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REMOVAL OF COPPER IONS USING FUNCTIONALIZED MESOPOROUS SILICA IN AQUEOUS SOLUTION

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REMOVAL OF COPPER IONS USING FUNCTIONALIZED MESOPOROUS SILICA IN AQUEOUS SOLUTION

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ABSTRACT

Mesoporous silica was synthesized as a support for the removal of copper ions in aqueous solutions. The Sol-gel method in conjunction with neutral surfactants was used. The remaining surfactants were removed by either the Soxhlet or microwave extraction method. Both extractions resulted in the same pore structure of the mesoporous silicas. However, the microwave extraction method reduced the amount of solvents as well as the time required for removing the remaining organic surfactants. 3-(2-aminoethylamino)propyltrimethoxysilane was functionalized onto the mesoporous silica surface. The functional agent removed copper ions and was bonded to the silica surface via covalent bonding. In addition, it was hydrophilic in nature, which reduced external mass-transfer resistance. The removal capacity of mesoporous silica is about 10 times larger than that of a commercial silica, largely because the mesoporous silica has a larger surface area as well as uniform pore structure. The experimental results and model prediction

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were in good agreement. The results of sensitivity analysis suggested that the mass transfer rate was so fast that little resistance of external mass transfer and diffusion was possible.

INTRODUCTION

Processes for the removal of heavy metals using materials with impregnated ion-chelating agents have generated considerable interest (1–4). For a successful process, the impregnated materials need to be stable at both acid and alkaline conditions, be selective with respect to a specific heavy metal, and have a large capacity. Inorganic materials have been used for this purpose because they are mechanically and chemically stable and have a large surface area. However, the capacity of inorganic powder has limitations. For example, when the pores of inorganic silica are impregnated with bulky organic materials, the surface area available for metal removal is decreased. Mesoporous silica made via a templating mechanism (5–6) can reduce this bottleneck phenomenon because it is capable of achieving a uniform pore structure. In addition, it provides a much larger surface area than commercial silica. Several researchers reported the successful removal of mercury ions using mesoporous silica (7–9).

When mesoporous silicas are synthesized using templates, calcination or solvent extraction is generally used to remove the template compounds. The template-removal step is typically time consuming. If ionic surfactants are used to prepare mesoporous silica, the silica framework and the templates are bound by electrostatic force. The template, which is held together by electrostatic force, can be removed only by calcination. Instead of ionic surfactants, neutral surfactants ensure that the framework and the template are combined via hydrogen bonding, and the neutral template can be separated by simple solvent extraction (10–11). While calcination destroys the uniform pore structure, the solvent extraction method maintains its uniformity. In addition, the silica wall is thick and mechanically strong. However, it takes 1–3 days for the templates that remain inside the pores to be removed by Soxhlet extraction. Unlike Soxhlet extraction, which has been generally used in the preparation of mesoporous silicas, microwave extraction can greatly reduce the required time and the amount of solvent needed to remove the template from the silica. Microwave extraction has been used in solvent extraction, pretreatment for high-performance liquid chromatography (HPLC), gas chromatography, gel permeation chromatography, and organic synthesis (12). The technique has been shown to have no influence on the molecular structure of samples. This report describes a study about the effect of microwave extraction and Soxhlet extraction.

To remove heavy metal ions from aqueous solutions, the surface of mesoporous silica needs to be functionalized by a chelating agent that has a selective reactivity for the target metal ion. The chelating ligand should be capable of co-

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valent bonding; when the agent binds to the silica surface via physical adsorption, the immobilized chelating ligand can be easily eluted. In addition, the material should be hydrophilic. Many heavy metal–chelating agents are hydrophobic. The hydrophobic agents result in an increase of mass transfer resistance (13). This external mass-transfer resistance can be reduced when an appropriate hydrophilic agent is selected and functionalized. Khatib and Parish (14) and Taylor and Howard (15) reported that a primary amine has an excellent capacity for the removal of Cu ions in aqueous solutions. In this study, an amine functional group was selected as a functionalizing agent. In addition, mass transfer characteristics were investigated by modeling the process.

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MODELING EQUATIONS

The overall rate of metal uptake is dependent on the following steps: 1) external mass transfer of heavy metal ions from the bulk solution to the outer surface of the powder, 2) diffusion of heavy metal ions through the pores of the powder, and 3) the adsorption of heavy metal ions with functional agents on the pore surface.

The model is based on the following assumptions: 1) diffusivity is constant at constant temperature and pressure, 2) the powder particles are completely spherical, 3) the concentration of the functional agent is uniformly distributed within the powder, 4) the external mass-transfer coefficient and diffusivity are constant for various initial metal-ion concentrations, and 5) no surface diffusion of copper ion occurs. According to Leyden and Luttrell (16), the adsorption of copper ion to untreated silica is negligible when pH is below 4.

Metal-ion concentration change in the bulk solution is proportional to the concentration difference between the bulk phase and the outer surface of the powder.

$$-\frac{\partial C}{\partial t} = \frac{M_p 3k_f}{VR\rho_p}(C - C_R) \tag{1}$$

Where C is the concentration of metal ions in the bulk phase, and C_R is the concentration of metal ions at the outer surface of the spherical powder. R represents the radius of the powder; ρ_p is the density; and M_p is the total mass of the powders. V is the total volume used in the batch reactor, and k_f is the external mass-transfer coefficient.

The mass balance of metal ions within a powder is as follows:

$$\varepsilon_p \frac{\partial C_r}{\partial t} + \rho_p \frac{\partial q_r}{\partial t} = D_M \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial C_r}{\partial r}\right) \tag{2}$$

where D_M is the effective diffusivity of metal ion within the powder; ε_p is the porosity; C_r is the concentration of metal ions within the powders; and q_r is the concentration of functional agent–metal ion complex.

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The Freundlich isotherm ($q_r = KC_r^{1/n}$) can be used for the correlation of C_r and q_r.

$$\frac{\partial C_r}{\partial t} = \frac{D_M}{\varepsilon_p + (\rho_p K/n)C_r^{(1-n)/n}} \frac{1}{r^2} \frac{\partial}{\partial r}\left(r^2 \frac{\partial C_r}{\partial r}\right) \tag{3}$$

The initial and boundary conditions can be given as follows:

$$t = 0 : C = C_0, C_r = 0 \tag{4}$$

$$r = 0 : \left.\frac{\partial C_r}{\partial r}\right|_{r=0} = 0 \tag{5}$$

$$r = R : k_f\ (C - C_R) = D_M \left.\frac{\partial C_r}{\partial r}\right|_{r=R} \tag{6}$$

The modeling equation can be written into dimensionless forms,

$$-\frac{\partial X}{\partial \theta} = Bi\,\frac{3M_p}{V\rho_p}\,(X - X_R) \tag{7}$$

$$\begin{aligned}\frac{\partial X_r}{\partial \theta} &= \frac{1}{\varepsilon_p + (\rho_p K/n)(C_0 X_r)^{(1-n)/n}} \frac{1}{x^2} \frac{\partial}{\partial x}\left(x^2 \frac{\partial X_r}{\partial x}\right) \\ &= f(X_r) \frac{1}{x^2} \frac{\partial}{\partial x}\left(x^2 \frac{\partial X_r}{\partial x}\right)\end{aligned} \tag{8}$$

$$\theta = 0 : X = 1, X_r = 0 \tag{9}$$

$$x = 0 : \left.\frac{\partial X_r}{\partial x}\right|_{x=0} = 0 \tag{10}$$

$$x = 1 : \left.\frac{\partial X_r}{\partial x}\right|_{x=1} = Bi(X - X_R) \tag{11}$$

To solve the governing equations, a set of partial differential equations were changed to coupled ordinary differential equations using finite difference methods. The resulting equations may be written as

$$\frac{\partial X_i}{\partial \theta} = f(X_i)\left\{\frac{X_{i+1} - 2X_i + X_{i-1}}{(\Delta x)^2} + \frac{X_{i+1} + X_{i-1}}{i(\Delta x)^2}\right\} \tag{12}$$

Boundary conditions in equations (10) and (11) may be given as

At the center of the sphere, $i = 1$,

$$\frac{\partial X_1}{\partial \theta} = f(X_1)\left\{\frac{2(X_2 - X_1)}{(\Delta x)^2}\right\}$$

At the surface of the sphere: $i = \mathrm{N}$,

$$\frac{\partial X_N}{\partial \theta} = f(X_N)\left\{\frac{X_{N-1} + 2\Delta x Bi(X - X_N) - 2X_N + X_{N-1}}{(\Delta x)^2} + \frac{2Bi(X - X_N)}{i(\Delta x)}\right\}$$

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Table 1. Dimensionless Group

$X = \dfrac{C}{C_0}$,	$X_r = \dfrac{C_r}{C_0}$,	$Bi = \dfrac{k_f R}{D_M}$,	$\theta = \dfrac{tD_M}{R^2}$,	$x = \dfrac{r}{R}$

The total N + 1 coupled ordinary differential equation for $X, X_1, X_2, \ldots X_N$ can be solved using the Adams-Gear method. The IVPAG subroutine of the International Mathematics and Statistical Library was used to solve the coupled ordinary differential equations. The dimensionless groups used in this study are listed in Table 1.

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MATERIALS AND METHODS

Preparation of Mesoporous Silica Support

HMS (hexagonal mesoporous silica) was synthesized based on a neutral pathway (17). Dodecylamine, $CH_3(CH_2)_{11}NH_2$ (Aldrich Chemical Co), was used as a neutral template. After dissolving 1 g of dodecylamine in 15.8 mL of ethanol, 20 g of deionized water was added to the solution under vigorous stirring. Tetraethoxysilane of 4.5 g, $Si(OC_2H_5)_4$ (Aldrich Chemical Co), was then added drop wise to the rigorously stirred mixture. The silica mixture solution was aged for 24 h. The product was filtered and air-dried for 24 h at room temperature. The template that remained within the silica was removed by extraction. Both Soxhlet and microwave extractions were used. On hundred milliliters of ethanol per 1 g of the silica was used as a solvent for Soxhlet extraction, and 20 mL of ethanol was used for microwave extraction. A microwave extraction system (MES-1000, CEM Co) was used for the microwave extraction. Both the extracted silicas were washed with deionized water and dried in a vacuum for 1 h.

Functionalization of Mesoporous Silica

3-(2-aminoethylamino)propyltrimethoxysilane, $NH_2(CH_2)_2NH(CH_2)_3Si(OCH_3)_3$, (AAPTS) was used as a functional agent for the adsorption of copper ions from aqueous solutions. One gram of Soxhlet-extracted silica was dried at 100°C in an oven for 12 h to completely remove water. For impregnation with AAPTS, a vacuum was applied through a vacuum evaporator for 10 min, followed by the addition of 1 g of AAPTS mixed with 20 mL of toluene for 4 h. Functionalized silica was washed 3 times with 100 mL of toluene and 2 times with 100 mL of acetone. One gram of functionalized silica was solvent extracted with 100 mL of ethanol to remove the unreacted reagent. The silica was then washed with deionized water and kept in a dry oven for further use.

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A commercial silica (Fuji Silysia Chemical Co) was also used as a reference for comparison with mesoporous silica. The silica was washed 2 times with 100 mL of hydrochloric acid (0.1 mol/L), rinsed with deionized water, and then oven dried at 110ºC for 24 h. The process for the functionalization was the same as that for mesoporous silica.

Removal of Copper Ions

Equilibrium isotherms were obtained by equilibrating 0.3–3.0 mmol/L solutions of copper ions with 0.1 g of the functionalized silica powders at pH 3. $Cu(NO_3)_2 \cdot 3H_2O$ (Junsei Chemical Co) was used to prepare copper ion solutions. The buffer solutions were used to maintain a constant hydrogen ion concentration. A pH 3 buffer solution was prepared with 0.1 mol/L $C_8H_5KO_4$ and 0.1 mol/L HCl. Transient adsorption experiments were carried out using a packed-column reactor. A Pyrex tube (11 mm i.d.) was packed with 1.2 g of the AAPTS-functionalized silica powders. The apparatus also was comprised of a circulation pump (Cole-Parmer) and a flow meter. The 90-cm^3 feed solution containing 2 mmol/L of copper ion was fed into the reactor and recycled to the solution bath at a rate of 2.5 mL/min. The concentration of copper ions was measured using an atomic absorption spectrometer (Perkin-Elmer, Model 3110).

RESULTS AND DISCUSSIONS

Comparison of Mesoporous Silica and Commercial Silica

Results of Brunauer-Emmett-Teller BET analysis for a commercial silica and the Soxhlet- and microwave-extracted mesoporous silica are listed in Table 2.

Table 2. BET Analysis

	BET Surface Area (m^2/g)	Pore Diameter (nm)	Pore Volume (cm^3/g)
A commercial silica	294	14.7[a]	1.16
Mesoporous silica, Soxhlet extracted	1062	2.46[b]	1.15
Mesoporous silica, microwave extracted	995	2.47[c]	1.12

[a] Barrett-Joyner-Halenda adsorption average pore diameter.
[b,c] Pore diameter at maximum peak of pore size distribution.

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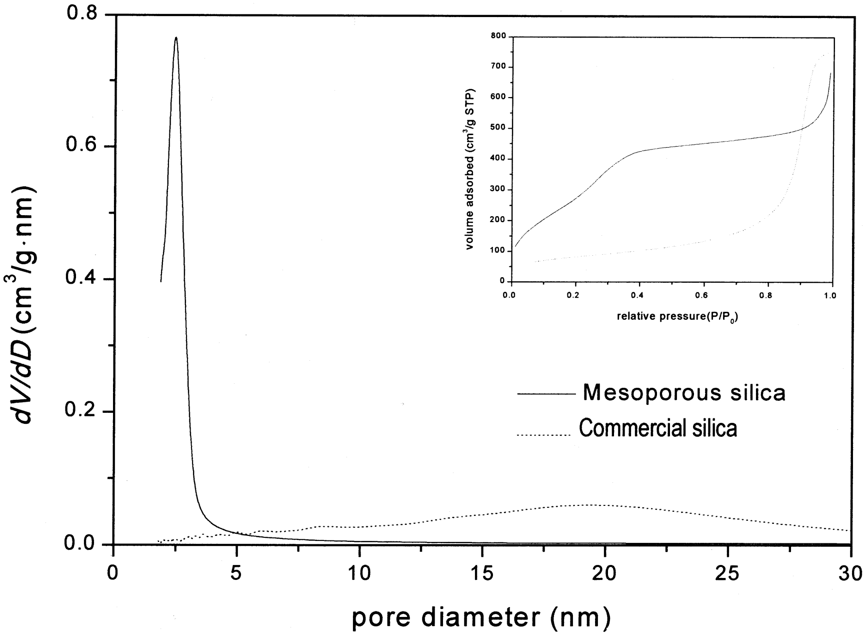

Figure 1. Pore size distribution based on Barrett-Joyner-Halenda method for mesoporous and commercial silica. Inner graph shows nitrogen adsorption isotherms.

While the pore volumes of the samples studied are similar, the surface area of the mesoporous silica shows more than three times larger than that of the commercial silica. This suggests that large amounts of functionalizing agents are capable of attaching to supports. The pore size distribution (PSD) for each silica is shown in Fig. 1. Mesoporous silica has narrow PSD, which represents uniform pore structure. The uniform pores prevent bottleneck phenomena after functionalization.

Effect of Extraction Methods

The advantages of microwave extraction are shown in Table 3. Microwave extraction requires much less time than does Soxhlet extraction. CHN analysis (Leco, CHNS-932) shows that a microwave extraction for 40 min has the same effect as a Soxhlet extraction for 36 h. The fraction of remaining nitrogen that expresses the amount of remaining surfactant is 0.21% for microwave extraction after 40 min and 0.22% for Soxhlet extraction after 36 h. Figure 2 provides BET (Micromeritic, ASAP 2010) and X-ray diffraction (XRD) (MAC/Science Co, MXP 18 XHF^{22} SRA) data of the Soxhlet- and the microwave-extracted silica.

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Table 3. A Comparison of Soxhlet Extraction and Microwave Extraction

	Soxhlet Extraction	Microwave Extraction
Time required	1–3 days	< 1 h
Solvent amount	100 mL/g	20 mL/g
Residue fraction of N-component	36 h: 0.22%	
	72 h: 0.08%	40 min: 0.21%

Both of BET and XRD results indicate no differences of silica pore structure exist, whether the templates were extracted using Soxhlet extraction and microwave extraction. While no differences were found in the pore structure between the two methods, microwave extraction clearly makes the synthesis process faster and more effective. The d_{100} values of both samples were equal to 4.20 nm. Each of the pore diameters, obtained from BET data, is 2.46 and 2.47 nm, and therefore, the pore wall thickness was determined to be 1.74 and 1.73 nm, respectively.

Immobilization of Functional Agent

A total of 2.43 mmol/g of AAPTS was functionalized onto the pore surface. After the functionalization of the AAPTS, the nitrogen content was determined. Fourier-transform infrared spectrometry (FTIR) (Jasco Co FT/IR-200) data are shown in Fig. 3 for each modification step. The data represent untreated silicas and silicas that had been functionalized with AAPTS. The peak around 3500 cm^{-1} was determined to represent an $-$OH group. This peak indicates that the silica surface was sufficiently activated. The broad peaks of the functionalized silica between 3500 cm^{-1} and 3000 cm^{-1} represent a complex of $-$OH and $-NH_2$ peaks. The peak at 1476 cm^{-1} of the functionalized silica represents the bending of a secondary amine. FTIR data show no corresponding peak for untreated silicas. The amine peak confirms the existence of covalent bonding between the functionalizing agent and the silica surface.

Capacity of Functionalized Silica

The removal capacity of silica that has been functionalized with AAPTS is shown in Table 4. A comparison shows that mesoporous silica had over 10-times larger copper removal capacity than does the commercial silica. This cannot be explained solely by an increase in surface area. The surface area of mesoporous silica was only about 3 times that of the commercial silica. These phenomena may be due to the uniformity of pore structure. Because the uniform pore structure re-

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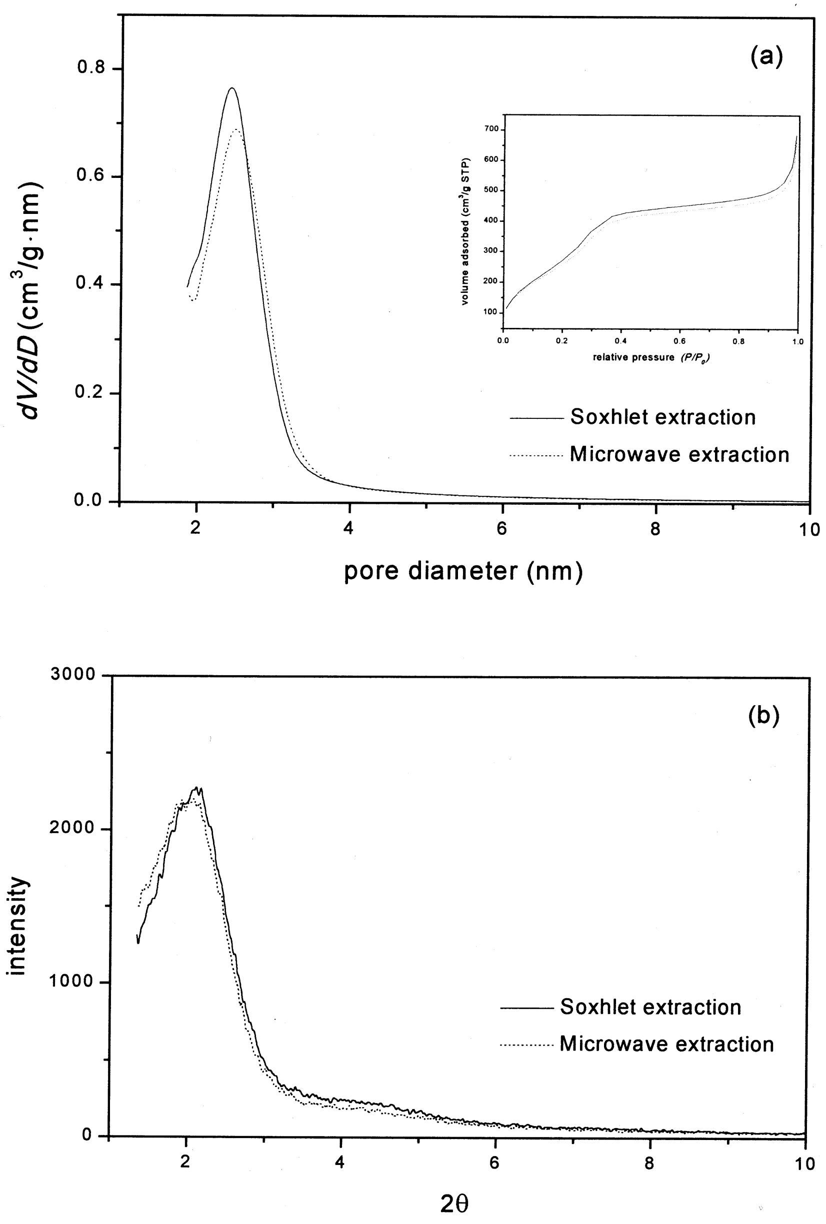

Figure 2. (a) Pore size distribution. (b) Powder X-ray diffraction patterns for Soxhlet and microwave extracted mesoporous silica.

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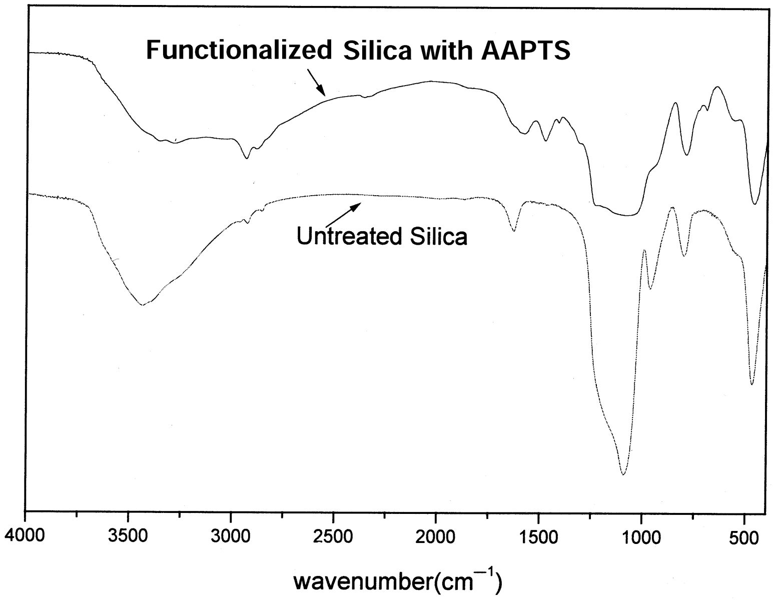

Figure 3. FTIR for untreated and treated silica.

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sulted in no bottleneck phenomena, the increase in capacity was much larger than the increase in surface area.

Removal of Cu Ions in a Semibatch Reactor

To determine the value of K and n in the isotherm equation $q_r = KC_r^{1/n}$, equilibrium isotherms were obtained. As a result of regression, $K = 0.2370$ and $n = 1.54$ were obtained. An experiment in a semibatch reactor was performed.

Table 4. Removal of Copper Ions by Functionalized Silica

Kind of Silica		Removal Capacity (mmol/g)
Untreated Silica	Commercial Silica	0.001
	Mesoporous Silica	0.004
Functionalized Silica	Commercial Silica functionalized with AAPTS	0.012
	Mesoporous Silica functionalized with AAPTS	0.107

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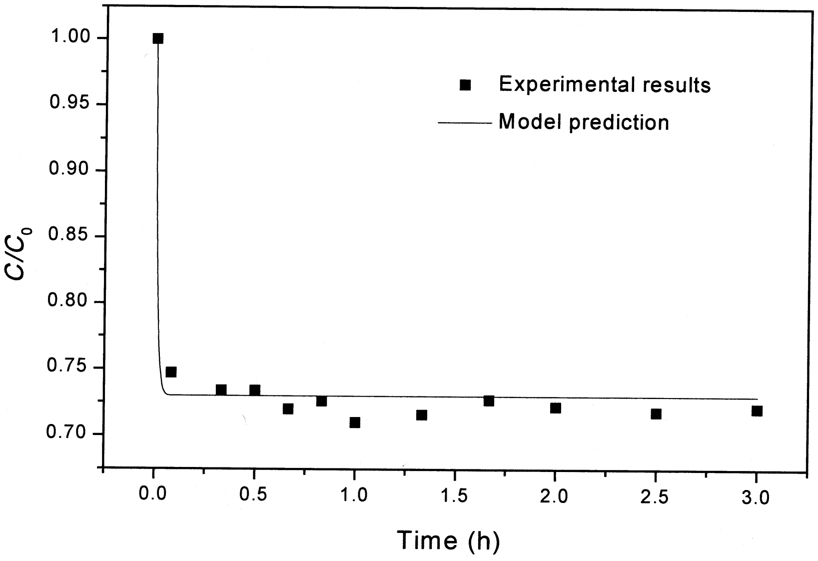

Figure 4. Comparison of experimental data and simulation results for Cu removal in semibatch reactor.

Figure 4 shows that copper ions were removed very rapidly at the beginning of the experiment. Five minutes after the start of the reaction, steady state was reached.

Modeling was performed to explain experimental results. The external mass-transfer coefficient (k_f) and the effective diffusivity (D_M) were unknown parameters in the model equation. The effective diffusivity can be expressed as $\varepsilon_p D_{AB}/\tau$ because D_{AB}, a molecular diffusivity of copper ions in aqueous solution, is known (4); the unknown parameter is tortuosity, τ. The tortuosity for solids is generally 2–8 (18). In this modeling, the tortuosity of mesoporous silica was assumed to be the same as that of the commercial silica. We found in a previous study (13) that the tortuosity of a commercial silica is 4.4. The estimated $D_M = 7.76 \times 10^{-7}$ cm^2/s.

To determine k_f, the correlation equation for a packed bed was used (19):

$$k_f = 1.17\mathrm{Re}^{-0.415}\,\mathrm{Sc}^{-2/3}\,v_0$$

The kinetic parameters used in this study are shown in Table 5. For this system, k_f was calculated as 2.2×10^{-3} cm/s.

The comparison of experimental results and the model prediction, illustrated in Fig. 4, shows good agreement. Sensitivity analyses for changes of k_f and D_M were performed. Figure 5 represents the effect of k_f on model prediction results. If k_f is 10–100 times smaller than the estimated value (2.2×10^{-3} cm/s), the initial

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Table 5. Material Properties and Operating Conditions for the Copper Ion Removal System

C_{M0}	2 mmol/L	μ	0.0089 g/cm·s
pH	3	M_p	1.2 g
R	0.005 cm	V	90 mL
ε_p	0.283	Q	2.47 mL/min
ρ_p	0.246 g/cm^3	Diameter of bed	1.1 cm

removal rate was slower. However, when k_f values exceed the estimated value such as 1×10^{-2} cm/s, the removal rate remained unchanged. Because the external mass transfer is sufficiently fast for ion removal, the increase in the external mass-transfer rate has no influence on the entire removal process. If a hydrophobic material was used as a functionalizing agent, the external mass transfer would be the rate-limiting step (13). Because a hydrophilic functionalizing agent that has an amine group is used in this study, the external mass-transfer problem can be avoided.

The effect of tortuosity was examined. For tortuosity of 2–8, the modeling results show little difference among them. This confirms that the possible error in tortuosity was negligible in the final model prediction.

Figure 6 shows the effect of diffusivity. If D_M is 10–100 times smaller than the specificed value (7.76×10^{-7}cm^2/s), the removal rate becomes slower. How-

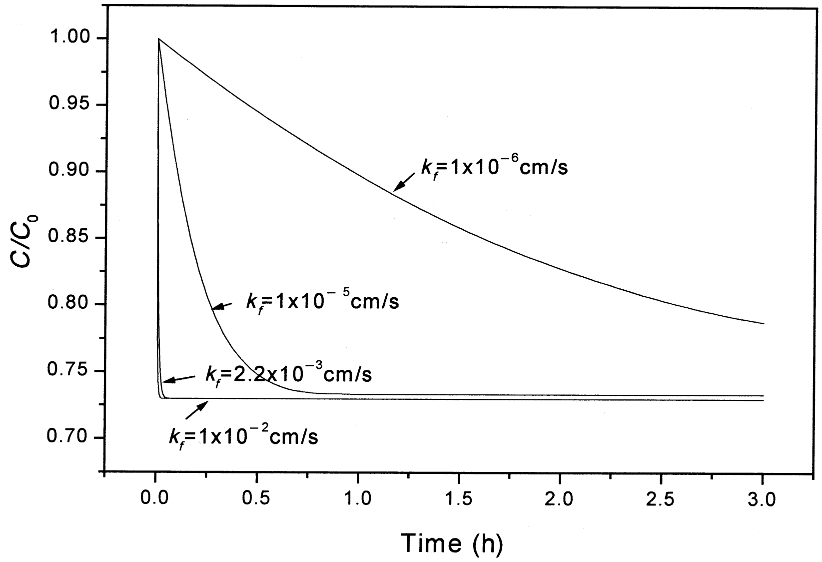

Figure 5. Effect of external mass-transfer coefficient on model prediction.

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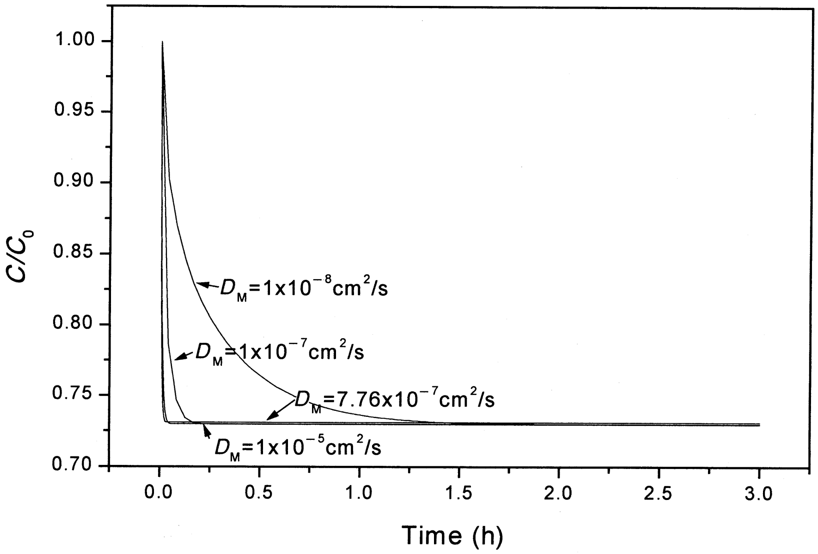

Figure 6. Effect of effective diffusivity on model prediction.

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ever, when D_M is larger than the estimated value, the removal rate is similar to that of the estimated value. As with the case of external mass transfer, diffusion has little resistance. This is due to textural mesoporosity, which is a unique property of HMS produced using neutral surfactants (20). The textural mesoporosity that results from the aggregates of small particles facilitates the diffusion of copper ion into the silica.

CONCLUSIONS

Mesoporous silica was manufactured for copper ion removal. A neutral amine surfactant was used to facilitate the removal of the remaining surfactant and then prevented the destruction of the pore structure. Silicas using Soxhlet and microwave extraction methods have the same pore structure. Microwave extraction has more advantages because the time required to complete the process is much smaller than it is with the Soxhlet method. An ideal functionalizing agent should remove copper ions selectively and bind with the silica surface via covalent bonding. In addition, it should be hydrophilic to avoid external mass-transfer resistance. An agent for which these conditions were satisfied, 3-(2-aminoethylamino)propyltrimethoxysilane (AAPTS), was immobilized on the mesoporous silica surface. FTIR data confirm the existence of the covalent bonding between

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the silica surface and amine. The functionalized mesoporous silica removed the copper ions from aqueous solution. The removal capacity of mesoporous silica is over 10 times larger than that of the commercial silica. This is the result of the large surface area and the uniform pore structure. A semibatch reactor with a fixed bed was used to examine the characteristics of mesoporous silica for mass transfer. The experimental result and model prediction are in good agreement. The results of sensitivity analysis confirm that the mass transfer rate was so fast that there was little resistance of external mass transfer and diffusion. Because hydrophilic functionalizing agents were used, there was little external mass-transfer resistance. In addition, the textural mesoporosity can reduce diffusion problems.

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NOMENCLATURE

C	concentration of metal ions in bulk phase (mol/cm^3)
C_0	initial concentration of metal ions in bulk phase (mol/cm^3)
C_R	concentration of metal ions at the outer surface of the spherical powders (mol/cm^3)
C_r	concentration of metal ions within the powders (mol/cm^3)
D_M	effective diffusivity (cm^2/s)
K	pre-factor in the isotherm equation (mol$^{(n-1)/n}$/g·cm$^{3/n}$)
k_f	external mass-transfer coefficient (cm/s)
M_p	total mass of powders in the packed bed (g)
n	exponential index in isotherm equation
q_r	concentration of functionalizing agent–metal ion complex (mol/g)
R	radius of powder (cm)
Re	Reynolds number
Sc	Schmidt number
V	total volume used in batch reactor (cm^3)
v_o	superficial velocity (cm/s)

Greek Symbols

ε_p	Porosity of powders
ρ_p	Density of powders (g/cm^3)
τ	Tortuosity of powders

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