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Comparison of Novel and Patented Silica–Polyamine Composite Materials as Aqueous Heavy Metal Ion Recovery Materials

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ABSTRACT

A novel silica–polyamine composite material, WP-1, was synthesized according to a new patented procedure for aqueous heavy metal ion removal. The effects of pH and initial concentration of metal ions on adsorption were investigated. Results showed that WP-1 has metal ion capacities in the order Cu(II) $>$ Ni(II) $>$ Fe(II) and generally works best in the 2–4 pH range. Kinetic studies showed the Cu(II) adsorption reaction occurs in a second-order fashion with a rate constant of $4.4 \times 10^{-4}\ \mathrm{s}^{-1}$. Two similar silica–polyamine materials, prepared by different procedures cited in the literature, were compared with WP-1 for Cu(II) ion capacity and mechanical durability. These tests showed that capacities were more than twice as high when the new patented procedure was used, indicating much better coverage of the silica gel. During repeated metal loading and unloading tests, WP-1 maintained up to 94% of its initial Cu(II) capacity and its mechanical integrity for 3000 cycles, whereas testing of the other materials had to be stopped prematurely due to degradation of the materials.

INTRODUCTION

The use of silica gel as a matrix for grafting organic molecules is well known and has many applications in separation technology (1). The chief

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drawback of silica gel is that incomplete coverage of the surface with a functionalized silane reagent renders the composite susceptible to dissolution at pH extremes (3a). In Wirth's study of preparing silica-based materials for application in high-performance liquid chromatography (HPLC), it was found that humidification of the gel yields a monolayer of water adsorbed to the silica surface (2). Subsequent horizontal polymerization of mixed trifunctional silanizing reagents produces a silanized material with increased substrate coverage compared to conventionally prepared silica gel. These steps protect the material from degradation at pH extremes by significantly reducing the number of exposed silanol groups on or near the silica surface.

Traditionally, chelating groups are bound to silica gel by first reacting the chelating group with a functionalized silane followed by bonding to the silica surface (Fig. 1B and C) (3). These organosilanes hydrolyze then bind to the silanol sites on the silica through the process of hydrogen bonding followed

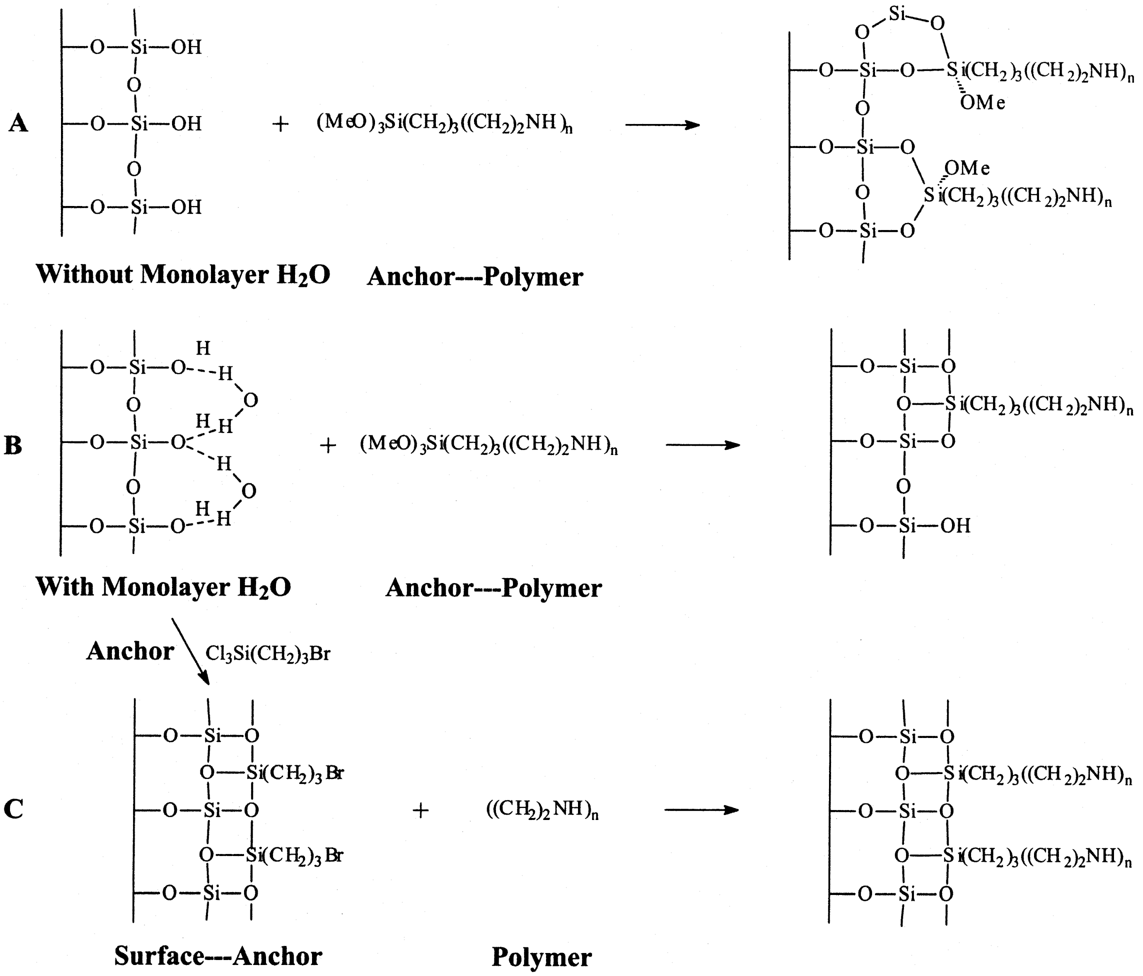

FIG. 1 Syntheses of (A) Ramsden Method, (B) hydration + Ramsden Method, (C) WP-1.

by covalent bond formation with concomitant loss of water (4). When large molecules such as polymers are introduced, steric hindrance becomes a factor in preventing uniform coverage of the silica surface (Fig. 1A and B). Typical silica surface coverage with organochlorosilanes for reverse-phase chromatography coatings is less than 50% due to steric effects (5). The presence of water in the hydrolysis step (either added, on the substrate surface, or from the atmosphere) will produce polymeric oligimers, increasing steric effects and causing the polymer to deposit on the silica surface in clumps rather than in uniform sheets. As a consequence, many silanol sites on the silica surface remain unreacted. The regeneration of many chelating materials involves a step in which the material is rinsed in base. Attack of the unreacted silanol groups by base results in eventual disintegration of the silica, rendering the silica–chelate systems prepared in this manner inappropriate for use in remediation or industrial recovery projects.

A patent was granted to the University of Montana in December of 1997 for the technology developed in our labs for the application of an organosilane anchor to the silica gel surface (6). The silica gel is first cleaned with acid, then humidified to produce a monolayer of water on the silica surface as previously applied by Wirth to HPLC silica gel (4). A small-chained anchor, $Cl_3Si(CH_2)_3Br$, is attached to the silica surface in the absence of excess water (Fig. 1C). Attachment of this organosilane to the hydrated gel results in a horizontally polymerized silica surface, providing nearly complete coverage with organosilane groups and few exposed silanol groups.

With the greater coverage, amine-based polymers are then attached to the organosilane anchor. Two advantages of the numerous amine groups “embedded” in the polymers are that first, the polymers themselves act as heavy metal ion chelators, thereby increasing the potential number of metal binding sites in the material. Second, additional chelators can be covalently bonded to amine sites, providing a means to modify the polymers readily, as appropriate, to extract specific metals.

Ramsden synthesized a chromatographic packing material by reacting poly(ethylene-iminopropyl) trimethoxysilane (available from Unified Chemicals) directly with unmodified silica gel, followed by heat curing (Fig. 1A). This produces a material which at first glance appears to be identical with our WP-1 material (that is, silica gel-Si-propyl-PEI) (7). However, we propose that the different synthetic route to WP-1—hydration of the silica surface, followed by the addition of a short-chained anchor before binding of the polymer—leads to an intrinsically different material. To investigate the capacity and durability differences between WP-1 and the Ramsden material, copper ion capacity and material lifetimes tests were performed.

A third silica composite material was synthesized by first hydrating the silica gel, then continuing in the same fashion as the Ramsden material synthesis (Fig. 1B). Examination of this “Hydrated Ramsden” composite allows a direct comparison between how the binding of a small-chain organosilane linker to the silica surface prior to polymer addition provides improved silica surface coverage over an immediate polymer–organosilane reaction, as demonstrated by material performance and mechanical durability.

In this paper we present solid-state CP-MAS ^{13}C-NMR studies performed on unmodified and hydrated silica gel to demonstrate differences in surface coverage. Adsorption of a 1 mM Cu(II) solution onto WP-1 was studied over time to provide kinetic information. The effects of pH and initial concentration of metal ions on the adsorption capacity of WP-1 were investigated in batch experiments.

Two sets of experiments were carried out to compare the performance characteristics of WP-1, Patent 4,540,486 (Ramsden), and Hydrated Ramsden. The first experiment tested the dynamic (flow) capacity of each material using a constant metal ion concentration for five loading, elution, and regeneration cycles. The practical lifetime of the materials was determined by continuing the cycle tests and the checking the capacity at predetermined intervals up to 3000 cycles. Further, scanning electron microscope (SEM) studies were performed on WP-1 and Ramsden before Cu(II) adsorption and after Cu(II) loading.

EXPERIMENTAL

Materials and Reagents

WP-1 and Ramsden were synthesized as outlined in United States Patents 5,695,882 (see sample procedure below) and 4,540,486, respectively. Hydrated Ramsden was synthesized in an identical fashion to the Ramsden material, except hydrated silica gel was used. Deionized water was used to prepare all solutions and for all rinses unless otherwise noted. Metal solutions were prepared from reagent-grade metal salts ($CuSO_4 \cdot 5H_2O$, $FeSO_4 \cdot 4H_2O$, or $NiCl_2 \cdot 6H_2O$, Mallinckrodt) and the pH of the solutions was adjusted as required using reagent grade H_2SO_4 (J. T. Baker Chemical), and NH_4OH (EM Science). Sulfuric acid (4 M) and ammonium hydroxide (4 M) solutions were prepared from the same reagent-grade sulfuric acid and ammonium hydroxide, respectively.

Apparatus

Dynamic experiments were carried out using a column fashioned from a 5-mL disposable syringe fitted with frits at both ends and filled with the material being tested. The column was attached to a variable flow FMI Lab Pump Model QG150 (Fluid Metering Inc., Syosset, NY), set to a flow rate of 10 mL/min (2 column volumes/min). Solution intakes were controlled by computer-activated solenoid valves (Cole-Parmer) using a PC with software developed for this application by Gamble and Associates Ltd., LLC (Pasadena, CA).

Equipment

UV-Vis data were measured on a Perkin-Elmer Lambda-II Spectrometer. Copper concentrations were measured by determining the solution absorbance at 800 nm and comparison to a standard Beer's law plot. Flame atomic absorption data were measured on Unicam 969 Flame Atomic Absorption (FAA) Spectrometer. Copper measurements were cross-checked by comparison of the UV-Vis and AA data to ensure that the UV-Vis data were not affected by contaminants having appreciable absorbance in the 800-nm region. ^{13}C-NMR data were obtained on a Varian Unity Plus 400 MHz NMR with CP-MAS solid-state attachments. Batch samples were shaken on a Mistral Multimixer at speed setting 4. Samples were mounted for SEM with carbon adhesive tape to aluminum studs, coated with 100 Å chromium in an IBS/TM200S ion beam sputterer (VCR Group, Inc., South San Francisco, CA) and viewed on a S-4500 cold field emission scanning electron microscope (Hitachi Ltd., Japan).

Synthesis of the Silica Polyamine Composite WP-1

Our materials consist of various polyamine moieties bound to Crossfield silica gel (90–105 μm particle size, 150 Å pore size). To synthesize the silica–polyamine composite materials, the procedure outlined in US Patent 5,695,882 was followed (8). To prepare 200 g WP-1, 200 g of silica gel is first cleansed with 800 mL 1 M nitric acid (reagent grade) by refluxing at 100°C for 6 hours. The gel is then washed with 3 × 800 mL distilled water and 3 × 800 mL methanol and air dried overnight. It is then oven dried at 100°C to obtain a dry weight. Weight loss for the cleansing step is typically 6.4–7.1% but varies due to relative humidity. The gel is then hydrated by passing moisturized air from a saturated KBr solution through the gel so that a fountain-like appearance persists. The weight gain is usually 4.2–4.6% after 16 hours. Dry heptane (705 mL) and freshly distilled $BrPrSiCl_3$ (95 mL) are mixed and slowly added to the gel. Vigorous HCl gas evolution and an orange color are evidence of a reaction. When the gas evolution slows, the mixture is degassed for 5 minutes and then spun slowly on a rotational stirrer overnight (16 hours). The slurry is then filtered and washed with heptane (3 × 800 mL), methanol (3 × 800 mL), distilled water (3 × 800 mL), and methanol (3 × 800 mL). The gel is air and oven dried; typical weight gain is around 30.4–32.5%. Polyethyleneimine (300 g) (PEI, Aldrich), 100 mL distilled water, and 300 mL methanol are mixed and added to the gel. The mixture is degassed and then spun slowly overnight. The gel is then filtered and washed with distilled water (3 × 800 mL), 0.5 M sulfuric acid (1 × 800 mL), distilled water (10 × 800 mL), 1 M ammonium hydroxide (1 × 800 mL), distilled water (10 × 800 mL), and finally methanol (3 × 800 mL). The gel is then air dried and ready to use. This procedure was modified when new materials were synthesized due to immense excesses of solvents used.

Batch Tests

WP-1 (0.2000 ± 0.0001 g) was weighed into a glass vial with a screw top. A metal ion solution (20 mL) at an initial pH of 3.4 and 25°C was added to the vial via a volumetric pipet and the vial capped. The pH was not maintained or monitored further. It is inappropriate to use buffers for this type of experiment. For concentration studies, the initial solution concentrations were 0.003125, 0.00625, 0.0125, 0.0250, 0.0500, 0.100, and 0.200 M. For all other studies, the solution concentrations were 1.0 mM. After 24 hours of shaking, each solution was filtered, preserved with 1 drop of trace metal quality concentrated HNO_3 (Fisher Scientific), and tested for metal ion concentration.

Kinetic Study

These tests were performed as for the above batch tests with the samples removed from the shaker between 1 minute to 24 hours before filtration and analysis, and were performed with solutions containing 1.0 mM copper. The general equation $1/C = 1/C_0 + kt$ was used to calculate the second-order rate constant k, where C is the concentration of the solution at time t and C_0 is the concentration at $t = 0$. The slope of the plot of $1/C$ vs time yields the rate constant k.

pH Studies

These tests were identical to the batch tests, except that the initial pH of each solution was adjusted as necessary before the experiment. Samples of each solution were analyzed by FAA before and after adsorption.

Dynamic Capacity Tests

For each test, a column containing ~5.5 cm^3 of material [2.50 g of WP-1, 1.75 g of Patent 4,540,486 (Ramsden), or 1.75 g of Hydrated Ramsden] was assembled. The column was attached to the pump, and 50 mL of H_2O was run through the column to wet the gel surface. Depending on the material being tested, 40, 60, or 80 mL of 50 mM copper ion solution was pumped through the column at 10 mL/min (1.8 column volumes/min), followed by a 40-mL H_2O rinse. Copper ion solution volumes were chosen to ensure full loading of the column with a minimum volume of metal solution. The breakthrough curve for WP-1 for this set of conditions is shown in Fig. 2. The total flow-

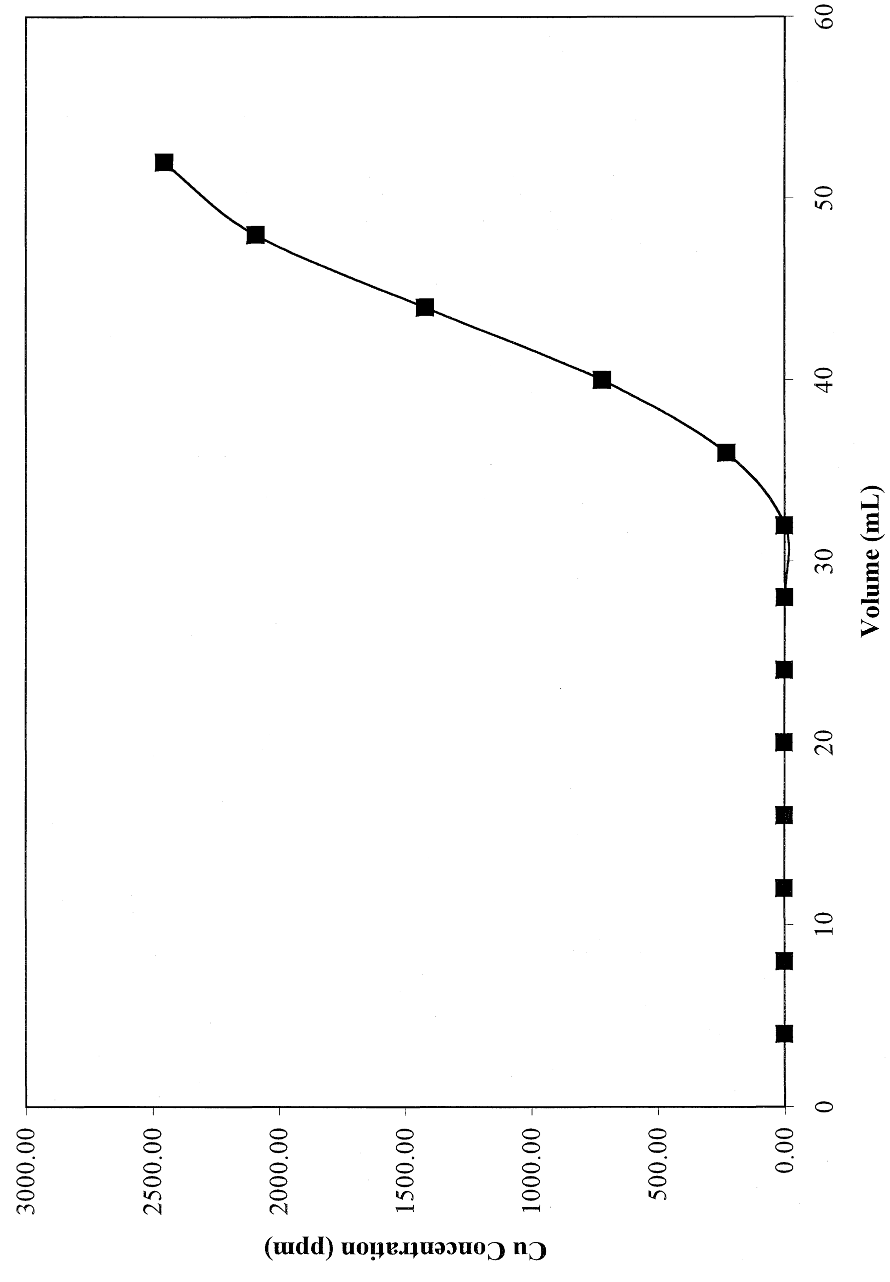

FIG. 2 Copper breakthrough curve for WP-1 in the dynamic capacity tests.

through volume was collected for analysis by UV-Vis. The Cu(II) on the column was eluted with 5 mL of 4 M H_2SO_4, followed by 15 mL of H_2O to create an elution volume of 20 mL which was also collected for UV-Vis analysis. The column was rinsed with an additional 85 mL of H_2O. Regeneration with 10 mL of 4 M ammonia was followed by a final H_2O rinse (100 mL). This cycle, excluding the first (wetting) step, was repeated 5 times for each column.

Material Lifetime Test

The initial capacity of the materials for copper was determined as for the dynamic capacity tests, and the capacity of each material was determined after 50, 100, 250, 500, 1000, 1500, 2000, 2250, 2500, 2750, and 3000 cycles (as permitted by the material). Between capacity measurements the cycle was modified to the following protocol: the pump flow rate was increased to 50 mL/min, none of the flow-through was collected, and the volumes of solutions were changed to 5 mL of copper sulfate, 2.5 mL of water rinse, 5 mL of 4 N H_2SO_4, 12.5 mL of water rinse, 8.3 mL regeneration with 4 N NH_4OH, and a final 7.13 mL of water rinse.

RESULTS AND DISCUSSION

Materials Synthesis

The basic approach to our synthesis of grafted polymer metal chelators is shown in Fig. 1(C). Commercially available silica gel is humidified to yield a surface possessing a monolayer of water (4). Our process provides a surface which is at least 80% coated with a functionalized silane anchor $[Si(CH_2)_nY]$ to which chelating groups can be attached. According to ^{29}Si analysis by Wirth, a comparison of the mole ratio of covalently bonded $\equiv SiR$ groups to the total original surface silanols showed that a coverage of 94% could be reached (3a).

The synthesis of the Ramsden materials suffers in two ways from the use of $(MeO)_3Si(CH_2)_3PEI$. First, the addition of such a large reagent sterically hinders complete, uniform coverage of the silica surface by the pendant silane groups. Second, although water promotes bonding of the reagent to the silica surface, it also inhibits complete uniform deposition of silane groups by assisting the water-catalyzed self-polymerization of $(MeO)_3Si(CH_2)_3PEI$ in solution before bonding, which induces clumping of this material. Thus, although the outer surface may appear to be covered by the $—Si(CH_2)_3PEI$ group, the silica surface has not been covered effectively, leaving it vulnerable to degradation by base.

By initially binding $Cl_3Si(CH_2)_3Br$ to the hydrated silica surface in the presence of only trace amounts of water (specifically, that present as the monolayer on the silica surface), we can maximize lateral polymerization of these groups as well as reduce steric hindrance, resulting in more complete coverage of the silica surface. This can be seen in the comparison of solid-state CP-MAS ^{13}C-NMR spectra for the organosilane anchor —$Si(CH_2)_3Br$ bound to unmodified silica gel (Fig. 3b) and to hydrated silica gel (Fig. 3a). The spec-

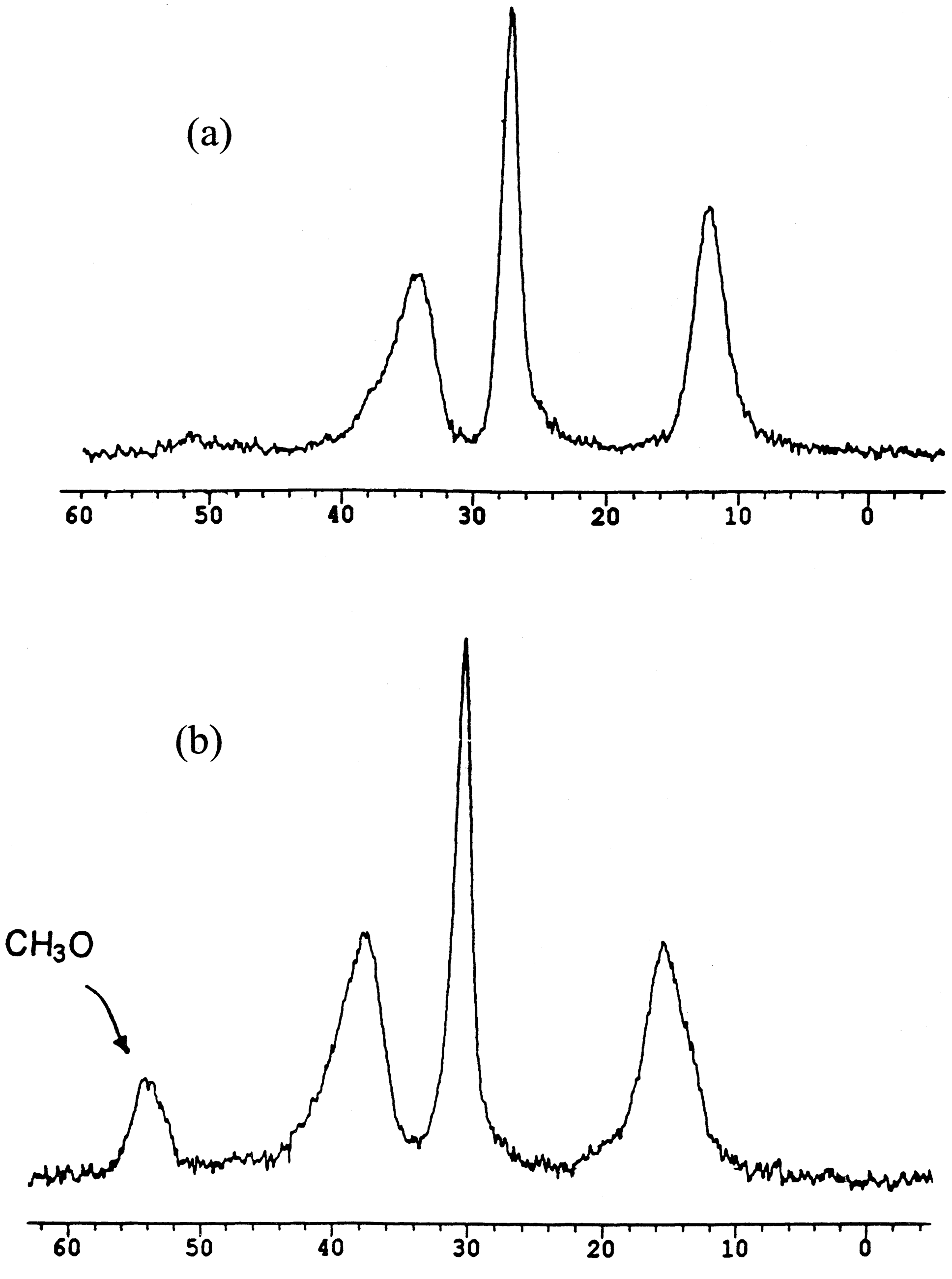

FIG. 3 100 MHz CP-MAS ^{13}C-NMR of functionalized propylsilane grafted to (a) hydrated and (b) nonhydrated silica gel.

trum of the nonhydrated gel shows a methoxide peak due to the reaction of exposed chlorosilane with a methanol wash. The presence of the methoxide peak indicates incomplete surface coverage of the silica surface with polymer. The same peak is barely visible in the spectrum of the hydrated gel, and shows that not only is our surface coverage better using the hydrating process, but that ^{13}C-NMR can be used to determine the relative silica surface polymer coverage. A more complex ^{29}Si analysis, which led to the same conclusion, was previously reported (3a). Additionally, the use of a dry hydrophobic solvent (in this case, heptane) acts in two ways to improve surface coverage. First, it keeps the monolayer of water on the silica surface intact, and second, it prevents self-polymerization of the polymer before reaching the silica surface.

The next step in the gel synthesis is the addition of the polymeric chelator PEI, a highly branched polymer with an approximate 1:2:1 distribution of primary:secondary:tertiary amine sites. The PEI polymer gels work on a “fishnet” principle of metal gathering, so-called because of the highly branched network within the gel. The tertiary sites are not amenable to further modification and may not be available for coordination to the metal.

Equilibrium Studies

In order to better understand the performance of WP-1 in kinetic terms, its adsorption of Cu(II) was monitored with time. Samples were shaken for 1, 2, 10, 15, and 30 minutes, 1, 2, 4, 6, and 24 hours. As seen in the adsorption profile (Fig. 4a), maximum adsorption of Cu(II) is accomplished in approximately 4 hours. The (pseudo) second-order rate constant of $4.4 \times 10^{-1}\ \mathrm{M}^{-1}\,\mathrm{s}^{-1}$ was determined from a linear plot of $1/C$ vs t, as shown in Fig. 4(b), where C is the Cu(II) concentration at time t (seconds). This rate constant is comparable to the pseudofirst-order rate constant reported by Huang et al. for the removal of Fe(III) with their sulfonated catechol ligand (8) (no other reports of similar kinetic data were found in the literature). WP-1 is therefore at least as efficient as polystyrene-based materials from a kinetic point of view.

Effect of Initial Concentration of Metal ions

Adsorption capacities of Cu(II) and Ni(II) by WP-1 are presented as a function of the initial concentration of the metal in solution in Fig. 5. The initial concentrations vary from 0.003125 to 0.200 M in the respective metal ion. The adsorption capacity of WP-1 initially increases with increasing metal ion concentration, reaches a plateau between values of 0.20 to 1.00 mM, then increases again to maximum capacities of 0.93 mmol/g for Cu(II) and 0.51 mmol/g for Ni(II) at a final tested concentration of 2.00 mM. The higher adsorption capacity of WP-1 for Cu(II) than Ni(II) corresponds to the preference of ethyleneamine for copper ions over nickel ions (9).

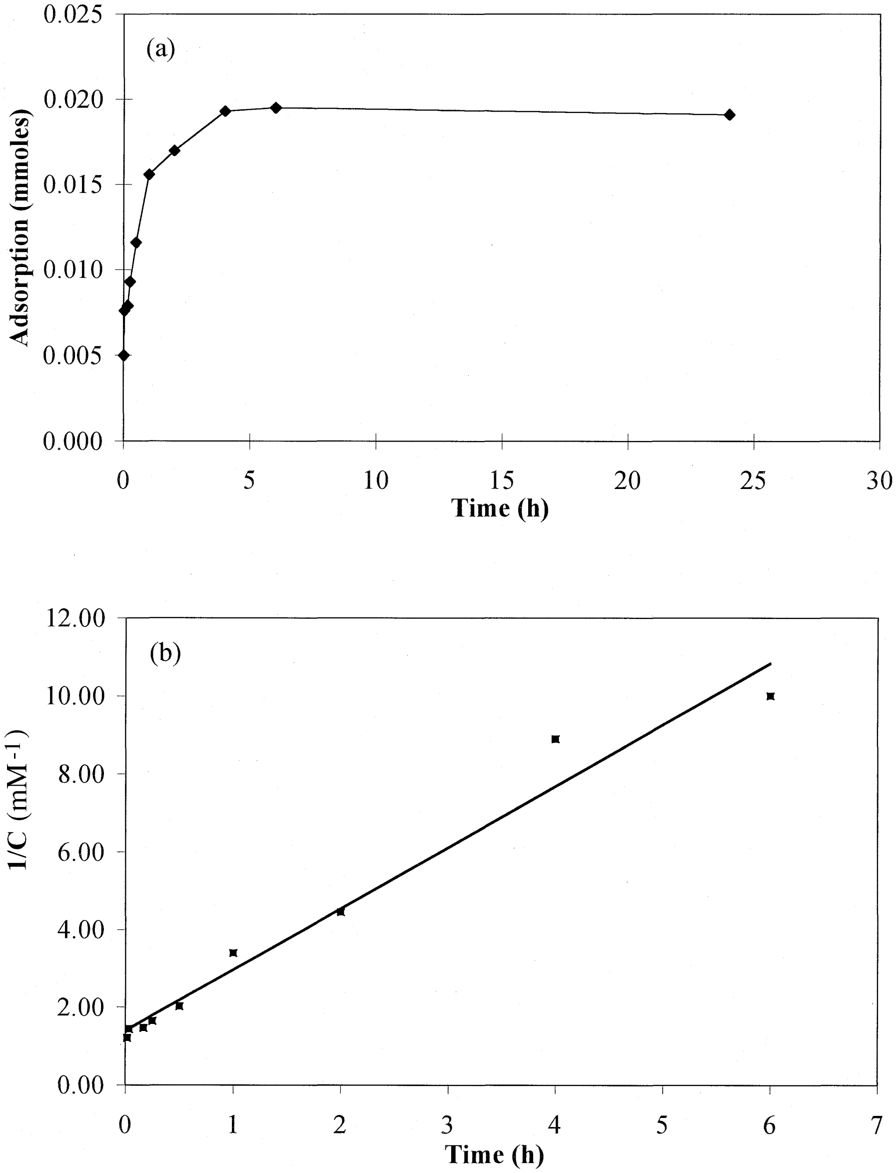

FIG. 4 (a) Loading of WP-1 using 1.0 mM Cu(II) at pH 3.4 and 25°C as a function of time. (b) Kinetic plot of $1/C$ vs t (hours) for Cu(II) removal.

Metal ion adsorption capacities reported in the literature are as low as 0.016 mmol/g for adsorption of Cu(II) and Ni(II) onto functionalized sporopollenin (10), and for Cu(II), Ni(II), and Fe(II) adsorbed onto modified alumina oxide (11). The dye Congo Red, bound to modified methacrylate microbeads, adsorbs Cu(II) at a level of 0.046 mmol/g (12), and Pluddemann's silica-bound 8-hydroxyquinoline material adsorbs at a maximum of 0.086 mmol/g (5b). These materials were tested for their capacities only at low metal ion concen-

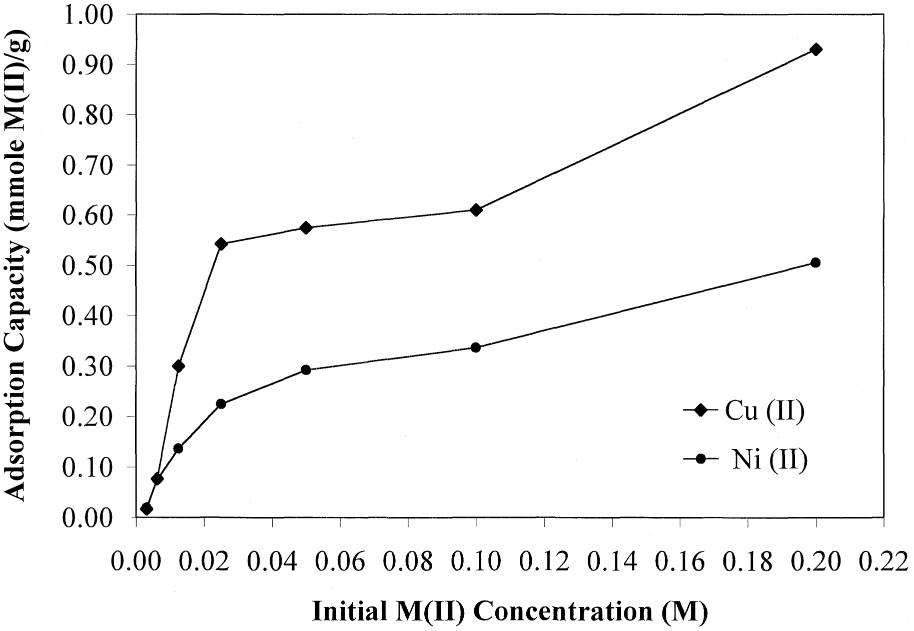

FIG. 5 Loading of WP-1 using Cu(II) or Ni(II) at pH 3.4 and 25°C as a function of concentration.

trations (2×10^{-4} to 0.001 M), however, and thus may possess higher capacities at higher concentrations. Only the nitrogen-containing cellulose derivatives synthesized by Nakamura and Amano were tested in higher Cu(II) concentrations (up to 0.01 M) and possess Cu(II) adsorption capacities which compare to ours—0.33 to 0.45 mmol/g (13).

Effect of pH

In order to establish the effect of pH on the adsorption of metal ions onto WP-1, batch equilibrium experiments were repeated at various pH values in the 0.5 to 8.0 range and at an initial metal concentration of 0.1 mM. Copper and iron precipitate above pH 4, and therefore we were unable to obtain capacity for these two metals above this pH. Figure 6 shows the adsorption data of Cu(II), Ni(II), and Fe(II) ions. The removal of Cu(II) from solution is relatively high initially, increases toward pH 2, where it declines slightly until pH 4 is reached. The Fe(II) ion has a much lower initial adsorption than Cu(II) under highly acidic conditions, then climbs to a maximum plateau between pH 2 and 4. WP-1 adsorbs Ni(II) best in the pH range 3–6, and its capacity drops off in more acidic or alkaline conditions. Interestingly, the data indicate that the preference of WP-1 for Cu(II), Fe(II), or Ni(II) can be modified by changing the pH of the ionic solutions. At pH greater than 3, adsorption of Ni(II) is only slightly higher than that of Fe(II). At pH 2, however, WP-1 has a significantly higher adsorption capacity for Cu(II) and Fe(II) than for Ni(II) (0.0205 and

0.0178 vs 0.0067 mmol/L adsorbed). This could have important uses in selective heavy metal ion separation/recovery applications.

Comparison vs Previously Reported Polyamine Silica Composites

The most prominent physical difference between our gels and the Ramsden and Hydrated Ramsden gels was their density; WP-1 is 41% more dense than Ramsden and Hydrated Ramsden. (WP-1 has a working density of about 0.45 g/cm^3 vs about 0.32 g/cm^3 for the Ramsden gels). When wet, Ramsden and Hydrated Ramsden appear more translucent than WP-1. During the first five cycle tests of Ramsden material, a small void pocket began to form on the inlet side of the column. After 100 cycles this had become a 2-mm void, and it increased to 5 mm by 500 cycles. Hydrated Ramsden also formed a small void pocket during the initial capacity test. During the lifetime cycle test a 1-mm void formed at 50 cycles which increased to 4 mm by 1000 cycles. In contrast, the WP-1 column showed no change in occupied volume in either test.

As shown in Fig. 7, the maximum Cu(II) ion capacity per gram of the Ramsden and Hydrated Ramsden materials were only 59 and 64% of the highest capacity of WP-1 (0.50 mmol/g for Ramsden and 0.54 mmol/g for Hydrated Ramsden vs 0.84 mmol/g for WP-1). In industrial and remediation applications, capacity per volume of gel is also important. Based on 5.5 mm^3 of gel material per column, WP-1 has an average copper capacity approximately 145% of the maximum capacity for both Ramsden and Hydrated Ramsden materials.

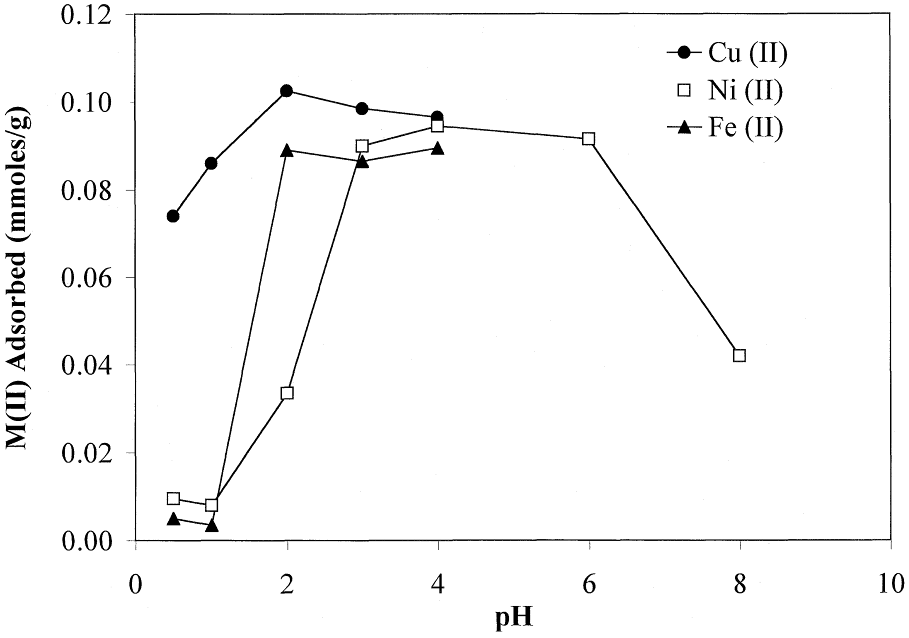

FIG. 6 Adsorption of Cu(II), Ni(II), and Fe(II) by WP-1 as a function of pH.

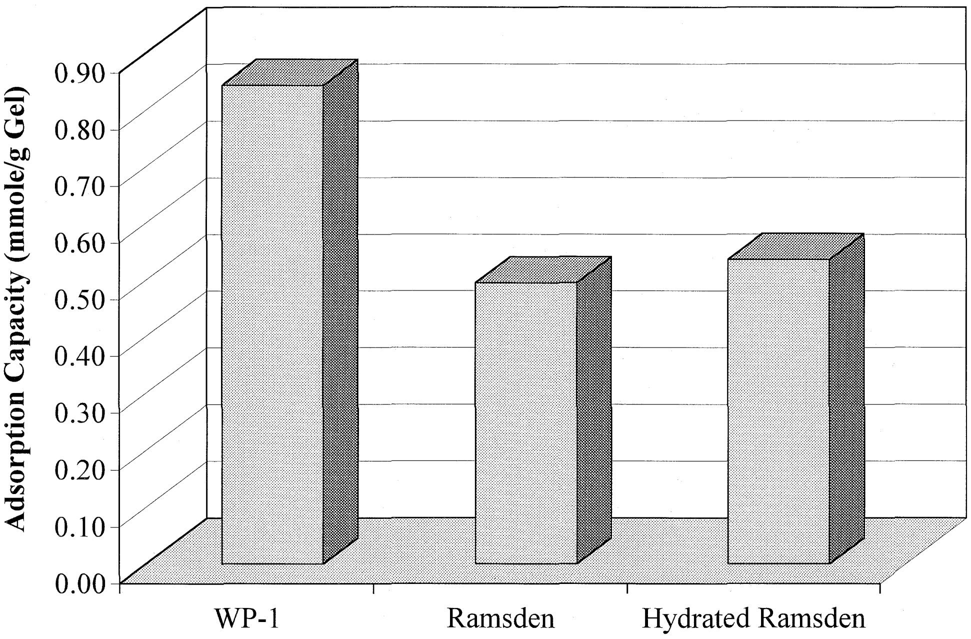

FIG. 7 Cu(II) adsorption capacities of WP-1, Ramsden, and Hydrated Ramsden under flow conditions.

Of utmost importance in industrial and remediation applications is how long a material will maintain its original performance characteristics. The cycle test was designed to determine how repeated use affects the capacity of gels. Figure 8 shows the comparison of lifetime cycle tests of WP-1, Ramsden, and Hydrated Ramsden materials. After 3000 cycles there was no visible change in the volume of WP-1 and the capacity was 94% of the highest capacity recorded. On the other hand, testing of the Ramsden gel was stopped after 500 cycles due to an increase in backpressure that compromised the structural integrity of the column. Similarly, Hydrated Ramsden testing had to be stopped prematurely due to increased backpressure. While there are not enough data points to comment conclusively on the capacity behavior of the Ramsden materials, the data do indicate a steep and steady decline in the capacities of Ramsden and Hydrated Ramsden even if the gels remained useable. The compression of Ramsden and Hydrated Ramsden suggests a deterioration of the materials due to instability of the unprotected silica surface when exposed to base.

A more physical view of our materials can be gained from SEM, which enables us to visualize differences in the gross topography of the surfaces of metal-free and metal-containing gels. Micrographs of the surfaces of metal-free WP-1 and the Ramsden materials are indistinguishable from that of bare silica gel. Micrographs of the copper-loaded composite materials reveal a surface that appears to be more densely packed and uniform for WP-1 than for the Ramsden material (Figs. 9A and B). This difference is consistent with an

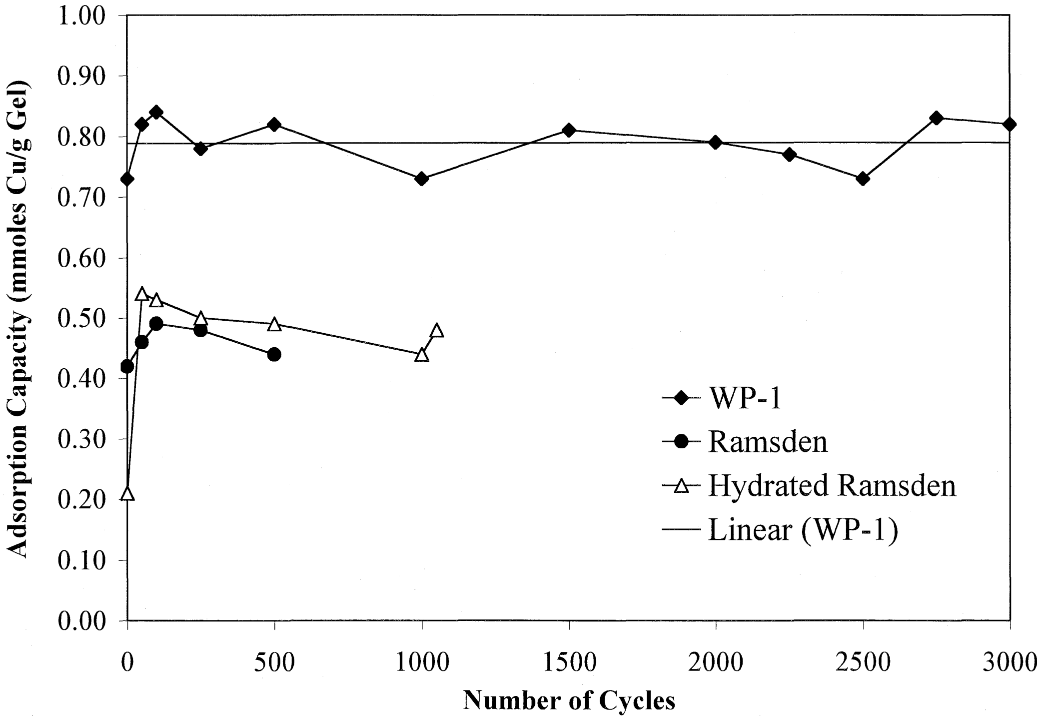

FIG. 8 Lifetime Cu(II) adsorption capacities of WP-1, Ramsden, and Hydrated Ramsden under flow conditions.

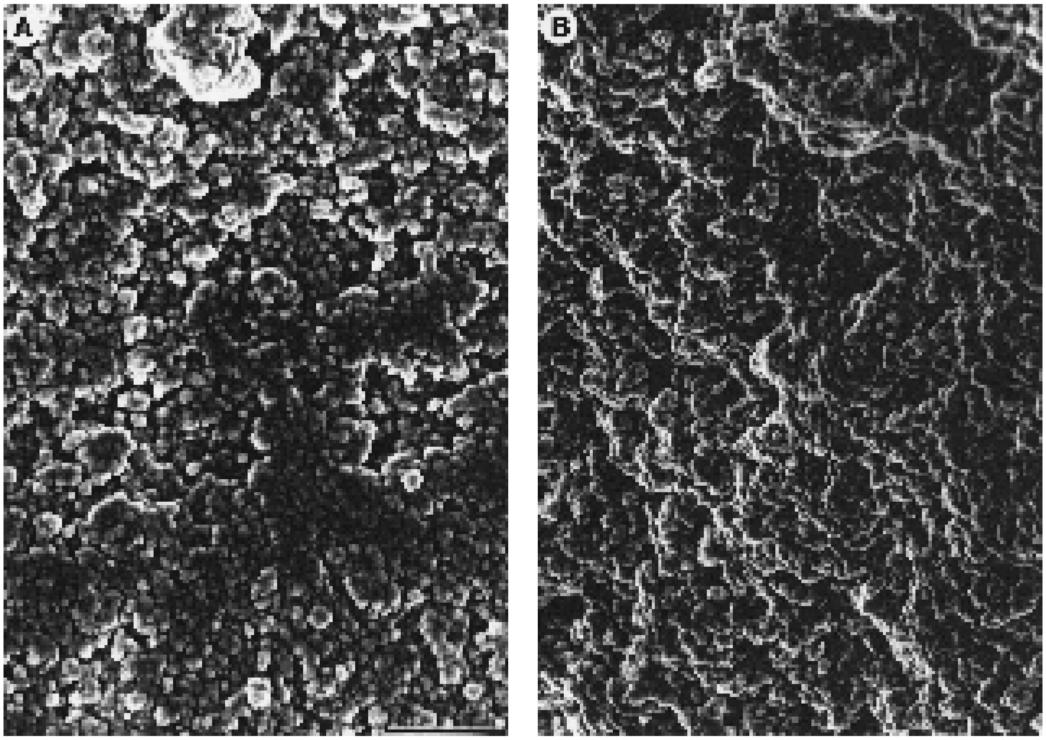

FIG. 9 SEM of Cu(II)-loaded (a) Ramsden and (b) WP-1 materials (scale bar = 0.5 μm).

improved surface coverage of the silica surface using our two-step synthetic method.

At this time Hydrated Ramsden has not been investigated by SEM. The Ramsden gel used in lifetime tests is currently being investigated by SEM to determine the extent of silica gel decomposition which has theoretically led to the breakdown of the material.

CONCLUSIONS

We have demonstrated that silica gel hydration, in combination with the stepwise addition of a small-chain organosilane linker followed by polyamine bonding, results in a new silica–PEI material (WP-1). WP-1 shows durability and 94% of its original adsorption capacity to 3000 repeated testing cycles, in addition to a markedly increased copper-ion capacity over the previously patented material, Ramsden, and its hydrated silica analogue, Hydrated Ramsden.

The adsorption capacity of WP-1 increases as metal ion concentration increases, up to 0.93 and 0.51 mmol/g for Cu(II) and Ni(II), respectively, at a maximum studied concentration of 0.200 M (200 mM) for each metal. The general trend for metal ion adsorption onto WP-1 is Cu(II) $>$ Ni(II) $>$ Fe(II), and adsorption is best under acidic conditions (pH 2–6).

Based on the results reported here, WP-1 would be a superior material for repeated use in high flow rate applications such as those found in industry and wastewater treatment projects. The key factors in producing these materials with high metal ion capacity and long-term stability are the combined employment of the procedures previously applied to HPLC and the order of organosilane anchor/polyamine binding to the silica surface.

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