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Preparation of Functionalized Mesostructured Silica Containing Magnetite (MSM) for the Removal of Copper Ions in Aqueous Solutions and Its Magnetic Separation

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ABSTRACT

The removal of copper ions from an aqueous solution by both adsorption onto mesostructured silica containing magnetite (MSM) and magnetic separation were investigated. Magnetite (core) was used as a magnetic carrier material for magnetic separation, while amine-functionalized mesostructured silica (shell) was used as a heavy metal ion adsorbent. The pore properties, magnetic properties, and phase of the prepared materials were measured by a N_2 sorptometer, a vibration sample magnetometer, and powder x-ray diffraction (XRD), respectively. After silica coating, the magnetite-core of the MSMs maintained their magnetic properties. The prepared adsorbent had a large loading capacity for Cu ions; up to

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0.5 mmol of Cu per g of adsorbent. The recovery process of the metal ion loaded adsorbents by an electromagnetic force was very rapid and effective.

Key Words: Adsorbent; Magnetic separation; Magnetite; Mesoporous silica; Removal of heavy metal ions.

INTRODUCTION

The preparation of improved adsorbents that can remove heavy metal ions from an aqueous solution has attracted much attention in the area of wastewater treatment. Several types of functionalized materials have been prepared by grafting of chelating ligands (i.e., mercapto, amine, etc.) on to the surface of the supports to remove metal ions from aqueous solution. These include activated carbon, zeolites, clays, and silica.[1–4] However, their small and irregular pore structures limit their access to the chelating ligands. This, in turn, lowers the metal loading capacities. To overcome these drawbacks, mesoporous molecular sieves, prepared by a self-assembly of inorganic precursors in solution containing structure-directing surfactants were used as adsorbents.[5–10] Feng et al reported a heavy metal ion adsorbent based on the mercapto functionalization of calcined MCM-41 silica.[5] Mericier et al prepared an analogous adsorbent by grafting the mercapto moieties to the pore channels of the hexagonal mesoporous silicas (HMS).[7–9] Liu et al prepared mercapto- and amine-functionalized adsorbents using SBA-15 silica.[10]

Functionalized mesoporous silica is a fine powder, which makes it difficult to recover metal ions loaded adsorbents in batch tests. This can be overcome through magnetic separation of the metal loaded adsorbent. Basically, this method involves incorporation of magnetic materials into the nonmagnetic materials to increase their magnetic susceptibility and allow these agglomerates to be separated by magnetic separation. There are many reports of the preparation of magnetic iron oxide composites embedded in silica or zeolite matrix.[11–15] In general, there are three major preparative methods. In the first method, colloidal iron oxides or ions are entrapped inside the silica matrix pores, and then the entrapped iron oxide or ions are reduced to magnetic iron oxide (magnetite, Fe_3O_4) in H_2 condition at high temperature. Although this method leads to the formation of magnetic phases supported on the silica matrix, their iron oxide loading is low ($<5\%$). This makes it necessary to use the extreme experimental conditions for magnetic phase formation.[11] The second approach is based on the use of zeolites. Most zeolites are rich in Na^+, K^+, and Ca^{2+}, which can be exchanged for metal ions. Aldrich et al investigated on the removal of Pb, Cu, and Cd ions from dilute solutions by sorption onto clinoptilolite (zeolite type), together with magnetite-$Fe(OH)_3$ coprecipitation and magnetic filtration.[12] The sorption capacities of magnetically enhanced zeolites depend on the particle size. The third method involves the fabrication of inorganic and hybrid coatings on the particles, such as solid-core inorganic/hybrid-shell particle preparation.[13–15] Using the precipitation method, where the coating material is precipitated directly onto the core, Ohmori and Matijevic prepared spindle-type hematite particles coated with uniform silica layers by tetraethylorthosilane (TEOS) hydrolysis in 2-propanol with ammonia as the precipitation catalyst.[13] This method should be also reduced to magnetite to use magnetic separation when nonmagnetic hematite is used as a core material. Therefore, pure magnetite was used as a magnetic carrier material.

In this study, magnetite-core/mesostructured, silica-shell agglomerates were prepared for use as metal adsorbents. Amine groups were selected as a metal-chelating ligand considering its metal uptake capacity and hydrophilic properties.

EXPERIMENTAL

Synthesis of Core-Shell Structure

Mesostructured silica containing magnetite (referred to as MSM) was synthesized by the electrostatic interaction between large magnetite particles (20 nm to 5 μm, mainly 100 nm) and nanostructured silica (3 nm of pore diameter). Figure 1 shows a schematic diagram of the mesostructured silica-shell (HMS) containing magnetite-core structure. HMS (hexagonal mesoporous silica) based on a neutral pathway was synthesized.[7,8] The silica precursor was self-assembled with the surfactant micelle via hydrolysis and condensation. Subsequently, the magnetite was wrapped with the mesostructured silica oxides. Mesostructured silica on magnetite was prepared by a neutral self-assembly process using hexadecylamine (Fluka) as a template and the surfactants were removed by solvent extraction or calcination. The HMS was obtained by dissolving 6.6 g of the primary amine in 46 mL of ethanol, adding water to the mixture and followed by adding 22.33 mL of TEOS (Fluka) under vigorous stirring. After 1 hour, 1 g of magnetite (Aldrich) was added to the mixture and stirred using a nonmagnetic stirrer for 20 hours. The product (denoted as MSM) was filtered and air-dried. The surfactant was, finally, removed by either solvent extraction (MSM-e) or calcination (MSM-c).

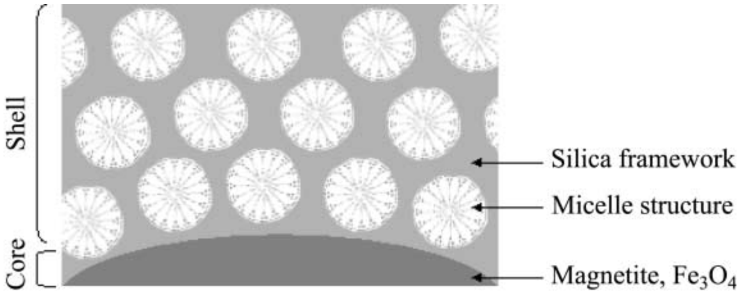

Figure 1. Schematic diagram of a mesostructured silica-shell (HMS) containing a magnetite-core structure.

Functionalization of Mesostructured Silica Containing Magnetite

A 1 g of vacuum dried MSM-e was refluxed in 25 mL of toluene containing 1 g 3-(2-aminoethylamino)propyltrimethoxysilane (Fluka) for 24 hours. The dried material was subsequently recovered by filtration and washed with toluene, methylchloride, acetone, and ethanol. Hereinafter, the functionalized magnetite/HMS is referred to as 2N-MSM-e.

Adsorption Test of Copper Ion

An adsorption test for aqueous copper ions was performed using a pH 4 buffer solution, which was prepared with 0.1 M of potassium hydrogenphthalate (Aldrich), 0.1 M hydrochloric acid (Aldrich), and de-ionized water.[16] The adsorbents 0.05 g were stirred with 10 mL of copper(II) nitrate trihydrate [$Cu(NO_3)_2 3H_2O$, Junsei] solutions of 0 to 20 mmol/L. The reaction mixtures were then shaken at room temperature for 12 hours. The adsorption capacities were measured from the difference between the initial concentration and those of the residual solutions by inductively coupled plasma-atomic emission spectrometry (ICP-AES, ICPQ 1000, Shimadzu).

Characterization

To determine the crystallinity of magnetite and the prepared samples, powder x-ray diffraction (XRD, M18XHF-SRA, MAC/Science) patterns were recorded using CuK_α radiation at 50 kV and 100 mA. Small angle x-ray scattering (SAXS, GADDS, Bruker) was used to measure the crystallinity of the mesostructured silica on magnetite at 40 kV and 45 mA. The nitrogen adsorption/desorption isotherms were examined at 77°K on a Micromeritics ASAP-2010 sorptometer (Buruker). The temperature at which the material decomposes or undergoes any phase change was measured in air by differential thermal analysis (DTA, SDT-2960, TA Instruments) at a heating rate of 10°/min between the temperature 25 and 400°C. The magnetic properties of the MSMs were measured using a vibration sample magnetometer (VSM, VSM-735, Lake-Shore Cryotronics) in an applied field of 4 kOe. The MSM morphology was observed by both transmission electron microscopy (TEM, JEM-200CX, Jeol) and scanning electron microscopy (SEM, JSM-T200, Jeol).

RESULTS AND DISCUSSION

Adsorbent Characterization

All MSMs exhibited a single peak in the small angle x-ray scattering (SAXS) spectrum, and showed an intense d_{100} scattering peak around 4.5 nm at $2\theta = 1.95$ (Fig. 2 and Table 1). The absence of higher angle peaks suggests that the inorganic walls of these materials are amorphous. Although single SAXS peaks are an indication of a lack of long-range order, they suggest the presence of a disordered hexagonal or sponge-like pore structure.[7] As shown in Table 1, the ordering lengths of the MSMs are 44 to 48Å. Template removal (MSM-e and MSM-c) from the mesostructures as compared to the MSM is observed to cause an increase in the peak intensities. The increase in the peak intensities indicates an opening of the filled framework pores with the organic templates.

The N_2 adsorption/desorption isotherms of the prepared materials shown in Fig. 3 yielded hysteresis loop-type IV isotherms with inflections observed between partial pressures of 0.15 to 0.55. These features illustrate the presence of framework mesopores. From these isotherms, the BET surface areas of the prepared materials were determined (see Table 1) and were found to be within the range expected for mesostructure materials. The BJH (Barret, Joiner, and Halenda) pore-size distributions (see Fig. 3 and Table 1) further verified the presence of 2-3 nm mesoporous channels. The narrow pore-size distributions found for all materials attested to the porosity of their uniform framework. Upon grafting the aminosilane groups to the framework pore walls, the pore diameter and pore volume decreased significantly due to the presence of ligating amine moieties in the framework channels. Despite the greater pore

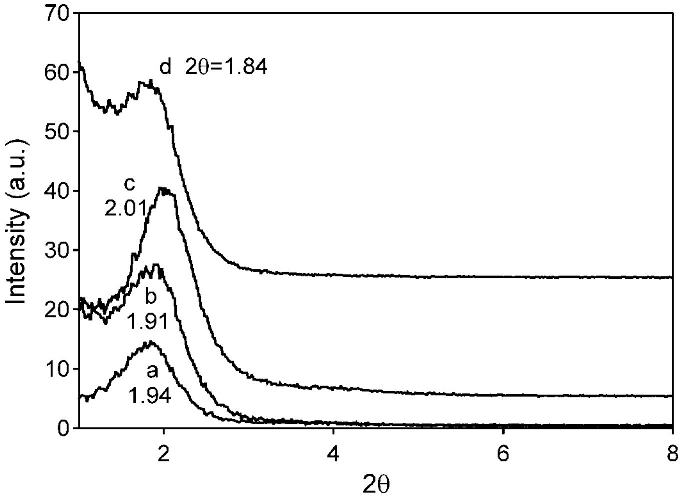

Figure 2. Small angle x-ray scattering patterns of (a) MSM, (b) MSM-e, (c) MSM-c, and (d) 2N-MSM-e.

channel constriction in 2N-MSM-e, this material retained significant mesoporosity. The parent mesostuctured material (MSM-e) of the adsorbent had a SiO_2/Fe_3O_4 weight ratio of 5.06, which was measured using an electron probe microanalyzer (EPMA, JXA-8900R, Jeol). The pore properties of the amine-functionalized adsorbent and their parent mesostructure are summarized in Table 1.

The removal template by calcination (MSM-c) was found to be more efficiently done than by solvent extraction (MSM-e). The surface area and pore volume of MSM-c (1003 m^2/g and 1.05 cm^3/g) was larger than that of MSM-e (672 m^2/g and 0.75 cm^3/g). From the SiO_2/Fe_3O_4 weight ratio, the surface area and pore volume of MSM-e based on only silica was actually 804 m^2/g and 0.90 cm^3/g, respectively. However, calcination at 460°C for 5 hours in air deformed the phase and color of the magnetite-core material (see Table 1). The color of MSM-e was dark gray, while MSM-c turned dark brown, which is similar to that of partially oxidized iron, maghemite (γ-Fe_2O_3), or hematite (α-Fe_2O_3). In addition, upon the removal of the surfactant at high calcination temperatures, significant dehydroxylation of surface hydroxyl groups on the pore walls was observed. This limits the amount of organosiliane that could be grafted in the channels. The XRD pattern in the wide range ensured the phase transformation of magnetite to maghemite and/or hematite after calcination (Fig. 4).

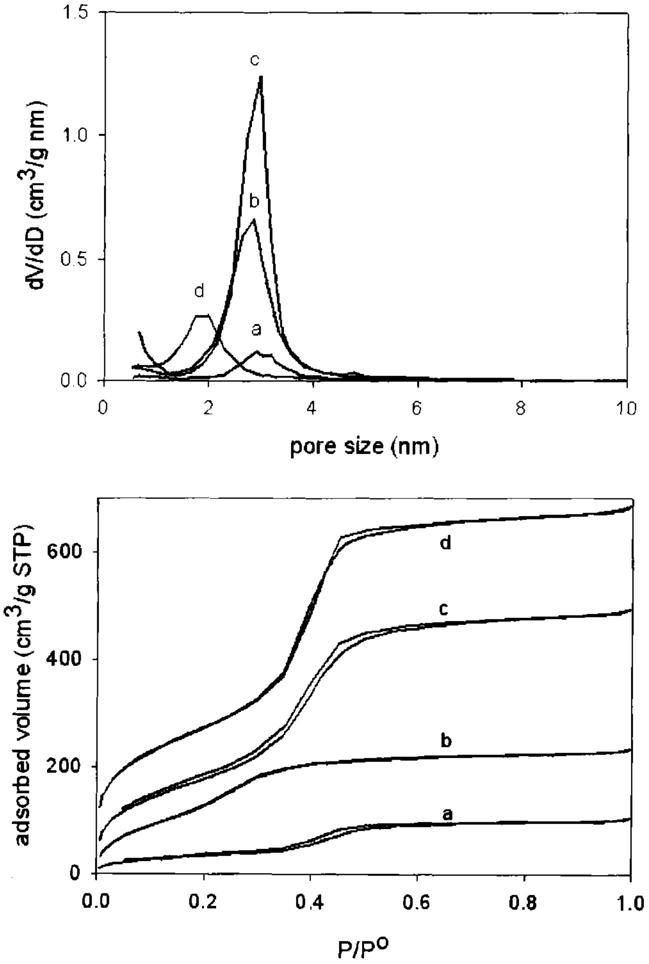

Figure 3. Pore-size distribution and N_2 adsorption/desorption isotherms of (a) MSM, (b) MSM-e, (c) MSM-c, and (d) 2N—MSM-e.

The structure of the parent materials and the calcined material were studied and confirmed by powder XRD. The phase identification was performed by comparing the measured diffraction pattern of prepared materials with that of pure magnetite and the reported data on the JCPDS database.[17,18] All the lines of the magnetite-core material (see Fig. 4) match well with those for reported well-crystallized Fe_3O_4 with a cubic structure.[18]

Table 1. Pore properties and magnetic properties of magnetite and MSMs.

Material designation	Pore diameter (Å)	BET surface area (m^2/g)	Pore volume (cm^3/g)	d_{100} spacing (Å)	Coercive force (Oe)	Specific magnetization (emu/g)
Magnetite[a]	—	2	—	—	287	82.6
MSM	29	132	0.15	45.46	—	—
MSM-e	29	672	0.75	46.22	274	10.9
MSM-c	30	1003	1.05	43.92	282	1.5
2N-MSM-e	20	513	0.35	47.97	313	6.9

[a] Nonporous material ($FeOFe_2O_3$).

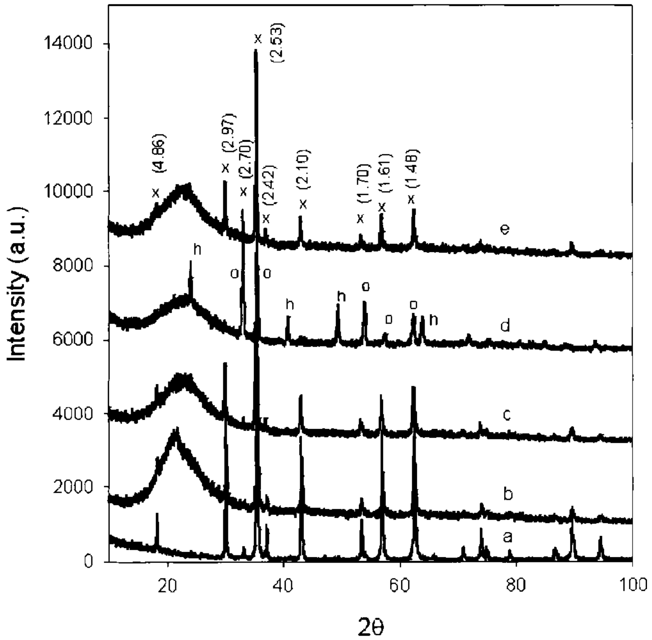

Figure 4. XRD patterns of (a) magnetite (reference), (b) MSM, (c) MSM-e, (d) MSM-c, and (e) 2N-MSM-e. Where the insert symbols, x, o, and h are magnetite, maghemite, and hematite, respectively. The lattice spacing of each peak is represented in parenthesis.

Except for MSM-c, the XRD patterns of the other confirmed that the core of the MSMs was magnetite (see Fig. 4). The characteristic peaks of each phase are illustrated in Fig. 4, and the magnetite and maghemite characteristics are seen to have similar diffraction patterns, except for the lattice spacing 4.86, 2.97, 2.42, and 2.08, when compared to magnetite itself. After calcination, the phase of MSM-c shows those of maghemite and hematite. This is due to magnetite to maghemite oxidation, and a partial transformation of maghemite to hematite. The MSM-c could not be used as a support for the metal adsorbent. Therefore, the MSM-e material, which maintained the phase of the magnetite-core, was used as a support for the metal adsorbent.

In addition, the silica coating magnetite materials had a broad peak that presented a halo band around 20°, which is usually indicated the short-range orderliness of the arrangement of the constitute atoms.

A more detailed description of the mesoscopic order in the prepared material was obtained by TEM. The morphology of the silica-coated magnetite was obtained by SEM. As shown in Fig. 5, pure magnetite was observed to have a glassy surface [Table 1 and the TEM image shown in Fig. 5(c)] and its particle size varied between 20 nm to 5 μm, mainly 100 nm. Figure 5(b) shows a typical SEM image of the mesostructured silica containing magnetite. The figure shows a completely visible silica coating on magnetite. The magnetite is irregularly surrounded with mesoporous silica. These aggregates are magnetically sensitive, and can be easily removed by magnetic filtration. The HMS channels on magnetite are uniform mesopores (see Fig. 5(d)), and appear to present a disordered hexagonal or sponge-like pore structure in agreement with the SAXS results.

Figure 6 shows the DTA curve of pure magnetite and MSM-e. The DTA curves of pure magnetite [see Fig. 6(a)] exhibited two broad exothermic peaks at about 260 and 330°C. The first peak is attributed to a Fe_3O_4 transformation to γ-Fe_2O_3 due to oxidation and the latter to a γ-Fe_2O_3 transformation to α-Fe_2O_3. Ohmori and Matijevic reported that the DTA trace of magnetic oxides, which were prepared using $FeCl_3$, shows a very broad exothermic peak in the range between 100 and 400°C.[13] Similarly, Reddy et al reported the DTA characteristics of $Fe(NO_3)_3$ and obtained γ-Fe_2O_3 and α-Fe_2O_3, wherein they observed broad exothermic peaks at 130°C and 520°C.[18] However, the mesostructured silica containing magnetite (MSM-e) had only one exothermic peak at 340°C, which was also caused by partial oxidation of magnetite with partial transformation to α-Fe_2O_3. This suggests that the coated magnetite has a higher transformation temperature than pure magnetite. Therefore, the thermal stability of the silica-coated magnetite can be said to have been good up until 300°C.

The magnetic properties (coercive force, H_c, and the specific magnetization, M_s) were measured using a VSM in an applied field of 4 kOe. Figure 7 shows

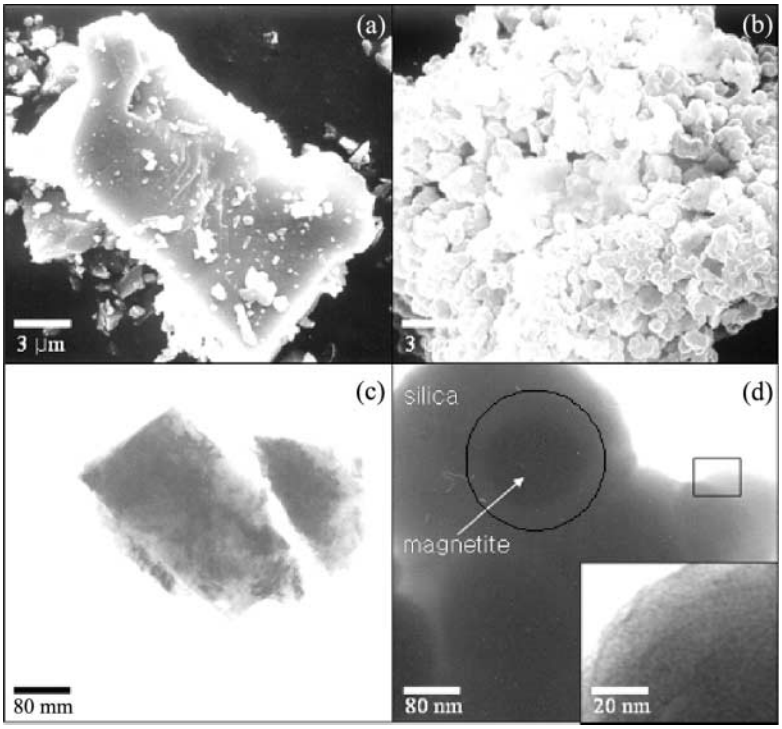

Figure 5. TEM and SEM images of pure magnetite (a,c) and MSM-e (b,d).

the magnetization hysteresis loops of the prepared materials. The value of M_s for magnetite/HMS (see Table 1) is lower than that of pure magnetite due to the presence of the nonmagnetic mesoporous silica coating. The specific magnetization value of MSM-c (1.5 emu/g) is lower than that of pure magnetite (82.6 emu/g) and MSM-e (10.9 emu/g) due to the phase transformation and oxidization during calcination. Therefore, MSM-c may be unsuitable to act as a support of the adsorbent. MSM-e and 2N-MSM-e are seen to better maintain their magnetic properties. In addition, the coercive force was not affected by the method of template and silica coating removal.

Copper Ion Adsorption Test

Previous investigations into mesoporous silica adsorbents using various amine functional groups reported that the metal loading capacity of

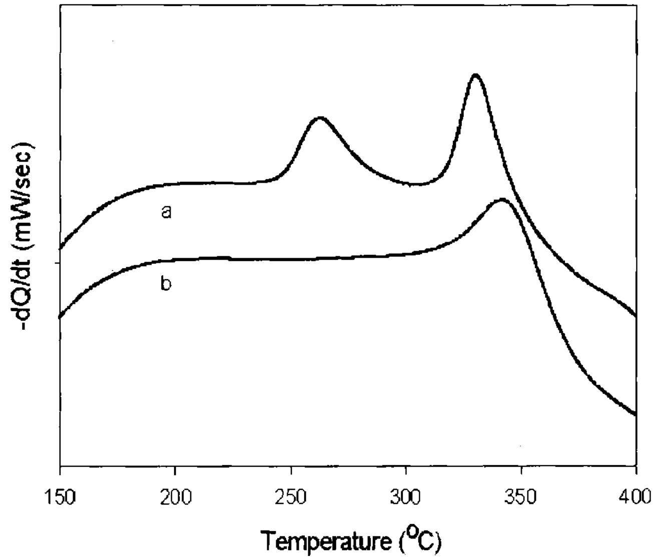

Figure 6. DSC curves of (a) magnetite and (b) MSM-e.

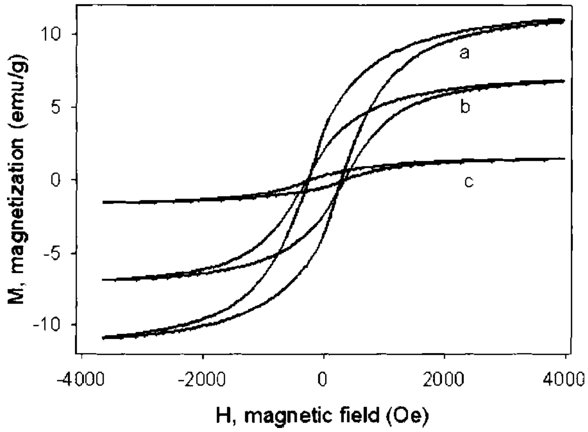

Figure 7. Magnetization hysteresis loops of (a) MSM-e, (b) 2N-MSM-e, and (c) MSM-c.

the adsorbents using aminosilane with 2-amine groups was higher than that of the adsorbents using aminosilane with only 1-amine group and 3-bulky amine groups.[19] Therefore, the 2-amine functional group was chosen for this study.

The C, H, and N concentration of 2N-MSM-e were analyzed by an element analyzer (EA1110, CE Instrument) and were used to determine the quantity of amine moieties grafted to the framework channels (13.61 wt% C, 3.85 wt% H, and 5.66 wt% N). The high amine content of 2N-MSM-e can be said to be attributed to the more abundant hydroxyl groups present in the parent mesostructure when compared to that of the calcined material. On the basis of the loading and BET surface area of the unfunctionalized MSM-e, the amine group densities on the pore walls of the adsorbents was calculated. The amine group content and density were found to be 4.04 mmol/g and 3.62 nm^{-2}, respectively.

Figure 8 shows that the equilibrium Cu-loading capacity of 2N-MSM-e is dependent on the copper concentration. The results followed a Langmuir isotherm curve; $q = Kq_mC/(1 + KC)$. Fitting by the least-squares method yielded K and q_m values of 1.1 L/g and 0.5 mmol/g (32 mg/g), respectively (where K is the Langmuir adsorption constant, and q_m is the maximum amount of Cu that can be absorbed by the 2N-MSM-e). This high removal capacity may be due to the uniformity of pore structure with relatively large pore size (3 nm). When the pores show high tortuosity with nonuniformity, the pores can be easily blocked during the functionalization process. In nonuniform pores, functionalization reduces the diameter of pores, which in turn, causes

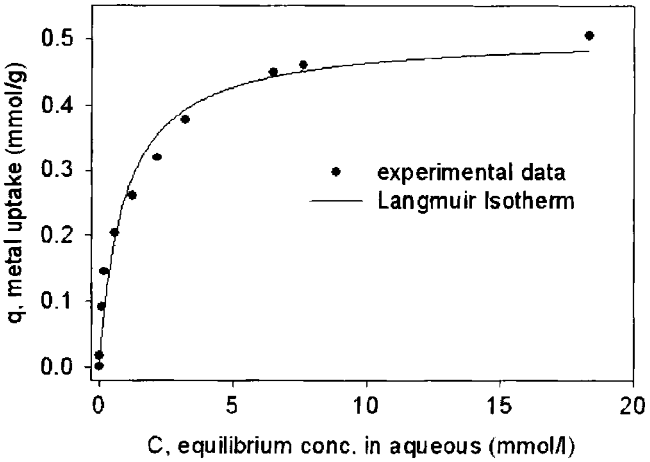

Figure 8. The Langmuir sorption isotherm of copper ions in a pH 4 buffer solution.

the pores to become more easily blocked. Blocked pores can no longer be used in metal ion adsorption. In the case of uniform pores, the pores are still wide open after the functionalization, allowing copper to diffuse into the inner part of particle. Therefore, mesoporous silica (average pore size of 3 nm) with uniform pore structure tends to show higher uptake in terms of removal of metal ion than silica with nonuniform pore structure.[3]

Metal uptake capacity was dependent on the content of functional group on the surface of support. In a previous study,[3] mesoporous silica adsorbent without magnetite was prepared via the same procedure. The use of adsorbent with 2.43 mmol/g of amine-functional group showed 0.11 mmol/g Cu ion uptake. Its molar ratio of the adsorbed copper ion to the amine-functional group is 0.045. In this study, 4.04 mmol/g of amine-functional group was loaded on the MSM-e. Its copper uptake for the same copper solution was 0.20 mmol/g. The molar ratio is 0.049. These results implied that magnetite-core was not affected on the metal uptake capacity.

After contacting with copper solution, the adsorbents were collected by a magnet. The magnet attracted the adsorbents from the solution and consequently, the solution became clear, as shown in Fig. 9. The recovery process of the metal ion loaded adsorbents by the magnetic or electromagnetic force is very rapid and effective.

In addition, it is important to recycle the adsorbent for industrial and environmental aspects. Used adsorbent was treated using 100 mL of 0.1 M HCl for the regeneration. After elemental analysis, the nitrogen contents of

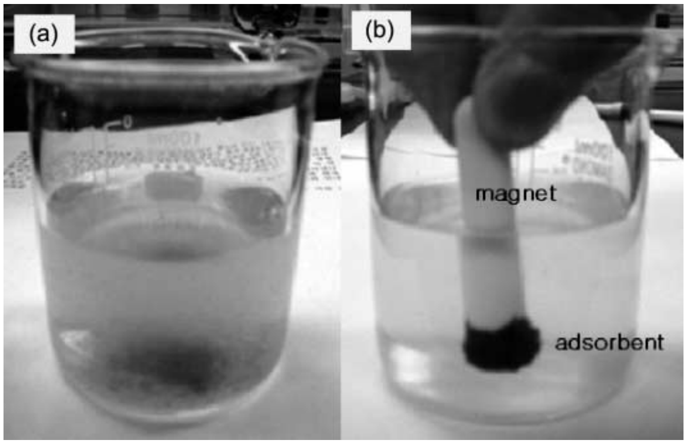

Figure 9. Pictures of (a) copper solution with dispersed adsorbents and (b) adsorbents collected by the magnet attraction.

fresh adsorbent and regenerated adsorbent were 5.6 wt% and 5.3 wt%, respectively. This result confirmed that only a little loss of amine functional group occurred during the regeneration step. Thus, regenerated adsorbent could be reused as a heavy metal adsorbent.

CONCLUSION

The high surface area of the mesoprous silica with the covalent bonding of the amine group containing magnetite as a core was prepared for removal of Cu ions from aqueous solutions. The resulting material allows for the rapid and effective recovery of the adsorbents by an electromagnetic force. The preparation technique suggested in this study is found to have more distinctive advantages than the existing metal separation method. The results show that (1) the absorption data follows a Langmuir isotherm, (2) the maximum absorption capacity could be as high as 0.5 mmol of Cu per g of adsorbent, and (3) silica containing magnetite is able to maintain its magnetic properties.

ACKNOWLEDGMENTS

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