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ENHANCED IONIC RECOGNITION BY A FUNCTIONALIZED MESOPOROUS SOL-GEL: SYNTHESIS AND METAL ION SELECTIVITY OF DIAMINOETHANE DERIVATIVE

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ABSTRACT

A newly developed double-imprinting methodology was extended to synthesize mesoporous sol-gels that contain a diaminoethane functional group. Formation of a *bis*[(3-trimethoxysilyl)propyl] ethylenediamine metal complex, followed by hydrolysis and condensation with tetraethylorthosilicate in the presence of dodecylamine surfactant resulted in the formation of the solid xerogel. Acid washing protonated the amino groups that release the metal ions. This resulted in the formation of binding sites that are uniquely designed with the coordination environment the metal ion prefers. Mesopores were formed by the extraction of the surfactant micelles to give this material relatively large surface areas and good mass-transfer characteristics. A copper (II) imprinted gel

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showed significantly more enhancement of copper (II) uptake capacities at various concentrations than did a nonimprinted gel made without the metal ion template. The imprinted material also exhibited improved selectivity for removal of copper (II) from Cu^{2+}-Zn^{2+} aqueous solutions. A sample of the copper imprinted sorbent, which absorbed a total of 99.3% of the copper from a 10^{-4} mol/L aqueous solution, removed 95% within 15 minutes. This material has copper distribution coefficients (K_d) as high as 12 000 at 10^{-4} mol/L. A separation factor, $K > 85$, with respect to copper (II) was achieved with an aqueous Cu^{2+}-Zn^{2+} system at pH 5.0.

INTRODUCTION

Molecular imprinting involves the incorporation of a template guest species into a host matrix through a mixture of the template with host monomers that undergo polymerization around the template. Subsequent removal of the template results in a material that contains imprints with a favorable size, shape, and chemical environment to rebind the template. The imprinting approach was first developed by Wulff and Sarhan (1) who used this technique to produce polymers for the resolution of racemic mixtures. It has since been utilized in the development of artificial enzymes (2), antibodies (3,4), chromatographic resins (5), and metal ion sorbents (6).

The discovery of MCM-41 mesoporous molecular sieves by scientists at the Mobil R&D Corp (7–9) has led to many advances in the area of surfactant template synthesis of mesoporous sol-gels. Charge matching between cationic or anionic surfactants and charged inorganic precursors leads to the S^+I^- and S^-I^+ synthetic pathways (10,11). An electrically neutral assembly pathway (S^0I^0) using neutral amine surfactants has been used to produce HMS molecular sieves (12–14). The large surface areas and ordered mesostructure of these materials makes them ideal for many applications, such as catalyst supports (15) and metal ion sorbents (16,17).

Organically functionalized mesoporous molecular sieves have been shown to exhibit much higher capacities (18) and selectivities (19) for target metal ions than did amorphous silica gels with similar surface areas. Unlike an amorphous silica gel, which contains irregular pore spaces that are susceptible to blockage by organic functional groups, the cylindrical mesopores of HMS and MCM-41 allow for metal ion access to all functional groups. Furthermore, the use of different surfactants (20) and reaction conditions (21) allows one to choose the desired pore size for a specific organic functional group and metal ion.

We have been interested in harnessing the unique properties of molecularly imprinted materials for the selective removal of metal ions from mixed solutions

(19,22–24). By combining the best attributes of molecular imprinting, organic functionalization of silica, and the surfactant template approach to mesoporous silica, we have recently developed 3 unique methodologies to functionalize mesoporous silica sorbents: 1) imprint coating (19), 2) ion exchange coating (23), and 3) double imprinting (24). We describe the preparation of a mesoporous sol-gel that contains the diaminoethane functional group and is imprinted with Cu^{2+} or Zn^{2+} through the use of the double imprinting methodology. Dodecylamine (DDA) was used as the surfactant to engineer mesoporosity via the S^0I^0 neutral assembly pathway. The resulting material was characterized by nitrogen gas adsorption. The capacity, selectivity, and overall kinetics of metal ion uptake were measured by batch analysis.

In our newly developed process, surfactant micelles and metal ions both act as templates in these doubly imprinted sorbents. The metal ion and the surfactant are removed from the silica matrix via acid leaching and ethanol extraction, respectively. This results in the formation of different sized imprints of specific function within the silica matrix. On the microporous level, the removal of the metal ion from the complex leaves cavities that exhibit ionic recognition. These pores give the sorbent enhanced selectivity for the given ion. On the mesoporous level, the removal of the surfactant micelles results in the formation of relatively large pores, which give the gel an overall porosity that includes large surface areas and excellent metal-ion transport kinetics. Because the whole process utilizes template or imprinting synthesis twice and on different length scales, it can be viewed as a hierarchical double-imprinting process.

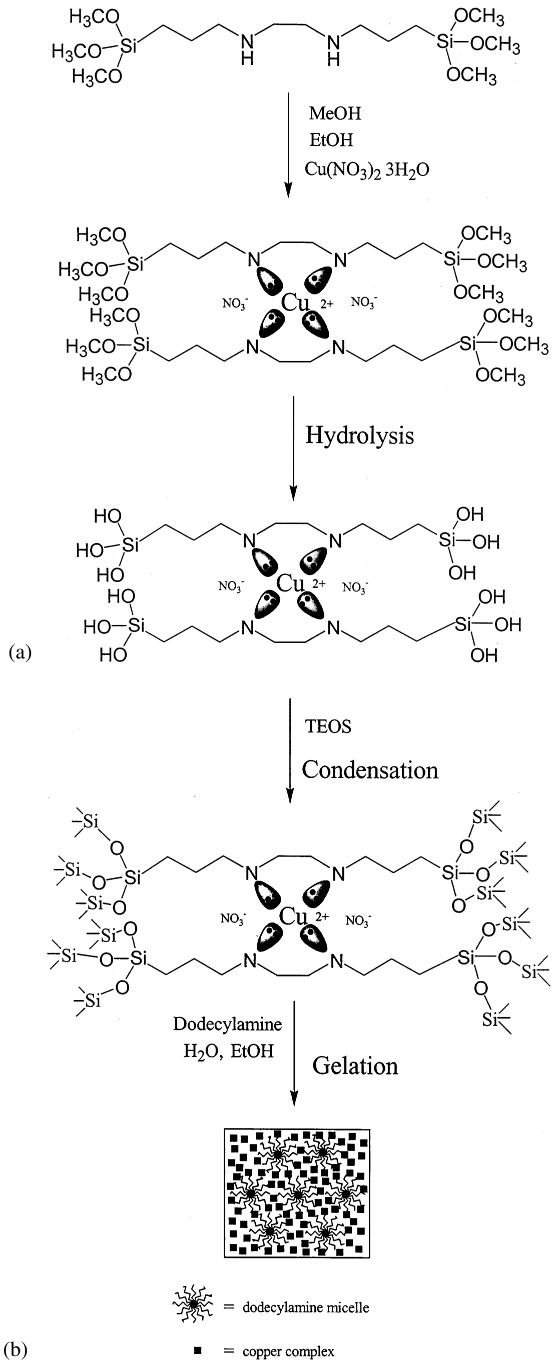
EXPERIMENTAL SECTION

Materials

Sixty-two percent *bis*[(3-trimethoxysilyl)propyl]ethylenediamine (BTMSen) in methanol was obtained from Gelest, Inc. All other chemicals were obtained from Aldrich. All chemicals were used as received.

Synthesis

In a typical procedure to produce the copper imprinted sorbent, DDA was added to ethanol and deionized water and stirred to form a micellar solution. In a separate beaker, $Cu(NO_3)_2 \cdot 3H_2O$ and BTMSen were added to ethanol in the proper stoichiometric amounts to form the 2:1 ligand to metal complex, $[Cu(BTMSen)_2]^{2+}$, which was stirred for 15 minutes. Tetraethylorthosilicate (TEOS) was then added to the metal complex solution, which was stirred for an additional 10


MeOH
EtOH
Cu(NO3)2 3H2O
Hydrolysis
(a)
TEOS
Condensation
Dodecylamine
H2O, EtOH
Gelation
= dodecylamine micelle
■ = copper complex
(b)

minutes. The dodecylamine solution was then added to the TEOS-metal complex mixture, which was covered and stirred until gelation, after which it was cured at ambient temperature for 12 hours (Fig. 1). The gel was then placed under vacuum at 80°C for an additional 12 hours. The molar ratios of the reactants were: 480 H_2O:170 EtOH:16 TEOS:4.3 DDA:2.8 BTMSen:1.4 $Cu(NO_3)\cdot 3H_20$. A nonimprinted sample was made with the identical procedure but without added metal salt. A zinc imprinted sorbent was synthesized using $Zn(NO_3)\cdot 6H_2O$, but less metal salt was used, resulting in a 3:1 ligand to metal complex, $[Zn(BTMSen)_3]^{2+}$. All sorbents were synthesized with the same amount of BTMSen.

Postsynthetic Processing

Following vacuum drying, samples were placed in excess 1 mol/L HNO_3 and stirred for 1 hour. This process resulted in protonation of the ligand amino groups and leaching of the metal from the gel. Although it contained no metal salt, the nonimprinted material was treated in an identical manner to insure the accuracy of the experimental results. Samples were then recovered by vacuum filtration and refluxed in excess EtOH-HCl solution at 90°C for 12 hours to extract all the surfactant (Fig. 2). The gels were then recovered and washed with plenty of EtOH. The resulting powders were placed in deionized water and titrated with 1 N NaOH to a pH of 7.5. The neutralized sorbents were then placed under vacuum at 80°C for 3 hours.

Batch Procedures

All metal ion solutions were buffered to a specific pH with sodium acetate–acetic acid (0.05 mol/L). In a typical run, 0.1 g sorbent and 10 mL metal ion solution were placed in a capped plastic vial and sonicated for 1 hour. The resulting mixture was filtered and the filtrate was analyzed via an inductively coupled plasma optical emission spectrometer to measure the metal ion concentration. The overall capacity of the sorbent for a given metal ion was then determined by calculating the change in concentration between the filtrate and the original metal-ion solution.

Figure 1. Synthesis of copper imprinted mesoporous sol-gel. Formation of $[Cu(BTMSen)_2]^{2+}$ in MeOH/EtOH, followed by hydrolysis and condensation with tetraethylorthosilicate (TEOS) in the presence of the dodecylamine micellar solution yields the solid product.

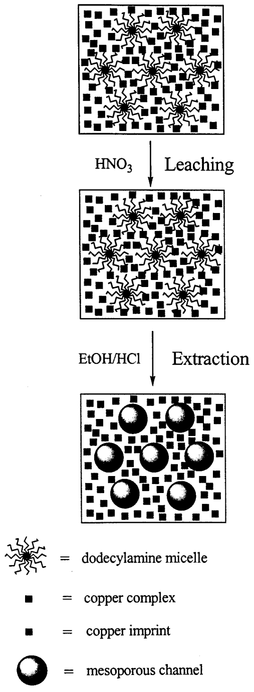


Figure 2. Postsynthetic processing. Acid leaching with 1M HNO_3 removes the Cu^{2+} ions and creates imprints. Extraction of dodecylamine micelles results in the formation of mesoporous channels.

Analysis

All metal ion concentration analyses were performed with a Thermo Jarrel Ash Iris inductively coupled plasma spectrometer. Surface areas and pore volumes were measured on a Micromeritics Gemini 2375 surface area analyzer (Micromeritics Corp). Nitrogen was used as the adsorbent. Adsorption isotherms were measured at 77 K after the samples were degassed at 80°C for 3 hours.

RESULTS AND DISCUSSION

Cu(II) Uptake Capacity

The copper imprinted sol-gel showed a greater capacity than did the non-imprinted gel for the adsorption of copper ions from aqueous solutions. The ad-

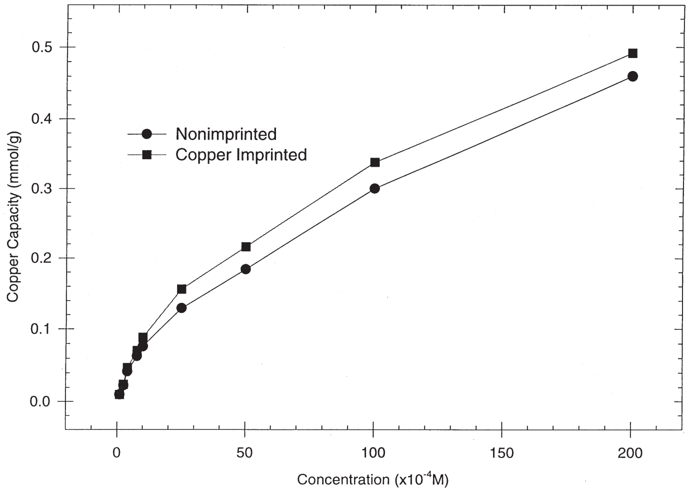


Figure 3. Copper adsorption isotherms for the copper imprinted (square) and nonimprinted (circle) sol-gels. Solutions were buffered at pH = 5.0 with HAc/NaAc (0.05M). 0.1 grams sorbent was equilibrated with 10 ml metal ion solution for one hour.

sorption isotherm at various concentrations and a pH of 5.0 is shown in Fig. 3. The ability of a sorbent to remove a specific ion from solution can be expressed in terms of a distribution constant (K_d),

$$K_d = \left(\frac{C_i - C_f}{C_f}\right) \times \left(\frac{\text{solution volume (mL)}}{\text{mass sorbent (g)}}\right) \quad (1)$$

where C_i and C_f are the initial and final concentrations of the ion in solution. Table 1 summarizes the copper uptake of the sorbents from solutions that range from 10^{-4} through 10^{-3} mol/L Cu^{2+}. A direct comparison shows the higher affinity of the imprinted gel for the Cu^{2+} and the resulting distribution coefficients. The imprinted sample absorbed more copper than did the nonimprinted sample at all concentrations studied.

Nitrogen Adsorption

Following the postsynthetic processing, a nitrogen adsorption analysis was performed on each sample. The adsorption isotherms of the copper imprinted and nonimprinted gels (Fig. 4) are very similar. The Brunauer, Emmett, and Teller (BET) surface areas (25), as calculated from the isotherms, were 286 and 294 m^2/g for the copper imprinted and nonimprinted gels, respectively. The nearly identical

Table 1. Copper Uptake Capacities and Distribution Coefficients of Copper Imprinted and Nonimprinted Sol-Gels

Sorbent	Solution Concentration (mol/L)	% Cu Absorbed	Capacity (mmol/g)	Copper *K*d
Nimp	1.0×10^{-4}	97.9	9.8×10^{-3}	4 700
Cu-imp	1.0×10^{-4}	99.3	9.9×10^{-3}	12 000
Nimp	2.5×10^{-4}	90.7	2.3×10^{-2}	979
Cu-imp	2.5×10^{-4}	98.1	2.4×10^{-2}	5 110
Nimp	5.0×10^{-4}	83.6	4.2×10^{-2}	509
Cu-imp	5.0×10^{-4}	94.7	4.7×10^{-2}	1 770
Nimp	7.5×10^{-4}	83.5	6.3×10^{-2}	507
Cu-imp	7.5×10^{-4}	93.0	7.0×10^{-2}	1 330
Nimp	1.0×10^{-3}	76.0	7.6×10^{-2}	317
Cu-imp	1.0×10^{-3}	88.2	8.8×10^{-2}	746

Nimp: Nonimprinted control sorbent.
Cu-imp: Cu(II)-imprinted sorbent.

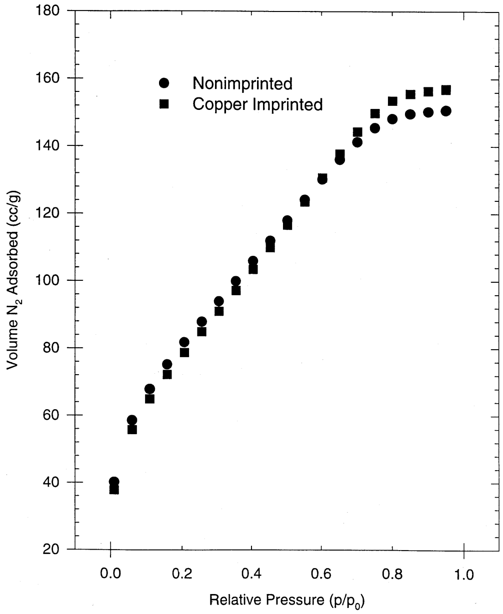


Figure 4. Nitrogen adsorption isotherms for the copper imprinted (square) and nonimprinted (circle) samples. Nitrogen volume is the standard temperature and pressure equivalent. P/P_0 is the ratio between the pressure at which the nitrogen was adsorbed and atmospheric pressure.

Table 2. Porosity Data on the Mesoporous Copper Imprinted and Nonimprinted Sol-Gels

Sample	BET Surface Area (m^2/g)	Total Price Volume (cc/g)	Pore Size (Å)
Nonimprinted	294	0.23	40
Cu-imprinted	286	0.24	45

Pore sizes represent the maximum values of the pore size distribution curve as calculated with the BJH method.

overall surface areas indicate that the increased affinity of the copper imprinted sample for the copper ion is not due to a larger available surface area. The maximum of the Barrett-Joyner-Halenda (26) pore size distribution is slightly larger for the imprinted gel, but both show a rather broad distribution in the mesoporous range. A summary of the nitrogen gas adsorption data is shown in Table 2.

Ligand Content

Based on the mass of the solid as synthesized copper imprinted material (2.43 g) and the original amount of BTMSen added (2.8 mmol), the total ligand in the material was determined to be 1.03 mmol/g. This calculation is based on the assumption that 100% of the ligand was polymerized and that none was lost during the postsynthetic treatments. The total copper added to the material was 0.52 mmol/g. In a batch test in which a relatively concentrated copper solution (0.02 mol/L) was used, the sorbents were effectively "flooded." All of the available sites were filled with Cu^{2+}. This setup can be used to find a rough estimate of the total number of sites and therefore the ligand content. In this batch test, the Cu^{2+} capacity of the copper-imprinted gel was 0.49 mmol/g, while the nonimprinted gel had a capacity of 0.46 mmol/g. Assuming that a 2:1 ligand to metal complex was formed, one can conclude that 0.98 and 0.92 mmol BTMSen per gram of gel, or 95% and 89% of the total ligand initially added, was incorporated into the material.

Kinetic Study

The copper adsorption study (Table 1) showed that 0.1 g of the imprinted sorbent removed 99.3% of the copper from 10 mL of a 10^{-4} mol/L solution. Because all the batch tests involved a 1 hour contact time, a series of tests were run with lower contact times to deduce how fast the adsorption process occurs. The re-

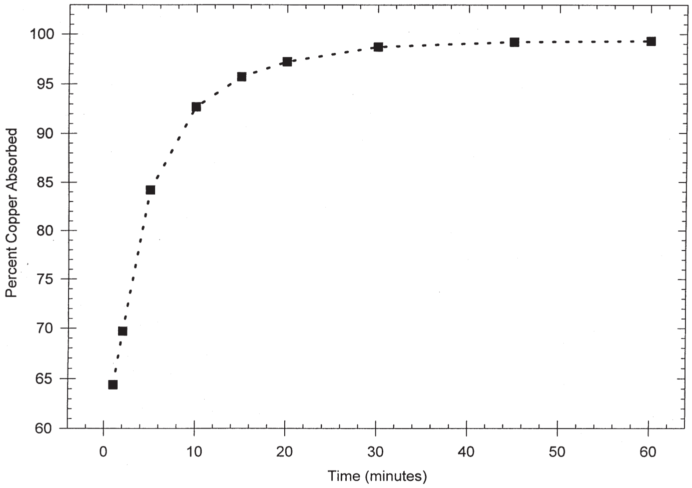


Figure 5. Percent copper absorbed from 10^{-4}M solution (pH 5.0) versus contact time for the copper imprinted sol-gel. 0.1 grams sorbent was placed in 10 ml metal ion solution for each data point.

sults (Fig. 5) show that approximately 84% of the copper was adsorbed in the first 5 minutes and that over 95% adsorption occurred within 15 minutes. The overall kinetics of these functionalized mesoporous sol-gels with respect to metal ion adsorption are clearly better than those of microporous materials (27) and most polymer-supported reagents, but they are not as fast as surface functionalized mesoporous materials (17).

Metal Ion Selectivity

Competitive ion binding studies were run with Cu^{2+} and Zn^{2+} to measure the selectivity of the imprinted material. The Zn^{2+} was chosen as the competitor species because it has the same charge, nearly identical size, and binds well with the diamine ligand. Zinc is also usually present in industrial effluents containing copper, such as electroplating waste and acid mine drainage (28). A selectivity coefficient, K, for the binding of a specific metal ion in the presence of a competitor species can be obtained from equilibrium binding data (6) according to Eq. (3):

$$M_1(\text{solution}) + M_2(\text{sorbent}) \leftrightarrow M_2(\text{solution}) + M_1(\text{sorbent}) \tag{2}$$

$$K = \left(\frac{[M_2]_{\text{solution}}\,[M_1]_{\text{sorbent}}}{[M_1]_{\text{solution}}\,[M_2]_{\text{sorbent}}}\right) = \frac{K_d(\text{Cu})}{K_d(\text{Zn})} \tag{3}$$

The K values for the imprinted and control blank gels show the effect that imprinting has on the metal ion selectivity for a given material. The results of competitive ion-binding batch tests at pH 5.0 are summarized in Table 3. As expected, due to the higher stability constants of copper with the diamine ligand (29), both the imprinted and nonimprinted sorbents absorbed more copper than zinc. When equilibrated with solutions containing the same concentration of both ions, the imprinted gel absorbed more copper than zinc over the blank gel. This results in a substantial increase in the copper distribution coefficient for the imprinted material, while the K_d values for zinc stay nearly the same. The values of K show that the imprinted sample was more selective for the Cu^{2+} than was the nonimprinted sample. In a solution that contained a large excess of zinc ions (0.001 mmol/L Cu/0.01 mol/L Zn), the imprinted material absorbed less zinc than did the control blank. In this case, the total number of ions in solution exceeded the number of binding sites so the increased affinity for copper was more pronounced and resulted in a lower K_d for zinc.

Effect of pH on Metal Ion Selectivity

The pH dependence for sorption of Cu^{2+} and Zn^{2+} was investigated over the pH range 3.0 through 5.5 (Fig. 6). The concentrations of all solutions were 5×10^{-3} mmol/L with respect to both copper and zinc. The metal ion adsorption was enhanced for both metals by increased pH. Both the copper imprinted and nonimprinted gels absorbed more Cu^{2+} than Zn^{2+} over the entire pH range. At pH values less than 5.0 no zinc was absorbed.

Table 3. Competitive Loading of M_1 (Cu^{2+}) and M_2 (Zn^{2+}) by Copper Imprinted and Control Blank Samples

	Concentrated (mol/L)		% Absorbed		K_d		
Sorbent	Cu	Zn	Cu	Zn	Cu	Zn	K
Nonimprinted	.0005	.0005	93.5	28.5	1 430	40	36
Cu-imprinted	.0005	.0005	97.4	30.0	3 780	43	88
Nonimprinted	.001	.001	85.3	16.4	580	20	30
Cu-imprinted	.001	.001	90.1	17.7	914	22	42
Nonimprinted	.001	.01	82.2	6.1	463	6.5	71
Cu-imprinted	.001	.01	86.6	5.6	643	6.0	110

Concentrations are initial solution concentrations at pH 5.0 in HAc-NaAc buffer.

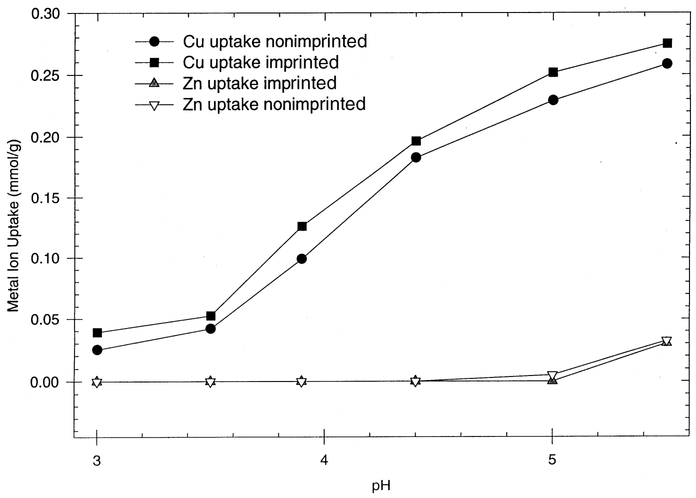


Figure 6. $Cu^{2+}$and Zn^{2+} uptake by the copper imprinted and nonimprinted sorbents in the pH range 3.0–5.5, buffered with HAc/NaAc (0.05M). All solutions were 5×10^{-3}M w.r.t. both copper and zinc.

Zinc Imprinted Sol-Gel

The synthesis of the zinc imprinted sorbent was similar to that of the copper imprinted sample with the exception of the complex stoichiometry. While the copper imprinted material utilized a 2:1 ligand to metal complex, the zinc imprinted gel was synthesized using a 3:1 BTMSen to metal complex, giving zinc the octahedral coordination environment that it prefers (30). Table 4 summarizes the results of competitive ion binding tests between Cu^{2+} and Zn^{2+} at a concentration of

Table 4. Competitive Loading of Cu^{2+} and Zn^{2+} by the Copper Imprinted, Zinc Imprinted, and Control Samples

	Concentration (mol/L)		% Absorbed		K_d	
Sorbent	Cu	Zn	Cu	Zn	Cu	Zn
Nonimprinted	10^{-4}	10^{-4}	97.2	36.4	3 470	57
Cu-imprinted	10^{-4}	10^{-4}	98.1	54.1	5 050	118
Zn-imprinted	10^{-4}	10^{-4}	99.0	98.1	9 460	5 090

Concentrations are the initial solution concentrations at pH 5.0 in HAc-NaAc buffer.

10^{-4} mol/L with the 3 different sorbents used in the study. The zinc imprinted sample demonstrates a dramatic enhancement in zinc uptake over the nonimprinted sample as demonstrated by an increase in K_d of nearly 2 orders of magnitude. Despite this, the thermodynamic advantage of copper over zinc with respect to ethylenediamine complexation (29) cannot be overcome via metal ion imprinting, as the zinc imprinted sample was unable to preferentially bind Zn^{2+} over Cu^{2+}.

CONCLUSIONS

The double imprinting methodology has been used to synthesize mesoporous sol-gel materials that exhibit enhanced ionic recognition. Metal ions and supramolecular assemblies of surfactant molecules are both used as templates in this system. Removal of the templates creates two types of pores, each with a specific function. Acid washing removes the metal ions and creates micropores that contain binding sites with the size, shape, and coordination environment that the metal ion prefers. Extraction of surfactant micelles results in the formation of mesoporous channels throughout the sorbent matrix, giving the material good metal ion transfer kinetics.

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