–base characteristics, molecular structure, and polarizability) and matrix geometry of the solid support material. Immobilizing ion-chelating agents on silica surfaces for selective removal of heavy and transition metal ions has gained more research interest in the last few decades; important work in this field was summarized nicely by Tavlarides and Lee.[1] To be useful, sorbent materials require high loading capacity, high selectivity for the target metal ions, rapid adsorption kinetics, a method for easy regeneration, and little or no generation of secondary wastes.

Self-assembled monolayers on mesoporous supports (SAMMS) is a new class of sorbent materials that meet all those requirements.[2–11] The SAMMS material combines the unique characteristics of mesoporous silica materials and self-assembled organic monolayers. The mesoporous silica supports provide an exceptionally high surface area (approximately 1000 m^2/g), compared to the 300 m^2/g, typical of powder-type silica (Aldrich Co, St. Louis, MO, USA). The silica supports of SAMMS have rigid, open-parallel pore structures that can be specifically adjusted from 2 nm to 50 nm in diameter. The high surface area provides a high binding capacity and the rigid, open-pore structure allows solutes easy access to the pore surfaces, leading to fast binding kinetics. A relatively uniform pore size distribution with moderate-size pore diameters is important in reducing the diffusion resistance in solid sorbent materials. Pores that are too small (i.e., < 2 nm) will cause lower utilization of the binding sites due to defects in the monolayer coverage.[12]

Molecular self-assembly is a unique process in which functional organic molecules aggregate on the surface throughout the mesoporous ceramic material. Bifunctional molecules can be chemically modified to contain hydrophilic head groups that form molecular bonds with the target contaminants and hydrophobic tail groups that form covalent bonds with the substrate as a closely packed monolayer. A wide range of applications is possible, depending on the selection of the functional groups. For example, a thiol group has been used for selective removal of mercury from aqueous liquid wastes,[3,4,13] a copper (II)-ferrocyanide group was used for the selective removal of cesium from acidic sodium- and potassium-bearing nuclear wastes,[5] and carbamoylphosphine oxide (CMPO) analog ligands were used for selective removal of lanthanides and actinides from nuclear wastes.[6,7] In short, functional groups can be tailored to have high affinity and selectivity for lanthanides, actinides, heavy metal ions, and oxometallate anions (e.g., chromate, arsenate, and pertechnetate).[2–14]

Phosphonic acid resins have been reported to successfully remove hard Lewis acid metal ions, such as Fe^{3+}, lanthanide, and actinide ions from aqueous solution.[5–7,15,16] Because phosphonic acid resins have better selectivity for heavy and transition metal ions in the presence of excess sodium, calcium, magnesium, and potassium than conventional cation exchanger resins (i.e., sulfonic acid resins), many studies have focused on using phosphonic acid resins as heavy and transition metal ion adsorbents.[17–23] Polymers were used as the support materials in these studies, and hence the adsorption of metal ions had slow binding kinetics as a result of the solvent swelling of the polymer supports.[24] Only a few studies[20,21] have focused on using silica supports with phosphonic acid ligands, however, their silica materials had low surface areas, and a correspondingly reduced number of binding sites. The pH range and number of metal ions studied to date, with phosphonic acid on both polymer and silica supports, are limited. For example, sorption of Mo^{6+} with phosphonic acid resins was reported for a pH range of 1 to 3,[19] sorption of a Ca^{2+} and Co^{2+} solution was examined at pH 9.5,[17] sorption of a multicomponent metal ion solution was tested at pH less than 3,[23] and sorption of a solution containing Pb^{2+}, Na^{+}, K^{+}, Ca^{2+}, and Mg^{2+} was evaluated at pH 5.[22]

Self-assembled carbamoylphosphonic acid on mesoporous silica support takes phosphonic acid resins to another level. In the CMPO ligand, carbonyl amide and a P═O double bond are arranged in a suitable fashion for chelation of actinide cations.[6] Gafted onto mesoporous silica supports, carbamoylphosphate ligand, a CMPO analog, was highly effective and fast at sequestering ‘‘hard Lewis acids,’’ like lanthanides and actinides.[6,7]

Hydrolysis of a carbamoylphosphate ligand yields a phosphonic acid ligand, which can bind heavy and transition metal ions.

The purpose of this study was to determine the viability of using acid forms of CMPO analog ligands on mesoporous silica material to sequester heavy and transition metal ions at a rapid adsorption rate. Specifically, acetamide phosphonic acid (APH) SAMMS and propionamide phosphonic acid (PPH) SAMMS were tested to determine the binding kinetics, selectivity, and loading capacity for selected metal ions (e.g., Cd^{2+}, Co^{2+}, Cr^{3+}, Cu^{2+}, Mn^{2+}, Pb^{2+}, Zn^{2+}, Ni^{2+}).

EXPERIMENTAL

SAMMS Preparation and Characterization

The mesoporous silica material (MCM-41) was synthesized according to Kresge et al.[25] The mesoporous silica MCM-41 had a surface area of 989 m^2/g and a nominal pore size of 5.0 nm, as determined by nitrogen adsorption and transmission electron microscopy (TEM). Once synthesized, the mesoporous silica was functionalized with acetamide phosphonate silane and propionamide phosphonate silane as previously described.[6,7] The final products are called AP-SAMMS and PP-SAMMS, respectively. The ester forms AP-SAMMS and PP-SAMMS were cleaved to the acid forms APH-SAMMS and PPH-SAMMS, respectively, using trimethylsilyl iodide (TMSI), followed by addition of excess water.[26,27] Solid-state[29] Si NMR studies found that AP-SAMMS and PP-SAMMS contained about 2.2 to 2.4 phosphonate silanes per nm^2 or about 2.0 mmol phosponate silanes per g of the material. The high silane population density indicates that the surface functionalization is a self-assembly process rather than a simple surface functionalization method, which typically result in coverage of 0.5 silanes/nm^2.

The acid conversion was 100% and the weight of the final material did not change much after the conversion, thus the APH-SAMMS and PPH-SAMMS contained about 2 mmol of phosphonic acid groups per g of the material, respectively. Figure 1 shows the schematic structures of the two different SAMMS: (a) APH-SAMMS and (b) PPH-SAMM.

pH Dependency of Sorption

The pH isotherms of metal ions on APH-, and PPH-SAMMS were measured in batch experiments. The experimental conditions are summarized in Table 1. A 0.05-g quantity of SAMMS and a 10-mL volume

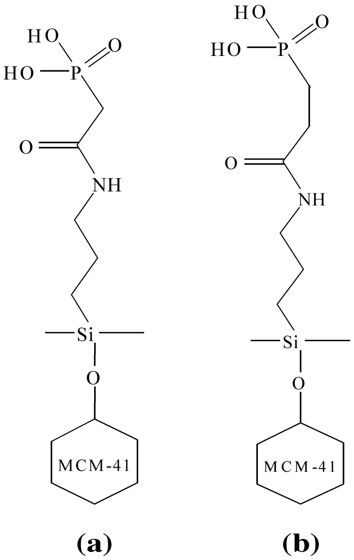

Figure 1. Schematic structures of (a) APH-SAMMS and (b) PPH-SAMMS.

(solution to solids ratio = 200) of a diluted multicomponent metal ion solution were shaken in a polyethylene bottle at the speed of 200 rpm and room temperature for a total contact time of 2 hours. Each metal ion, including Cd^{2+}, Co^{2+}, Cr^{3+}, Cu^{2+}, Mn^{2+}, Pb^{2+}, Zn^{2+}, and Ni^{2+}, had an initial concentration of 5 mg/L. To maintain essentially constant ionic strength and pH, the multicomponent metal ion solution was prepared by diluting the stock solutions (comprised of 10,000 mg/L each metal ion

Table 1. Typical experimental conditions.

Conditions	Values
SAMMS (g)	0.05
Metal ion solution (mL)	10
Initial concentration (ppm)	2–600
Background solution	0.05 M $NaNO_3$/ 0.05 M CH_3CO_2Na
pH	2.2–5.5
Contact time (h)	2
Mixing speed (rpm)	200
Temperature (°C)	25

in a 1 to 4% HNO_3 solution) with a diluent containing 0.1-M $NaNO_3$ (for pH 2) or 0.05-M sodium nitrate ($NaNO_3$) and 0.05-M sodium acetate (CH_3CO_2Na) solutions (for pH 4 to 6). The solution pH was then adjusted to a nominal pH of 2.0, 4.0, or 5.5 by adding 0.1-M HNO_3 solution and/or 0.1-M NaOH solution. The pH was controlled to less than 6 to prevent hydroxide precipitation of metal ions. The pH values of solution before and after each batch experiment were measured. The metal-loaded SAMMS material was then filtered through a 0.45-micron Nylon filter in a polypropylene housing (SAMMS particle sizes were 5 to 200 microns). Both initial and final solutions (before and after the batch experiment) were analyzed by ICP-OES (Optima 3000 DV, Perkin Elmer, Boston, MA, USA). The percent sorption is given by the percent change of metal ion concentration in solution before and after adding SAMMS. The adsorption capacity is given in mg of metal ion loaded per g of SAMMS.

Competitive Adsorption

To evaluate the competitive adsorption of metal ions on SAMMS, a 0.05-g quantity of APH-SAMMS was equilibrated with a 10.0-mL volume of solution containing an equimolar (0.5 mmol/L) of Cd^{2+}, Co^{2+}, Cu^{2+}, Mn^{2+}, Pb^{2+}, Zn^{2+}, and Ni^{2+} at pH 5.5. A mixture of 0.05-M $NaNO_3$ and 0.05-M CH_3CO_2 Na solutions was used to prepare the metal ion solution and the batch experiments were performed in the same fashion as the pH dependency study.

Sorption Isotherm Experiments

To determine the metal ion adsorption capacity of SAMMS, a 0.05-g quantity of APH-SAMMS and a 10.0-mL volume of cadmium ion solution were shaken in a polyethylene bottle in the same fashion as described in the pH isotherm measurement procedure. The cadmium concentrations ranged from 0.03 to 10.0 mmol/L, which were obtained by diluting the 10,000 mg/L cadmium nitrate stock solution with the 0.05-M $NaNO_3$ and 0.05-M CH_3CO_2Na diluent solution.

Metal Ion Adsorption Kinetics Experiment

Cadmium and nickel were selected for use in the study of adsorption kinetics. Kinetics experiments were performed in a similar fashion as the batch experiments. However, the 0.5-g quantity of APH-SAMMS was dispersed in a 100-mL volume of solution containing 2 mg/L of each metal ion, Cd^{2+} and Ni^{2+}. The aliquots were removed for ICP-OES analysis at 0, 0.5, 1, 2, 3, 4, 5, 10, 30, 60, and 120 minutes.

Regeneration Experiment

The initial batch contact was performed for 2 h, using a 0.05-g quantity of APH-SAMMS in 10.0-mL of a solution containing 10 mg/L of each of Cd^{2+}, Ni^{2+}, and Pb^{2+}. The metal-loaded SAMMS was then filtered through a 0.45-micron Nylon filter. A 5-mL volume of the filtrate was collected. A 10.0-mL volume of 20 wt% HCl solution (equivalent to 5.5-M HCl) was then passed through the filter containing SAMMS at a flow rate of 1 mL/min. The total eluent was collected. The filtrate from adsorption stage and the eluent from desorption stage were then analyzed for Cd^{2+}, Ni^{2+}, and Pb^{2+} using ICP-OES.

RESULTS AND DISCUSSION

pH Dependency of Sorption

Figure 2a and b show the extent of metal ion sorption as a function of solution pH on APH-SAMMS and PPH-SAMMS, respectively. The adsorption of metal ions on these acid forms of SAMMS materials behaves in the same fashion: adsorption increased as the pH increased from 2.2 to 5.5. Each metal ion shows a different sensitivity to pH conditions. On APH-SAMMS, for example, at pH 2.2 the extents of sorption for Cd, Cu, Cr, Mn, and Pb were between 50 and 75%, whereas those of Co, Ni, and Zn were between 10 and 20%. At pH 4.2, over 95% of all metal ions originally in the solution were adsorbed with the exception of Co, Ni, and Zn. At pH 5.5, over 97% of all metal ions were adsorbed with the exception of Co, Cr, and Ni. Cr(III) trends to hydrolyze at pH values less than neutral. Based on the $Cr(OH)_3$ solubility product constant (K_{sp}) of 6×10^{-31} at 25°C,[28] 5 mg/L Cr^{3+} solution starts to hydrolyze at pH 5.3, which may result in lower adsorption efficiency at that pH and above.

The reaction between diprotic functional groups (i.e., phosphonic acid) and divalent metal may have two mechanisms as follows:[29]

$$M^{2+} + 2R\text{-}(PO)(OH)_2 \leftrightarrow (R\text{-}(PO)(OH)(O))_2M + 2H^+ \quad (1)$$

$$M^{2+} + R\text{-}(PO)(OH)_2 \leftrightarrow R\text{-}(PO)(O)_2M + 2H^+ \quad (2)$$

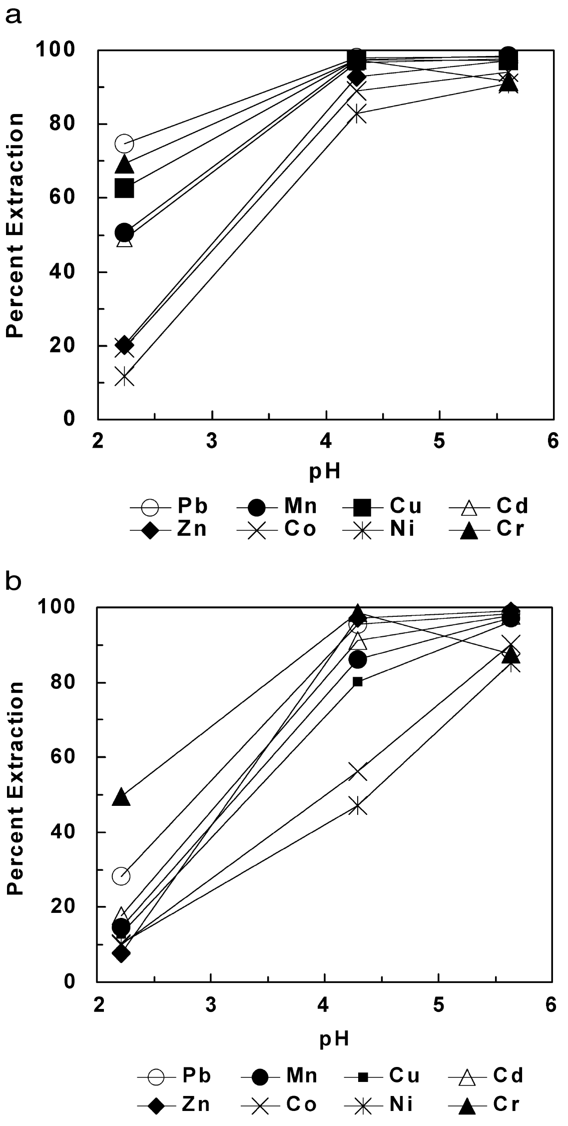

Figure 2. The extents of metal ion sorption as a function of solution pH on (a) APH-SAMMS, and (b) PPH-SAMMS, $C_{i,o} = 5$ mg/L.

where M^{2+} represents a divalent metal ion. However, the chelation between metal ions and carbamoylphosphonic acid may not follow only reactions (1) and (2) because of the presence of synergistic amide ligand. Alexandratos and Hussain[30] found that the binding between metal ions and ketophosphonate ligands [i.e., $COCH_2PO(OH)_2$ and $CO(CH_2)_2PO(OH)_2$] in nitric acid solutions occurred either by ion exchange or by coordination via intraligand cooperation and ring formation, depending upon the concentration of background nitric acid solution. The extents of sorption of most metal ions were generally higher on APH-SAMMS than on PPH-SAMMS. This may be because the six-membered ring chelate of APH-SAMMS favored the small metal ions more than the seven-membered chelate of PPH-SAMMS did.[7] Alexandratos and Hussain[30] argued that $CO(CH_2)_2$-$PO(OH)_2$ is much less likely to form a seven-membered chelate ring and the coordination is only through the phosphoryl oxygen. Further studies are needed to obtain the true binding mechanism between heavy and transition metal ions and carbamoylphosphonic acid ligands.

Since the experiments were performed in the presence of a large excess of sodium (460 times higher concentration than those of metal ions), the selectivity of SAMMS for these metal ions in the presence of sodium ion can be inferred from the metal ion distribution coefficients

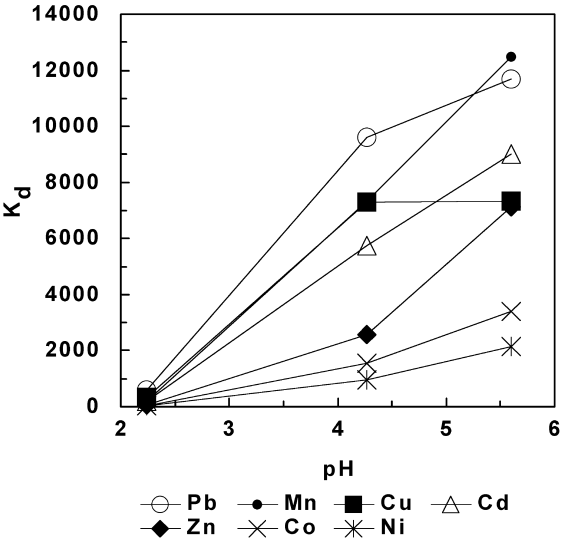

Figure 3. The distribution coefficients (K_d) of metal ions on APH-SAMMS.

(K_d). The distribution coefficients are mass-weighted partition coefficients of metal ions between the SAMMS phase and solution phase and are calculated by

$$K_d = \frac{(C_o - C_f)}{C_f} \frac{V}{m_s} \tag{3}$$

where C_o and C_f are the initial and final metal ion concentrations in solution (mg/L), V is the solution volume (mL), and m_s is the mass of SAMMS (g). The representative K_d values for metal ions on APH-SAMMS as a function of pH are shown in Figure 3. The K_d values are in the same order of magnitude ($K_d < 1000$) at pH 2.2 and increase significantly above pH 4 for most metal ions. At pH 5.5, for example, the K_d values are between 6000 and 12,000 for Zn, Cu, Mn, and Pb and between 2000 and 4000 for Co and Ni. The high magnitude of K_d values implies that the SAMMS materials have reasonably high selectivity for metal ions even at high concentration of sodium salt. For example, the manganese K_d value of 12,000 illustrates that at the equilibrium concentrations of 0.0001 mg Mn^{2+}/mL in 0.1-M sodium salt solution (equivalent to 2.3 mg Na^+/mL), there is 1.2 mg of manganese adsorbed onto 1 g of SAMMS contacting the solution.

Competitive Adsorption

The selectivity of a sorbent material toward different metal ions generally depends on the oxidation state of the metal ion, the geometry of the adsorption surface, and the physicochemical property of the functional groups incorporated on the surface.[1] The selectivity of a solid adsorbent is

Table 2. The extent of metal ion adsorption and distribution coefficients on APH-SAMMS.

Metal ion	Percentage sorption ± 1.0 S.D. (N = 3)	K_d ± 1.0 S.D. (N = 3)
Pb	70.0 ± 0.4	464.5 ± 8.6
Cu	66.3 ± 0.3	392.8 ± 5.5
Mn	63.1 ± 0.4	341.2 ± 5.1
Cd	56.3 ± 0.4	257.0 ± 4.1
Zn	50.5 ± 0.6	203.7 ± 5.0
Co	33.4 ± 0.9	100.0 ± 3.8
Ni	25.7 ± 0.9	69.0 ± 3.3

generally determined by equilibrating a unit mass of the material with a solution containing equimolar metal ions for a desired pH interval. Because of its superior adsorption activity relative to the other SAMMS for pH conditions around 5, APH-SAMMS was selected for further investigation. Table 2 summarizes the extent of sorption of metal ions on APH-SAMMS and their distribution coefficients at initial concentration of each metal ion ($C_{i,o}$) of 0.5 mmol/L and final pH of 5.5. In this study, each metal ion in the solution had equal initial molar concentration to obtain unbiased thermodynamically controlled selectivity toward metal ions of different molecular weights. At a solution to solid ratio of 200, the amount of each metal ion added corresponds to approximately 10% of the binding site content. As final concentration of each metal ion in solution ($C_{i,f}$) increased from $C_{i,f} \sim$ 1 to 4 ppm (see Figure 3) to $C_{i,f} \sim$ 10 to 30 ppm (see Table 2), the K_d values dropped by roughly a factor of 35.

Based on the K_d values and the extents of sorption, APH-SAMMS had an affinity for divalent metal ions in decreasing order as follows:

$$Pb^{2+} > Cu^{2+} > Mn^{2+} > Cd^{2+} > Zn^{2+} > Co^{2+} > Ni^{2+} \gg Na^{+}$$

At lower pH (pH 2), Yamabe et al.[23] also found that phosphonic acid on polymer support exhibited the highest selectivity toward Pb^{2+} and the lowest selectivity toward Ni^{2+} among common divalent metal ions. Our recent study found that the affinity of APH-SAMMS for Ca^{2+} was low and

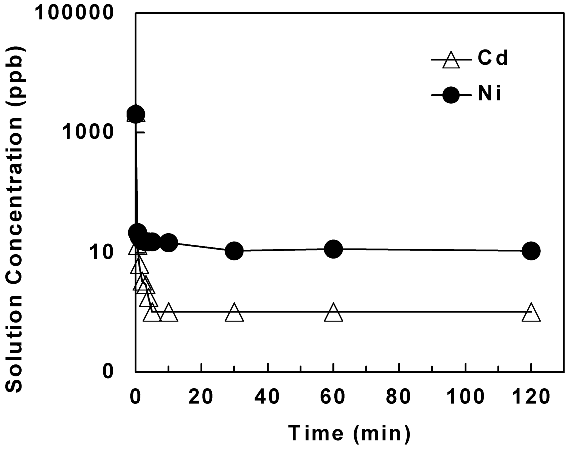

Figure 4. The final concentration of cadmium and nickel ions in solution contracting APH-SAMMS vs time profile, $C_{i,o}$ = 2 mg/L, pH = 5.5.

in the same order of magnitude as Ni^{2+}.[7] This differs from the order of affinity measured on sulfonated cation exchange resins,[31] which have relatively high affinity for calcium ion as follows:

$$Pb^{2+} > Ca^{2+} > Ni^{2+} > Cd^{2+} > Cu^{2+} > Co^{2+} > Zn^{2+}$$

Kinetics

Figure 4 shows the profile of Cd^{2+} and Ni^{2+} concentrations in solution over time. At a solution to solids ratio of 200 mL/g, APH-SAMMS reduced the Cd^{2+} concentration in solution from 2 ppm to less than 10 ppb within 1 minute and to less than 1 ppb within 5 minutes. It also reduced Ni^{2+} concentration in solution from 2 ppm to less than 20 ppb within 1 minute. From the competitive adsorption study, the affinity of APH-SAMMS for Ni^{2+} was less than for Cd^{2+}, and hence there was ten times higher concentration of Ni^{2+} left in the solution than Cd^{2+}. Nevertheless, the removal of more than 99% of Cd^{2+} and Ni^{2+} within the first minute indicates that there was little resistance to both external mass transfer and intraparticle diffusion. There was little external mass transfer resistance because of the hydrophilic properties of the functional groups on the surface, and there was very little intraparticle diffusion resistance because of the rigid, open-parallel pore structures with narrow distributed pore sizes of the mesoporous silica supports. Although chelating resins exhibit better selectivity for heavy and transition metal ions than ion exchange resins (i.e., sulfonic acid resins), the metal ion binding process in a chelating resin is often slower than that in an ion exchange resin. This is because chelation process is often controlled by chemical reaction, whereas ion exchange process is not.[31] In this study, the equilibrium was reached very fast because the functional groups in CMPO analog ligands were arranged in such a suitable way that there is no chemical resistance to the chelation.

Sorption Isotherm

Cadmium was chosen as a representative ion for measuring the loading capacity of APH-SAMMS because of its reasonably high K_d and high toxicity. The isotherm in Figure 5 represents cadmium adsorption capacity as a function of equilibrium concentration of cadmium ion in solution at room temperature. The data show an excellent agreement with Langmuir adsorption model, which is given by

$$Q = \frac{Q_{\max} K_L C_e}{1 + K_L C_e} \tag{4}$$

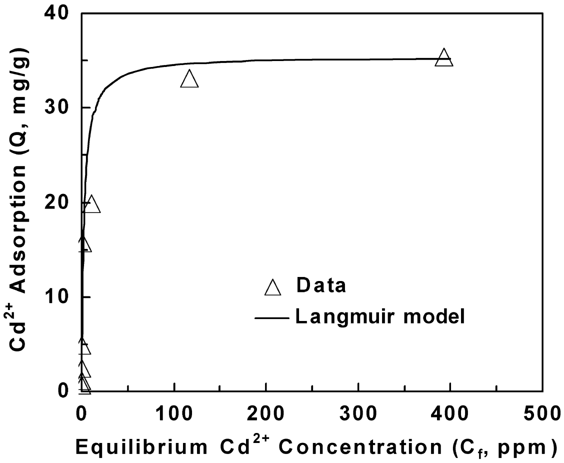

Figure 5. The adsorption isotherm data of Cd^{2+} on APH-SAMMS and the Langmuir adsorption equilibrium model, pH = 5.5.

where $Q_{\max}$ is the adsorption capacity (mg/g) when all adsorption sites are occupied, C_e is the equilibrium concentration of Cd^{2+}, and the Langmuir constant K_L (L/mg) is derived from the ratio of the adsorption rate constant to the desorption rate constant. A plot of C_e/Q vs C_e exhibited an almost perfect linear fit ($R^2 = 0.999$). The maximum adsorption capacity and the Langmuir constant K_L, calculated from the intercept and slope of the linear line, are 35.5 mg/g (equivalent to 0.32 mmol/g) and 0.367 L/mg, respectively. The maximum adsorption capacity of cadmium corresponded to 16% (molar basis) of the total binding site (2 mmol phosphonic acid/g APH-SAMMS). The extent of functional group utilization would be higher for those metal ions with better ligand-binding affinity than cadmium (i.e., Pb, Cu). The agreement between the data and Langmuir adsorption model suggested that the adsorption of Cd^{2+} onto the SAMMS interface occurred

Table 3. Regeneration experiment.

Metal ion	Cd	Ni	Pb
Metal ion adsorption capacity (mg/g)	1.97	1.97	2.11
Elution ratio (%)	84	99	90

as a single monolayer and was uniformly distributed across the pore surface, not nucleating or precipitating out of solution.

Regeneration Experiments

Table 3 summarizes adsorption capacities and the percent elution ratio of Cd^{2+}, Ni^{2+}, and Pb^{2+}. The elution ratio is defined as the ratio of the amount eluted into the acid solution to that originally adsorbed on the SAMMS. At the initial metal ion concentration of 10 mg/L, APH-SAMMS adsorbed over 99% of these metal ions. The regeneration of the metal-loaded SAMMS is fast and easy process. The adsorbed cadmium, nickel, and lead can be removed up to 99% by the 20 wt% HCl solution passing through the loaded SAMMS. After the stripping of these metal ions, the sorbent material can be reused. Our recent study shows that after ten cycles of regeneration by acid washing and reuse of SAMMS, there was no loss in binding affinity of the material.[7]

CONCLUSIONS

The CMPO analog ligands [i.e., acetamide phosphonic acid (APH) and propionamide phosphonic acid (PPH)] on mesoporous silica supports have a potential use as heavy and transition metal ion adsorbents. Adsorption of metal ions on SAMMS reached equilibrium within 1 minute. The CMPO analog ligands combines the P=O functional group with carbonyl amide in a fashion that reduces the resistances to chemical reactions and mass transfer. The fast binding kinetics is also a result of rigid, open-pore structure and a narrow distribution of pore sizes of the MCM-41 support material. The order of affinity of phosphonic acid SAMMS to divalent metal ions is $Pb^{2+} > Cu^{2+} > Mn^{2+} > Cd^{2+} > Zn^{2+} > Co^{2+} > Ni^{2+}$. The adsorption isotherm of cadmium ion on SAMMS can be described by a Langmuir equilibrium expression. Between pH 4.2 and 5.5, phosphonic acid SAMMS removed from 80% to 100% of metal ions each with 5 ppm initial concentration in the solution at a solution to solids ratio of 200. With the ability to sequester a high percentage of heavy and transition metal ions in trace concentrations within seconds, SAMMS can find its application in removing these toxic metal ions to a lower level than the EPA drinking water limit. Phosphonic acid SAMMS also has an advantage over conventional sulfonic cation exchanger resins when used to sequester heavy and transition metal ions in industrial waste streams. Unlike sulfonic cation exchanger resins, which often lose binding sites to the alkaline and alkaline earth metal ions, the phosphonic acid SAMMS is much less likely to take up excess alkaline and alkaline earth metal ions.

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