Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Heckman, B. , Martin, L. , Bertino, M. F. , Leventis, N. and Tokuhiro, A. T.(2008) 'Sol-Gel Materials for High Capacity, Rapid Removal of Metal Contaminants', Separation Science and Technology, 43: 6, 1474 — 1487
To link to this Article: DOI: 10.1080/01496390801955539
URL: http://dx.doi.org/10.1080/01496390801955539

Separation Science and Technology, 43: 1474–1487, 2008

ISSN 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390801955539

Sol-Gel Materials for High Capacity, Rapid Removal of Metal Contaminants

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Abstract: An environmental waste remediation method is presented where porous cylindrical monoliths are interposed as septa between a solution contaminated with metal ions and a solution of a precipitant. Precipitant and contaminant diffuse and generate precipitate nano- and micro-particles inside the monoliths. Two types of silica sol-gel monoliths were tested. One class of materials was prepared following a conventional base-catalyzed route which yielded fragile silica monoliths with pore diameters on the order of 7–10 nm. A second class of materials material consisted of templated silica macroporous monoliths that were cross-linked with diisocyanate. These materials had pore diameters on the order of microns and were mechanically extremely strong, having a Young modulus in excess of 400 MPa. Both types of silica gel monoliths proved very versatile, and allowed to precipitate a wide variety of metal ions, including toxic metals such as Cd^{2+}, and fission by-products such as lanthanides and Sr^{2+}. The capacity of the gel monoliths was also very high, at least 20 times higher than the capacity of conventional derivatized gels. Most importantly, precipitation inside the macroporous gels was a factor 7–8 more rapid than in microporous gels. The results indicate that macroporous cross-linked sol-gel monoliths are a

Received 5 September 2007, Accepted 21 January 2008

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promising material for the development of efficient, mechanically strong filter elements for environmental remediation.

Keywords: Sol-gel, nuclear waste, porous materials, precipitation, environmental remediation

INTRODUCTION

Removal of toxic and radioactive metals from waste water is a long-standing issue in environmental management. Over the years, a wide variety of solutions have been proposed and applied. In precipitation approaches, insoluble compounds are formed and precipitated by adding a suitable compound to the parent solution. Typically, sulfides are formed by adding a compound that liberates sulfur ions readily, such as Na_2S or thiourea (1). In complexation approaches, ions are strongly bound to an organic molecule. For example, calixarenes are used to remove radioactive Cs isotopes from liquid radioactive waste and sludges (2). The complexing agents can be attached to a solid substrate, like in the case of derivatized silica gels. Gels derivatized with a thiol group, for example, are a very effective means for capturing Hg^{2+} ions from potable water (3, 4). In exchange approaches, the solution is passed through an ion exchange column. For example, ion exchange resins have been developed to absorb Ag^{+} ions produced by photographic development and are used by large-scale photographic laboratories such as those of hospital complexes. In other ion-exchange approaches a solution is passed through a column containing a mineral that exchanges preferentially a certain type of ions. For example, tungstates can be employed to exchange Cs^{+} (5, 6), and hydroxyapatite can be employed to exchange Sr^{2+} and other divalent ions (7, 8). In phytoremediation approaches plants that need specific ions for their metabolism are grown on contaminated soil. For example, Alyssum murale has been used to recover nickel from soil in Canada. Leaves were found to be so enriched in nickel that the metal could be cost-effectively recovered by burning the leaves (9–11). Each of these techniques presents advantages and disadvantages. Precipitation is an extremely simple method with a high yield. However, the precipitate must be separated out of the parent solution, a non-trivial task when the precipitate is radioactive. Complexation is an extremely rapid and efficient method, but the complexing agents can be expensive, or hazardous. For example, calixarenes belong to the family of crown ethers, which are relatively difficult and expensive to synthesize. Furthermore, complexing of radioactive waste does not solve the problem of removal from solution and encapsulation of the waste in a stable matrix. Anchoring of complexing molecules to substrates like silica or polymer gels alleviates the encapsulation problem, but presents capacity issues. Adsorption occurs on the surfaces of gels, and even when high surface area materials are employed, the total capacity remains on the order of μmols per gram of dry material (4). Ion exchange is a very efficient method, but columns are relatively expensive, and are not made for long-term storage, i.e., radioactive ions may leach out. In the case of ion exchange on minerals, the capacity is again closely related to the surface area of the materials. Phytoremediation is a promising technique to clean large areas contaminated with a comparatively low metal concentration. However, the yield is relatively low, the level of contamination must be low, least the plants will be poisoned by the waste, and the plants used for phytoremediation cannot be used in all climates.

Presented here is a general method of precipitation of metals inside silica hydrogels which is based on well-established chemical principles, and that is cheap, versatile, and easy to implement. In our method, a cylindrical hydrogel monolith is interposed as a septum between two reservoirs. One reservoir contains a metal ion solution and the other reservoir contains a precipitant like Na_2S that reacts readily with metal ions at room temperature. The metal ions and the precipitant diffuse and form nano- and micro-particles inside the hydrogel monolith. Once formed, the nanoparticles are confined within the porous material and do not leach out as established by previous work by our groups (12). Our method can be adapted to absorb a wide range of metal ions, including ions that are frequently encountered in radioactive waste management, such as Sr^{2+} and lanthanides (Eu^{3+}, Nd^{2+}). We also compared the filtering characteristics of two types of sol-gel silica monoliths. One set of monoliths consisted of silica gels prepared following a conventional, base-catalyzed route. These gels were readily obtained, but had comparatively small pores (7–10 nm) and were fragile. A second set of monoliths consisted of silica gels with micron-sized pores, which had been cross-linked with polyurethane to increase their mechanical strength. For both materials, we found that the capacity of the monoliths is orders of magnitude higher than that of derivatized gels, and that the absorption rate is high and remains constant for long periods of time. Most importantly, we found that the absorption rate of macroporous gels is about 8 times larger than that of microporous gels, and is on the order of milligrams per hour. Thus, cross-linked, sol-gel monoliths represent a promising material for the development of efficient, mechanically strong filter elements for environmental remediation.

EXPERIMENTAL

Gel Synthesis

Microporous silica hydrogels were prepared following a conventional base-catalyzed route (13). In brief, the contents of vial A (4.514 mL of tetramethoxysilane–TMOS–; 3.839 mL of methanol) and of vial B (4.514 mL of methanol; 1.514 mL of water, and 20 μL of NH_4OH) were mixed thoroughly to form a sol that gels at room temperature in 10–15 min. The gels were left to age at room temperature for ~2 days. After aging, the gels were washed 4 times in methanol, and 4 times in water. The time interval between each washing was about 12 hours. To prepare microporous hydrogel filters, an acrylic tube with an inner diameter of 1.9 cm was used as a mold. About 20 ml of an about-to-gel sol were poured inside the mold, which formed a cylinder with a height of about 7.5 cm. After aging, the column was soaked 4 times in about 200 ml of methanol and left in the washing solution for at least 6 hours between each washing. The same washing procedure was then repeated with water. The mold containing the gel was then glued to two reservoirs as described in more detail in the discussion of Fig. 2. Mechanically strong, macroporous hydrogels were prepared by modifications of published procedures. Specifically, we based our synthesis on recent work by the Nakanishi group (14), which, in turn, is based on a modification of Stucky's method for SBA-15/MCF materials (15, 16). Nakanishi's approach yields monolithic silica with well-defined periodic macropores by reducing the amount of solvent (aqueous acid) in Stucky's process, thus obtaining gels rather than precipitates. In Nakanishi's method, however, the gelation solvent (water) was removed at 60°C under ambient pressure, and the templating agent (Pluronic P123– BASF–) was removed by calcination at 650°C. Solvent and templating agent removal lead to up to 50% volume shrinkage, which is not desirable if large, crack-free monoliths are to be prepared. We decided therefore to remove solvents swelling agents and surfactants by repeated washings and Soxhlet extraction (17). Our extraction procedure minimizes the shrinking and cracking of calcination treatments, and yields large, crack-free monoliths. In a typical synthesis, macroporous gels were prepared by dissolving four grams of P123 in 12 grams of a 1.0 M aqueous solution of nitric acid; to this solution, 3.1 grams of 1,3,5 trimethyl benzene (TMB) were added under vigorous stirring. After about 3 hours, the system was cooled to 0°C in an ice bath, and then 5.15 grams of TMOS were added under stirring. After 10 minutes the solution was poured into a mold. The mold was kept 60°C for 5x the gelation period (roughly 12–15 hours). The gel was then washed twice in ethanol, 8 hours each time. To the washings followed Soxhlet extraction using acetonitrile for two days to remove P123. The gels were then washed 4 times with acetone (8 hours). The mechanical stability of the gels was increased by cross-linking, as previously established by our groups. To cross-link, the macroporous gels were placed in 200 ml of acetone in which 22 grams of Desmodur N3200 (Bayer) had been previously dissolved. After bathing in Desmodur solution for 24 hours, the gels were placed in a sealed container and heated to 55°C for 3 days. The gels were washed 4x in acetone, (8 hours), methanol, and water. Porosity, density, mechanical strength and surface area of the two types of monoliths used in our experiments are reported in Table 1. Notice that the BET surface area of the cross-linked monoliths is more than 100 times smaller than that of microporous monoliths. This is

Table 1. Selected data for native and mesoporous, cross-linked monoliths. Adapted from (17)

Monolith type	Bulk density ($g \cdot cm^{-3}$)	Porosity (%)	BET surface area ($m^2 \cdot g^{-1}$)	Young modulus (MPa)
Microporous, non-cross-linked	0.33	83.8	714	<5
Macroporous, cross-linked	0.58	31.1	1.31	>400

because the cross-linking polymer clogs the nanopores while leaving the micropores nearly unscathed, as shown in Fig. 1. At the end of the process, the monoliths had a diameter of about 16 mm and a length of up to 55 mm. They were then glued to stainless steel washers which had an inner diameter of 8 mm and an outer diameter of 19 mm. The washers were snugly fit into the same acrylic molds used for the microporous gels, and silicon glue was then employed to waterproof the contact between washers and mold.

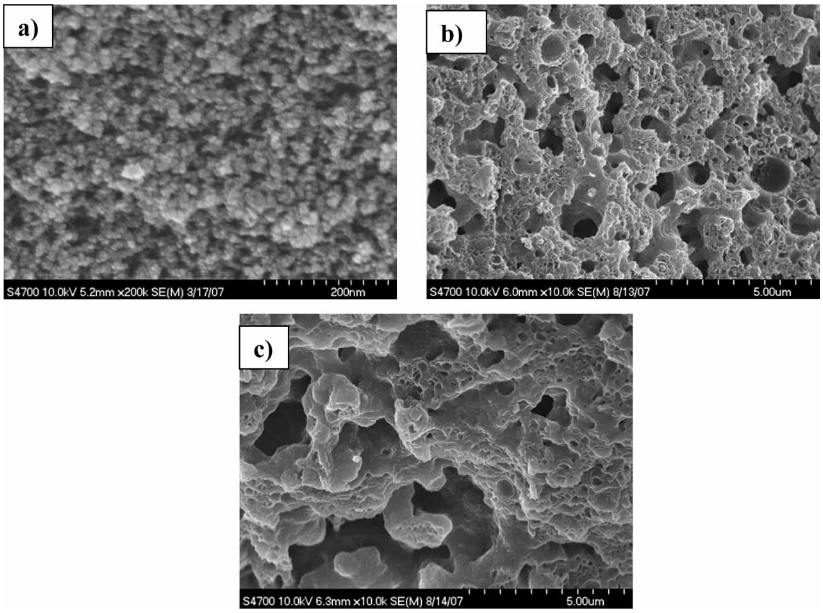

Figure 1. Scanning electron microscopy images of a) microporous silica gels, b) macroporous gels before cross-linking, and c) macroporous gels after cross-linking.

Characterization

Samples were characterized with flame atomic absorption (AA) spectroscopy, neutron activation analysis (NAA), transmission electron microscopy (TEM), scanning electron microscopy (SEM), and N_2 gas adsorption porosimetry using Brunauer-Emmett-Teller (BET) analysis. AA was used to determine the metal ion concentration of solutions containing Cd^{2+}, and data was taken on a Perkin-Elmer 2380 instrument. Samples for AA were prepared by diluting each sample with H_2O to reach the linear range of Cd^{2+} for the instrument ($2\,\mathrm{mg} \cdot \mathrm{l}^{-1}$). A 1% (v/v) HCl was added to the final product. NAA was performed to determine the concentration of Nd^{3+}, Eu^{3+}, and Sr^{2+}. Samples were activated by placing small plastic vials near the core of the University of Missouri – Rolla Reactor. This reactor is a light-water pool reactor with ^{235}U fuel rods that can operate at a maximum power of 200 kW. The neutron fluxes are a linear function of the reactor operating power. At maximum power, the fluxes of thermal, and, respectively, epithermal neutrons are $\Phi_{\mathrm{thermal}} = 1.86 \times 10^{12}\ \mathrm{n/cm^2sec}$ and $\Phi_{\mathrm{epithermal}} = 1.27 \times 10^{10}\ \mathrm{n/cm^2sec}$. For neutron activation analysis, samples with a volume of 2 ml were collected from the solution to be analyzed, and a 1% (v/v) of HNO_3 was added. HCl could not be used as an acidifier because of the large activation cross-section of Cl. The samples were then placed near the reactor core using a pneumatic system ("rabbit tube"). The samples remained in the rabbit tube for varying times and at different powers depending on the activation cross-section of the element of interest. Nd^{3+} samples were in the core for 60 sec at a power 10 kW (total neutron flux $\Phi_{\mathrm{neutron}} = 9.36 \times 10^{10}\ \mathrm{n/cm^2sec}$); Eu^{3+} for 60 sec at a power of 400 W (total neutron flux $\Phi_{\mathrm{neutron}} = 3.75 \times 10^{9}\ \mathrm{n/cm^2sec}$); and Sr^{2+} for 120 sec at a power of 1 kW (total neutron flux $\Phi_{\mathrm{neutron}} = 9.36 \times 10^{9}\ \mathrm{n/cm^2sec}$). After activation, the samples were retrieved and placed inside a gamma ray detector. The gamma ray detector was a Canberra Industries model 7–747 equipped with a high-purity Ge detector cooled with liquid nitrogen. The data was analyzed with Genie 2000 Gamma Acquisition and Analysis software, also from Canberra Industries. Great care was taken to ensure that the time elapsed between the retrieval of the sample and the beginning of the counting was the same for all samples. In addition, a series of centering jigs was designed to ensure that the samples were placed in the same location within the core and within the detector. These precautions allowed achieving a reproducibility of the measurements that was within 5%. TEM micrographs were taken with a Zeiss EM 109, operated at 80 kV. Samples were prepared by carving spots out of a monolith with a razor blade. The carved out regions were then crushed and placed on a 300-mesh lacey carbon grid. N_2 gas adsorption and BET surface area analyses were performed at NASA Glenn Research Center with an ASAP 2000 Surface Area/Pore Distribution analyzer from Micrometrics Instrument Corporation. The samples were outgassed at 80°C for 24 hrs before being analyzed.

RESULTS AND DISCUSSION

The major goal of our project was to devise a simple and reliable method for the removal of metal ions from concentrated solutions such as those produced in nuclear waste reprocessing plants. Table 2 reports the concentrations of metal ions in a reprocessing solution in a light-water reactor in France (18, 19). The composition was a barrel of typical reprocessed fuel irradiated to 33 $\mathrm{MW \cdot days \cdot kg^{-1}}$. The solution contains long-lived fission products, such as lanthanides, but also processing byproducts, such as Ni and Fe. The concentration of the ions can roughly be divided into two categories. Certain metals like Ag and Y are present in a comparatively low concentration, around and below $1\ \mathrm{g \cdot l^{-1}}$. Metals like Sr or Zr are typically present in higher concentrations, up to $7\ \mathrm{g \cdot l^{-1}}$. Therefore, in most of our experiments we compared solutions with concentrations around $1\ \mathrm{g \cdot l^{-1}}$ and around $5\ \mathrm{g \cdot l^{-1}}$. Among possible metals, cadmium possessed the most attractive features for our proof-of-concept experiments. Like most metals in Table 2, cadmium is spontaneously precipitated as the insoluble CdS when Cd^{2+} ions are contacted with S^{2-} ions. Furthermore, CdS has a bright yellow-orange color, thus its formation is easily detected by simple visual inspection of the hydrogel monolith. Finally, a large body of literature is available on the formation and characterization of CdS inside silica gels (20–25). The monolithic-gel filters used in our experiments consisted of two L-shaped PVC tubes connected by a clear acrylic tube. A schematic drawing and photograph of the set-up are shown in Fig. 2. The gel monolith was placed as a septum between the waste-simulating solution and the precipitant. Waste-simulating solutions of different ions were prepared, such as

Table 2. Elements found in typical nuclear waste containers. The specific data was obtained from a barrel of high-level waste from the reprocessing of light-water reactor fuel in France (18,19). Adapted from (18)

Fission products ($\mathrm{g \cdot l^{-1}}$)				Actinides ($\mathrm{g \cdot l^{-1}}$)	
Se	0.08	Cd	0.12	U	2.06
Rb	0.53	Te	0.71	Np	0.66
Sr	1.26	Cs	5.43	Pu	0.05
Y	0.70	Ba	2.42	Am	0.56
Zr	6.95	Gd	0.12	Cm	0.04
Mo	5.04	La	1.82	Corrosion products and additives ($\mathrm{g \cdot l^{-1}}$)	
Tc	0.85	Ce	3.56	Na	14.71
Ru	1.58	Pr	1.68	Fe	9.08
Rh	0.44	Nd	6.07	Ni	1.45
Pd	1.29	Sm	1.21	Cr	1.54
Ag	0.12	Eu	0.20	Al	3.78

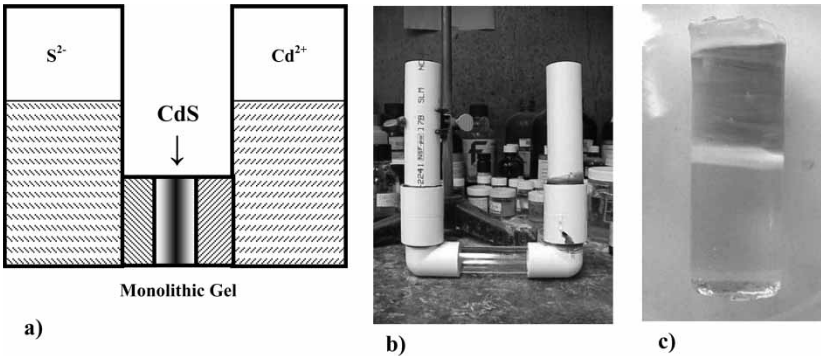

Figure 2. a) Schematic and b) photograph of the apparatus used for monolithic-gel filtration. The gel monolith was formed or glued inside a clear acrylic tube (1.9 cm inner diameter) and attached to two PVC pipes (3 cm inner diameter) with an elbow converter. Opposite tubes contained solutions of a waste simulant and of a precipitant, respectively. The contaminant and precipitant diffused into the gel and precipitates were formed, as shown in c) for CdS experiments.

Cd^{2+}, Sr^{2+}, Eu^{3+}, and Nd^{3+}. The solutions consisted of 125 mL of H_2O to which ion concentrations were added: $[Cd^{2+}] = 4.8\ g \cdot l^{-1}$ $[Sr^{2+}] = 1.3\ g \cdot l^{-1}$, $[Eu^{3+}] = 1.0\ g \cdot l^{-1}$, and $[Nd^{3+}] = 6.0\ g \cdot l^{-1}$. All simulated wastes were precipitated with a S^{2-} ion source, Na_2S, except for Sr^{2+}, which was reacted with a CO_3^{2-} ion source, $NaHCO_3$. Approximately every 12 hours, a 2 mL sample was collected from the simulant side and the ion concentration was measured. The metal concentration of the waste simulant solution was measured with atomic absorption for Cd^{2+} and with neutron activation for Sr^{2+}, Nd^{2+}, and Eu^{3+}. The measurements showed that the concentration of the ions in the simulant solution decreased steadily with time. The amount of metal absorbed by the gels was calculated from the decrease of the metal ion concentration in the waste simulant solution, and is shown in Fig. 3 for Cd^{2+}, and in Fig. 4 for Nd^{3+}, Eu^{3+}, and Sr^{2+} respectively. The absorption increased nearly linearly with time in all cases, and the absorption rates derived from linear fits to the data are reported in Table 3. We also noticed that the gels could absorb large amounts of metal without a noticeable decrease in the absorption rate. The filtering process for Cd^{2+} was stopped after 350 hours, at which point the gels had absorbed up to 1.17 mmol of Cd^{2+} per gram of dry gel. The capacity of the monolithic gels is therefore at least 35 times higher than the typical capacity of derivatized gels, which typically is between 20 and 50 μmol of metal per gram of dry gel (4). The minimum capacities of the monolithc gels are reported in Table 3. We notice that the capacity for Nd^{3+} was on the order of one mmole per gram of dry gel which is comparable to the capacity reported by the Phalippou group (26) using partially sintered aerogels, but with the advantages of an easier processing, and the potential re-usability of the filters.

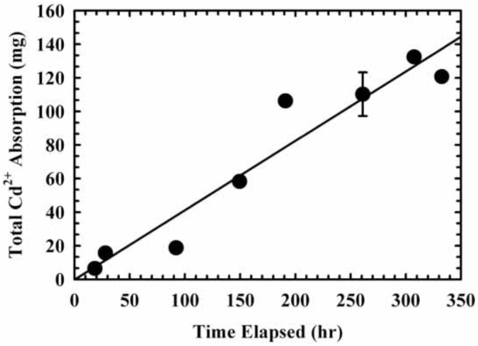

Figure 3. Absorption rate of Cd^{2+} by microporous monolithic gel filters. The contaminant concentration was $[Cd^{2+}] = 4.3\ g \cdot l^{-1}$.

The morphology of the precipitates was examined with TEM, which showed the presence of large particles with a diameter ranging from ca. 50 nm to a few microns embedded in a silica matrix. Figure 5 shows a representative image of the composites. Selected Area Diffraction analysis showed the characteristic reflections of the cubic CdS phase and further confirmed the chemical identity of the aggregates.

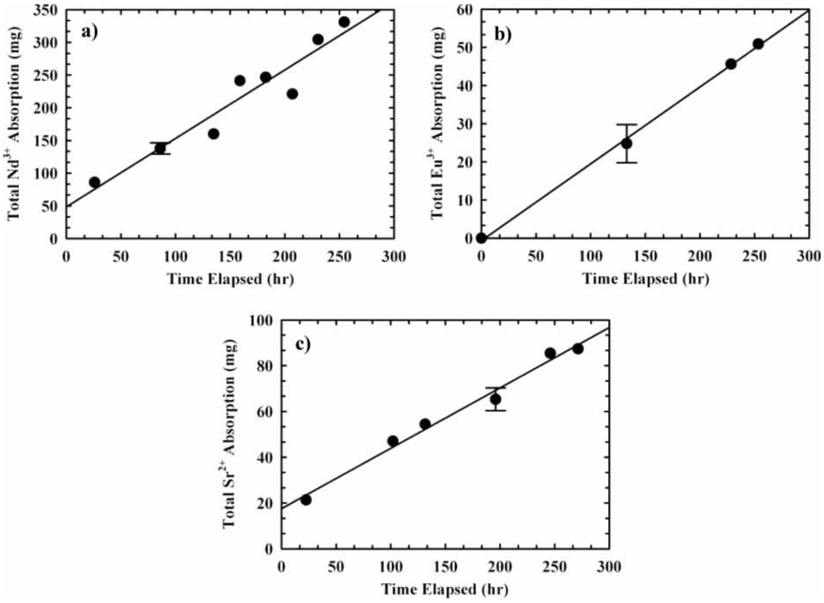

Figure 4. Absorption rates of nuclear waste simulants by microporous monolithic gel filters. The concentrations of the contaminants were $[Nd^{3+}] = 6.0\ g \cdot hr^{-1}$, $[Eu^{3+}] = 1.0\ g \cdot hr^{-1}$, and respectively $[Sr^{2+}] = 1.3\ g \cdot hr^{-1}$.

Table 3. Summary of results for monolithic gel filters. Notice that the values of the capacity were calculated based on the amount of metal absorbed at the time the experiments were stopped, typically 300 hours. Absorption had not been observed to saturate at that point and therefore the indicated capacities are to be interpreted as minimum values. The asterisk indicates the result obtained with macroporous cross-linked gels

Metal ion	Contaminant concentration ($g \cdot l^{-1}$)	Rate of absorption ($mg \cdot hr^{-1}$)	Minimum capacity ($\mu mole \cdot g^{-1}$ dry gel)
Cd^{2+}	4.3	0.442	1171
*Cd^{2+}	*4.3	*3.90	*670
Nd^{3+}	6.0	1.05	1147
Eu^{3+}	1.0	0.201	167
Sr^{2+}	1.3	0.264	498

The filtering ability of macroporous cross-linked gels was compared to that of the microporous gels by filtering a $4.3\ g \cdot l^{-1}$ solution of Cd^{2+}. The metal absorption rate is reported in Fig. 6. The data could be well reproduced by a linear fit, from which a rate of $0.692\ mg \cdot hr^{-1}$ was calculated. This rate is about 1.5 times higher than that of microporous gels, but has to be increased by another 5.6 times to account for the different cross-sections of the filters. Because of shrinking during the templating agent removal process,

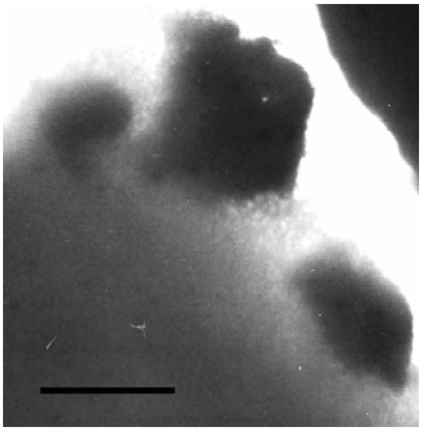

Figure 5. Bright field TEM micrograph of CdS particles formed within the bulk of silica gel filters. Dark CdS particles were observed embedded in a lighter silica matrix. The scale bar represents 200 nm.

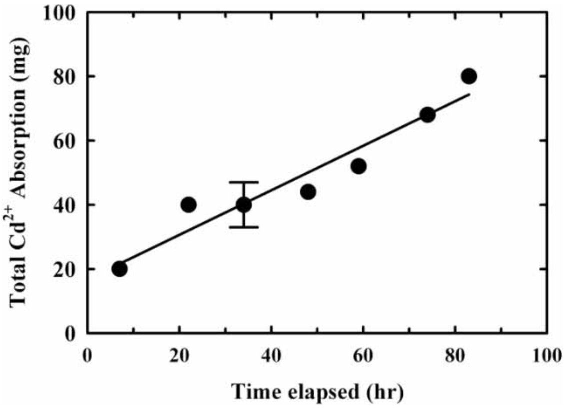

Figure 6. Absorption rate of Cd^{2+} through a macroporous gel. The contaminant concentration was 4.3 g · l^{-1}.

macroporous gels had a diameter about 2 mm smaller than the molds into which they were formed, and had to be glued to washers which had an inner diameter of 8 mm and an outer diameter equal to the inner diameter of the molds and. Microporous gels did not have any shrinking issues, and therefore the acrylic molds with a diameter of 19 mm into which they were formed could be glued directly to the PVC tubing, as shown in Fig. 2. Once the different effective diameters (8 vs. 19 mm) of the monoliths are accounted for, we obtain that absorption rates through macroporous gels are a factor 8–9 times higher than through microporous gels. The higher absorption rate of the macroporous gels is in apparent contrast with the porosity data reported in Table 1. The BET surface area of cross-linked macroporous gels is about 600 times lower than that of the microporous gels, and the porosity is a factor 2.5 lower. Thus, one would expect the absorption rate of microporous gels to be higher than that of the macroporous gels. This apparent contradiction can be explained by taking into account the interaction of the metal ions with the pore walls. Previous work by the Collinson group (27–31) has shown that the diffusion of chemical species within sol-gel materials depends on the pore size but also on the interaction between the chemicals and the pore walls. The diffusion velocity increases when the pore size is increased and it decreases when the interaction with the pore walls increases. In monoliths with narrow pores, most ions will be near the walls and interact with them. Thus, in microporous systems the interaction with the walls is the limiting factor. In systems with larger pores, the fraction of ions that interact with the walls will be much smaller, and therefore the interaction with the walls will be less important. The difference between micro- and macro-porous gels observed in our experiments can be explained in the same terms. In macroporous gels very large pores are available, a small fraction of the ions interacts with the walls, and diffusion is rapid. In microporous gels the pore density is higher but the pores are very small and diffusion is slow. Thus, the observed differences in absorption rates can be reconciled with the different diffusion velocities, which, in turn, are dictated by pore size and pore wall interactions. We think that the different termination of the pore walls in microporous and macroporous gels did not play a relevant role. In fact, the walls of microporous gels had a OH^- termination at the pH values used in our experiments ($pH > 3$ in all our experiments). These negatively charged groups probably interacted strongly with Cd^{2+} and decreased the diffusion velocity. Macroporous gels had a NH_2 termination, which might have also coordinated Cd^{2+}. However, the pores of the macroporous gels were so large that the interaction with the walls did not play a relevant role. Collinson, for example, showed that the diffusion coefficient in OH- terminated monoliths was comparable for anions and cations, provided that the pores had a diameter larger than about 20 nm. Thus, the results obtained with macroporous gels are in line with expectations, and show that macroporous cross-linked materials can be used as filter materials. The materials are also likely to be quite resilient to radiation. In fact, irradiation of polyurethane with gamma rays increases its mechanical strength due to radiation-induced cross-linking. For example, Young's modulus increased by a factor of 3 in polyurethane samples irradiated with gamma doses of 10 MGy (32). Thus, irradiation might actually increase the mechanical strength of our cross-linked materials. In the future, we plan to test the filters under more realistic and large-scale conditions. The filtering speed is probably too low for nuclear waste processing plants, where solutions with an ion concentration of several grams per liter are processed at a rate of liters per minute (33). However, the filters may be applied to waste tanks and to comparatively diluted waste streams, such as those of low-level waste.

CONCLUSIONS

We describe a method by which metal ions dissolved in water can be immobilized in sol-gel monoliths. Precipitation of metal ions inside microporous monolithic gel filters is a relatively slow, but steady process, and the capacity of monolithic gels is at least two orders of magnitude higher than for derivatized gels. More importantly, mechanically strong macroporous gels absorb metal ions at a rate on the order of milligrams per hour, which is about 8 times higher than that of microporous gels. These materials are therefore very promising for filtering applications.

ACKNOWLEDGMENTS

This work was supported by United States Department of Energy no. DE-FG07-04ID14592.

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