

Gold Removal and Recovery using Mesoporous Silica Adsorbents

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ABSTRACT

Two gold-selective adsorbents were prepared from MCM-41 by grafting amino and thiol groups. The mesoporous silica adsorbents possess higher adsorption capacity for gold compared to activated carbons. The OMS-NH₂ adsorbent was able to selectively remove and adsorb gold from solutions containing copper. Pure gold was recovered by a simple acid wash and the regenerated adsorbents could be reused. The OMS-SH also selectively adsorb gold, but always with a small quantity of copper (ca 1-5 at. %). In addition, the metals were irreversibly adsorbed on OMS-SH and can not be easily recovered.

Keywords: MCM-41, adsorption, separation, binary mixture, copper, gold

1 INTRODUCTION

The ordered mesoporous materials (e.g., M41S, FSM, HMS and SBA) belong to an important class of molecular sieve materials. Their large surface areas, ordered pore structures and nanometer-sized pores offer a unique environment for chemical separation and reaction [1,2]. The concept of 'supra-molecular templating' has enabled the design of mesoporous silica with adjustable pore sizes and structures [3]. Chemical modifications of the pore channels with metals, metal oxides and organic moieties [4-6] led to new materials with unique physical, chemical and catalytic properties.

The cylindrical pore structure and high degrees of pore symmetry found in MCM-41 make it an ideal system for testing new and existing adsorption and diffusion models. The simple pore geometry allows for easier mathematical description and the amorphous pore wall is a good approximation of an ideal Langmuir surface. The width of the pore channel restricts the size and shape of the molecules that can enter and leave the pores. This gives rise to molecular sieving effects that have many beneficial applications in separation. The chemical environment of the pore channels can be simply manipulated to affect the adsorption and diffusion of molecules by grafting surface chemical moieties. This provides new opportunities for solving difficult separation problems.

In the last few years there have been significant advances in the synthesis of ordered mesoporous silica

(OMS). The two main obstacles for the widespread industrial application of OMS are its cost and stability. In the manufacture of the ordered mesoporous silica, the surfactant template accounts for more than 80 % of the cost. Nondestructive methods for the removal and recovery of the surfactants and the use of cheaper polymer substitutes have substantially cut the cost of OMS [7]. Better thermal and hydrothermal stability is obtained by post-synthesis treatment of the OMS with metal alkoxides, salt solution and trimethylsilylation [8,9]. Although further cost reduction is needed for the economical application of OMS technology to general environmental problems, there are many specific cases where OMS technology is urgently needed. Feng and coworkers [2] are among the first to demonstrate the use of OMS for the removal of mercury and other toxic heavy metals from water. It is found that the modified mesoporous silica has high adsorption capacity for mercury ions. Our group has shown that it is possible to tailor OMS adsorbent to remove specific dye from mixtures, enabling their recovery and reuse [10]. The increasing use of precious metals such as gold and platinum in microelectronics, sensors and catalysts pose both economic and technical challenges for their recovery, purification and reuse. This work reports the use of OMS adsorbents for the selective removal and recovery of gold from solutions containing a base metal (i.e., copper).

2 EXPERIMENT

The synthesis of MCM-41 and its modifications to produce selective adsorbents are described along with the details of the single and binary components adsorption experiments.

2.1 Synthesis

The MCM-41 powder was prepared from an alkaline solution containing tetraethyl orthosilicate (TEOS, 98%, Aldrich), cetyltrimethylammonium bromide (CTABr, 99.3%, Aldrich), ammonium hydroxide (NH₄OH, 28-30wt%, Fisher Scientific) and double distilled, deionized water. Plate-shaped crystals with an average diameter of 0.9 ± 0.1 μm and a thickness of about 0.1 μm were crystallized from a synthesis solution with a molar composition of 6.58 TEOS: 1 CTABr: 292 NH₄OH: 2773 H₂O. The synthesis solution was stirred for 24 hours at room conditions after

mixing all the chemical components. The precipitate formed in the solution was filtered and washed with DDI water. After drying, the powder was calcined at 823 K for 24 h to remove the organic template molecules. Characterizations were conducted on the calcined powder. The recovered powder displayed the characteristic X-ray diffraction pattern of MCM-41 and the nitrogen physisorption measurement (Coulter SA 3100) gave a BET surface area of 1071 m²/g and a pore volume of 0.3805 cm³/g. An average pore size of 27.6 Å was calculated from the XRD (Philip 1080) and N₂ physisorption data. Routine chemical analysis of the sample by X-ray photoelectron spectroscopy (XPS, Physical Electronics PHI 5600) detected only silicon and oxygen atoms with carbons from adsorbed carbon dioxide and ambient hydrocarbons as the main surface impurities. The FTIR (Perkin-Elmer model GX 2000) spectrum of the powder displayed the characteristic bands for Si-OH groups at 3675 cm⁻¹, 950 cm⁻¹ and 800 cm⁻¹.

2.2 Post-modification

Amino and thiol-containing mesoporous silicas were prepared using the following procedures. OMS-NH₂ was obtained when 2.5 g of MCM-41 was refluxed in 250 ml dry toluene solution containing 0.1 mole of 3-aminopropyltrimethoxysilane (APTS, 97%, Aldrich) at 383 K for 18 h. After cooling to room temperature, the powder was collected by series of centrifugation and washing steps. OMS-SH was prepared using the same procedure but replacing APTS with (3-mercaptopropyl) trimethoxysilane (MPTS, 95%, Aldrich). The resulting adsorbent powders were analyzed by FTIR and thermogravimetric method to identify and quantify the grafted surface moieties.

2.3 Adsorption

Single component adsorption isotherms were obtained for 0.1 g of adsorbent in 100 ml aqueous solutions containing 0.5 to 4 mM of metal ions. Gold and copper solutions were prepared from AuCl₃ (99% Aldrich) and CuCl₂ (98%, Aldrich) salts, respectively. The batch adsorption experiments were at room temperature (295 ± 2 K) for 14 days with constant agitation. Metal concentrations were determined using an inductively coupled plasma-atomic emission spectrometer (ICP-AES) using reference standard solutions of gold and copper.

The adsorption behavior and selectivity of OMS-NH₂ and OMS-SH adsorbents were determined for binary solutions of gold and copper salts. The effects of pH, total metal concentration and metal composition were investigated. In the experiment, 0.1 g of adsorbent was added into 100 ml of metal salt solution. The pH of the solution was adjusted using hydrochloric acid. The pH at the start and at the end of the experiment rarely deviated by more than ± 0.2. The adsorption was conducted in a shaker bath at 295 ± 2 K. Experiments were carried out to study

the effects of metal composition on adsorption. Solutions with a total metal concentration of 2 mM, but different metal compositions were prepared. The adsorption was conducted at a fix pH (2.5) and temperature (295 K).

After the adsorption, the used adsorbents were collected by centrifugation and regenerated by washing with 1 M hydrochloric acid.

3 RESULTS AND DISCUSSION

The OMS-NH₂ displayed an I.R. absorbance peaks at 3360cm⁻¹ together with 3288 cm⁻¹ and 1600 cm⁻¹ belonging to the -NH₂ and C-N bond, respectively. A signal at 2580 cm⁻¹ assigned to S-H stretching vibration was detected in OMS-SH. Table 1 summarizes the physical and chemical properties of the OMS adsorbents.

Sample	Surface Area (m ² /g)	Pore Size ¹ (nm)	Concentration of Functional Group		Isoelectric point
			mmol/g	groups/n m ²	pH
MCM-41	1150	3.01	--	--	2.1
OMS-NH ₂	774	2.57	2.23	1.7	3.6
OMS-SH	887	2.76	1.27	0.9	4.0

Table 1: Physical and chemical properties of the mesoporous silica adsorbents.

In a simple stability test in aqueous solution, it shows that the mesoporous silica adsorbents were stable over a broad range of pH values (2 to 10), however at pH > 10, the organic moieties detach from the MCM-41 as the siliceous wall dissolved at these high pH. Both OMS-NH₂ and OMS-SH were also stable in solvents (e.g., toluene, acetone and ethanol), but were vulnerable to oxidation by strong oxidizing agents (e.g., H₂O₂).

Sample	Adsorption capacity (mmol/g)/[mg/g]	
	Au ³⁺	Cu ²⁺
MCM-41	~	~
OMS-NH ₂	1.69 [333]	0.82 [52]
OMS-SH	1.60 [315]	0.28 [18]

Table 2: Single component adsorption capacities for mesoporous silica adsorbents

From the adsorption results shown in Table 2, despite the enormous surface area, gold and copper adsorptions on

MCM-41 are negligible compared to the other two adsorbents. OMS-NH₂ and OMS-SH have comparable adsorption capacity for gold (Table 2), which is four times larger than the best value reported for activated carbon [11, 12]. OMS-SH adsorbs less copper suggesting that it can be the more selective gold adsorbent of the two. These results show the importance of the surface functionality for metal adsorption.

Figure 1 plots the adsorption data of OMS-NH₂ and OMS-SH for the binary metal solutions. Metal adsorption at different pH was conducted using solutions containing equimolar concentrations of gold and copper salts. It is clear from Fig. 1a that only gold ion is adsorbed by OMS-NH₂ in complete exclusion of copper. Also, analysis indicated that complete gold removal is achieved over the whole experimental pH range. OMS-SH also selectively removes and adsorbs gold from the solution (Fig. 1b), but at low pH (< 2.5) small quantities of copper (2.5 mg/g) is also adsorbed. Figures 1c and 1d plot the metal adsorbed as a function of metal composition in the solution. Gold-only removal without copper adsorption is obtained using OMS-NH₂ adsorbent. More than 90 % of the gold is adsorbed from the solution as shown Fig. 1e, and the removal efficiency reaches 100 % for solutions with dilute gold concentration making it an attractive adsorbent for gold recovery from dilute mining and recycling wastes. The OMS-SH adsorbent also selectively adsorbs gold from the solution (Fig. 1d), but the removal efficiency is lower (Fig. 1f) and small quantities of copper are always adsorbed.

More than 70 % of the adsorbed gold was recovered from OMS-NH₂ after a single wash with 1 M HCl solution. It was found that the gold concentration was increased tenfold after the adsorption and regeneration process. In contrast, less than 5 % of the adsorbed metals in OMS-SH were recovered even using more concentrated acid wash solutions (i.e., 5 M HCl). X-ray photoelectron spectroscopy suggested that gold and copper underwent a change in oxidation state during their adsorption on OMS-SH, which maybe responsible for the irreversible adsorptions of these metals. Therefore, although OMS-SH can selectively adsorb gold, it is not suitable for industrial use since the metal can not be easily recovered. The gold recovered from OMS-NH₂ is pure, requiring no further purification and can be reduced into metallic form using sodium borohydride. The regenerated adsorbent can be reused without loss in capacity by simply taking the precaution to pre-rinse with a small amount of ethanol.

4 CONCLUSIONS

This work clearly demonstrated the potential use of selective adsorption for the recovery of precious metals such as gold from the solution containing other metals. The OMS-NH₂ proved to have a large capacity and excellent affinity for gold, enabling its separation from mixtures and recovery as high purity gold.

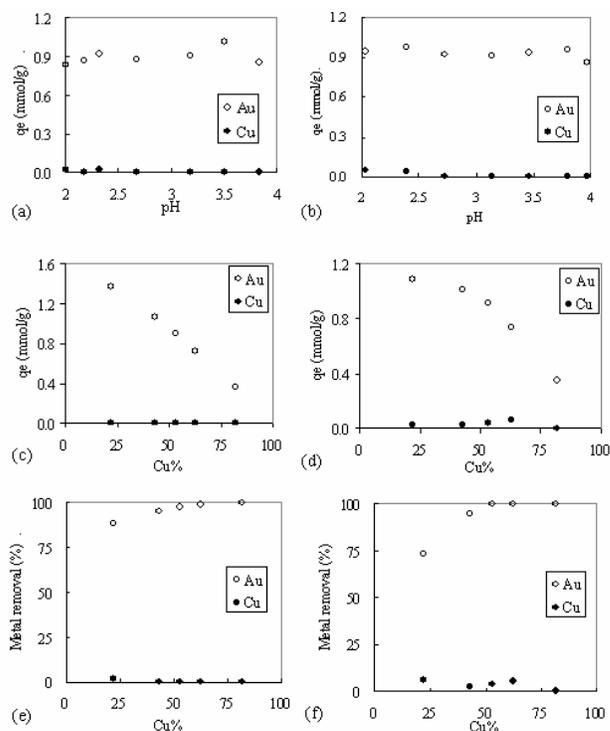


Figure 1: Binary metal adsorptions of copper and gold solutions at different pH for (a) OMS-NH₂ and (b) OMS-SH; Metal Adsorption vs At.% Cu for (c) OMS-NH₂ and (d) OMS-SH; Metal Removal vs At.% Cu for (e) OMS-NH₂ and (f) OMS-SH. (q_c is the adsorption capacity of metal ion in mmol/g).

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