

Removal of Silver Ions by Thiol-Functionalized Mesoporous Silica

Jayhyun Park¹, Jaikoo Park², Hyunjung Kim³ +

¹ R&D Team, Institute of Mine Reclamation Corporation, Coal Center, 30 Chungjin-dong, Jongno-gu, Seoul 110-727, Republic of Korea

² Department of Natural Resources and Environmental Engineering, Hanyang University, #17 Heangdang-dong, Seongdong-gu, Seoul 133-791, Republic of Korea

³ Department of Mineral Resources and Energy Engineering, Chonbuk National University, 664-14 Duckjin-Dong 1Ga, Duckjin-Gu, Jeonju, Jeonbuk 561-756, Republic of Korea

Abstract. An uptake of silver from aqueous solutions by ion exchange on functionalized mesoporous silica has been studied. Mesoporous silica with large pore (ca. 6 nm) was synthesized by condensation of siliceous solution using nonionic oligomeric polyethylene glycol block copolymer as surfactant in acidic medium, and the mesoporous silica was functionalized by 3-mercaptopropyltrimetoxysilane(MPTMS) for good selectivity and high adsorption capacity. The result of nitrogen gas adsorption(BET) and transmission electron microscopy show that silica adsorbate have ordered mesoporous structure with uniform pore size distribution. The removal efficiency of metal in various concentration of metal cations in aqueous solution was investigated and it is determined that in various concentration range, adsorption amount of metal cations on mesoporous silica match to Freundlich and Henry adsorption isotherm data which are used for calculation of ion exchange parameter.

Keywords: silver, adsorption, mesoporous, thiol

1. Introduction

The optimization of wastewater treatment process requires a development of new operations based on low cost materials with high pollutant-removal efficiency [1]. Numerous processes such as ion exchange, precipitation, adsorption, ultrafiltration, or reverse osmosis have been used for removing heavy metal ions [2,3]. These techniques have been successful, but they offer the disadvantages related to removal efficiency. A lot of adsorbents including activated carbon, clays, or zeolites are used for capture of metal ions, even though they have their inherent disadvantages which are wide distribution of pore size, heterogeneous pore structure, low selectivity, heterogeneous reactions, and relatively low metal loading capacities.

The use of functionalized mesoporous silica(FMS) materials as potential sorbents for the removal of heavy metal has been investigated recently [4,5]. Their synthesis and applications have attracted great interest because of the combined advantages of inorganic-organic composites and the mesoporous structure [6]. Their large surface area, uniform pore size distributions and open-framework pore structure make them potential environmental material candidates in the field of advanced catalysis and adsorption. The functionalization of mesoporous silicas has been mostly studied with a mercaptopropyl group [7]. A number of FMS for heavy metal loading were synthesized with pore sizes less than 3 nm though Yang reported that FMS with pore size larger than 3 nm has good selectivity of Hg and Cd [8]. Furthermore, main targeted metal ions onto FMS were mercury, cadmium, lead, and zinc [9,10], and most of these investigations focus on the metal loading amount, selectivity, and the distribution coefficient of heavy metal, but not adsorption isotherm.

+ Corresponding author. Tel.: +82-63-270-2860; fax: +82-63-270-2366.
E-mail address: kshjkim@jbnu.ac.kr.

In this work, silver and cadmium have been selected as target heavy metals. Silver is more valuable metal than general toxic heavy metal such as mercury, lead, zinc, cadmium, and cromate. In addition, silver is the highly potential adsorbate candidate for practical application of FMS in environmental field because of its broad usage in the photographic and imaging industry, electronics, silverware, and jewelry. Here, we report the preparation of mesoporous silica with large pore size(ca. 6 nm) by condensation of siliceous solution in acidic medium using nonionic oligomeric polyethylene glycol block copolymer(P123) as surfactant and the functionalization of 3-mercaptopropyltrimetoxysilane(MPTMS) on the surface of mesoporous silica. The synthesized FMS materials were used as silver ions adsorbents. Adsorption property of silver in FMS with large pore is also compared with that of cadmium which is known as one of high favorable metal cations on FMS.

2. Materials and Methods

2.1. Synthesis and characterization of absorbent

Stucky et al. [11] showed that non-ionic surfactants are good structure-directing agents of mesoporous silicate. In a typical preparation, 4 g of Pluronic P123(Aldrich Co.) was dissolved in 120 g of 2M HCl solution with stirring at room temperature. Then, 46 g of silicate solution made by dissolving 1M of solid state amorphous silica(Dongyang Chem. Co.) in 1M NaOH solution was added into the solution with stirring at 35 °C for 20 h. The mixture was aged at 90 °C for 20 h without stirring. The precipitated solid product was recovered, washed, and dried at 60 °C. Dried samples were calcined at 550 °C for 2h. The functionalization of thiol groups was followed by stirring the mesoporous silica in toluene. An 8 g of sample of the surfactant extracted mesoporous silica was then stirred for 24 h in 200 ml of toluene containing 8 g of MPTMS at 30 °C. The products were filtered, and washed with copious amount of ethanol to remove ungrafted MPTMS.

The surface and shape of the mesoporous samples were observed with a field-emission scanning electron microscope (JSM-6330F, JEOL). The specific surface area was measured with the N₂-gas adsorption method applying the BET apparatus (Nova1000, Quantachrome). The pore size distribution was calculated by the BJH method.

2.2. Adsorption test

The aqueous solutions of silver(AgNO₃) and cadmium(CdNO₃) used in all experiments were prepared with deionised water. A 0.1g of mesoporous sample was poured in 50ml of metallic solution in a glass bottle. The mixture solutions were shaken for 6 h allowing the adsorption to reach equilibrium at 25 °C. The pH value in all experiments was fixed at 5.5 using buffer solutions. The mixture was filtered afterwards. The initial and final metal concentrations of the solutions were measured with an ICP-AES(ICPS-1000IV, Shimadzu). Several metal cation solutions with different initial concentration were prepared.

3. Results and Discussion

3.1. Structural properties of mesoporous silica

All materials were prepared at a very low pH(< 1). Fig. 1a shows the morphology of mesoporous material. The aggregates of synthesized mesoporous materials had long fabric-like shape. TEM image of synthesized material confirm the existence of the ordered pore structures in the material (Fig. 1b).

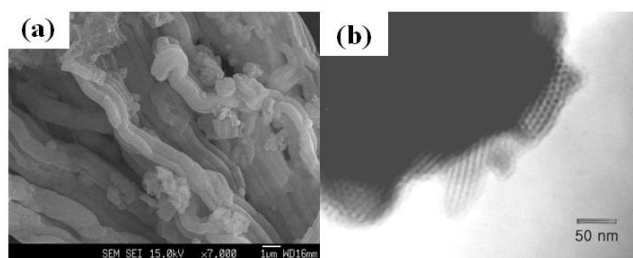


Fig. 1. (a)SEM and (b)TEM images of synthesized mesoporous silica material

The nitrogen adsorption-desorption isotherms of the synthesized material and functionalized materials are shown in Fig. 2. The adsorption-desorption isotherms exhibit typical Type IV isotherm patterns which is typical characteristic of a mesoporous material. The one steep slope at 0.7–0.8 of P/P_0 is characteristic of the porous adsorbents possessing narrow size distribution of pores, approximately 6.4 nm. They also showed a type A hysteresis loop of de Boer located at higher relatively pressure than that of the MCM-41 material. It is known that this kind of hysteresis loop is due to cylindrical pores open at both ends [12]. This hysteresis is caused by condensation and evaporation of a hemispherical meniscus produced in cylindrical pores. Fig. 2 and Table 1 show that the surface modification process by MPTMS led to the decrease in the nitrogen adsorption capacity, which resulted in the decrease in the specific surface area and pore volume of the sample. However, the mesopore diameter and the height of hysteresis, which are in proportion to the mesopore volume, were not changed after functionalization. The specific surface area and pore volume of the original mesoporous sample were ca. 768 m^2/g and 1.03 m^3/g , respectively. These results indicate that MPTMS functionalization had an effect on the reduction of micropore volume without any remarkable change on the structural ordering of mesopore and narrow mesopore size distributions of silica mesoporous materials.

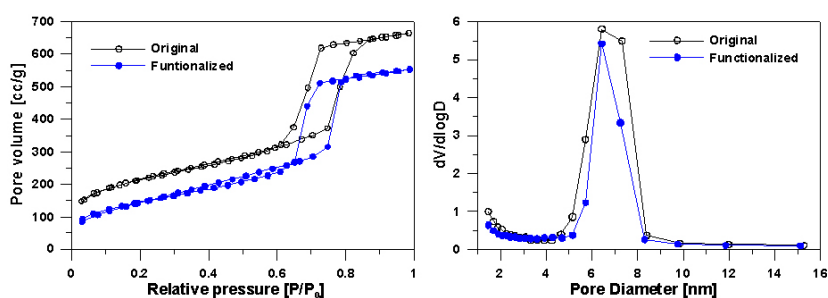


Fig. 2. Nitrogen isotherms of samples and their pore size distributions by BJH method

Table 1 Textural properties of the mesoporous silica materials

Sample	BET surface area (m^2/g)	Pore volume (cm^3/g)	Mesopore diameter (nm)
Original	768	1.03	6.42
Functionalized	538	0.85	6.42

3.2. Adsorption behavior of silver cations

Silver and cadmium ions adsorption capacities of functionalized mesoporous silica were investigated. The ion removal efficiency in solution at 30 °C by varying the ion concentration from 10 to 500 mg/L is shown in Fig. 3(a). The removal efficiencies in Fig. 3(a) were calculated using the following equations [1].

$$\text{The removal efficiency (\%)} = (C_i - C_f)/C_i \times 100$$

Where, C_i and C_f represent the concentrations (mg/L) of the metal ion in initial and final solutions, respectively.

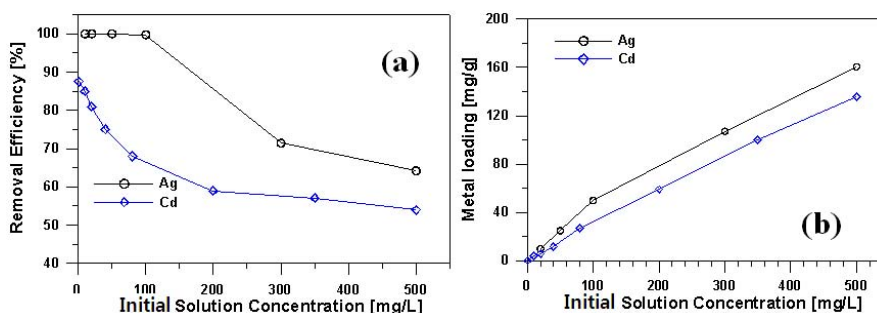


Fig. 3. (a) Removal efficiency and (b) metal loading of Ag and Cd ions according to initial concentration

The removal efficiencies for silver and cadmium ion decreased with increasing metal ion concentration in aqueous solutions. The removal efficiency of silver was higher than that of cadmium. When the silver concentrations of the influent water were under 100 mg/L, the silver concentrations of effluent water were under 0.1mg/L after ion exchange processes of adsorbent sample. This result indicates that thiol-functionalized mesoporous silica is the more efficient adsorbent for silver ions than cadmium ion from water containing lower metal concentrations.

The isotherms of adsorption of metal ions on the thiol-modified mesoporous silica are shown in Fig. 3(b). Silver and cadmium adsorption capacity continued to increase with the influent concentration, indicating that strong interaction took place between the ion exchangeable thiol-surface and the added metal cations. The relationship between the metal concentrations in water and the adsorbed amounts of metal can be approximated to the straight lines. Therefore, these adsorption isotherms can be expressed by Henry equation or Freundlich equation. The adsorption data for silver and cadmium cations over the concentration range from 10 to 500 mg/L at 30 °C have been correlated with Henry equation (Eq. 1) [13].

$$C_{ads}=K_h C_e \quad (1)$$

Where K_h is an adsorption constant, C_{ads} is an adsorbed amount of metal on the adsorbent(mg/g), and C_e is the equilibrium concentration of metal in solution(mg/L). The adsorption constants and statistical fits of the sorption data to the Henry equation are given in Table 2. The Henry equation effectively described the adsorption data with all R^2 values > 0.98 .

Table 2 Constants of adsorption equations for metal cations on functionalized mesoporous silica

Adsorbate	Henry Eq.		Freundlich Eq.		
	K_h (l/g)	R^2	K_f (mg/g)	1/n	R^2
Ag	0.337	0.989	0.846	0.831	0.996
Cd	0.279	0.998	0.071	0.990	0.994

The Freundlich adsorption isotherm has also been used for fitting the adsorption data over a wide range of concentrations. This isotherm gives an expression encompassing the adsorption on the non-uniform surface of adsorbent. The constant of Freundlich can be evaluated by linearization of equation (Eq.2) [14,15].

$$\ln C_{ads} = \ln K_f + 1/n \ln C_e \quad (2)$$

The constants K_f and $1/n$ were calculated and are shown in Table 2. The coefficient K_f is a parameter that reflects the amount of the active adsorption site. $1/n$ is a characteristic coefficient related to energy or intensity of adsorption [13,14]. The Freundlich model as well as the Henry model effectively described the adsorption data with almost value of $R^2 > 0.99$. Thus, the good agreement of isotherms with Freundlich and Henry model in quite high metal concentration range suggest that multilayer adsorption of metal ions takes place in uniform pore. Moreover, the higher values of K_f of adsorbed sample for silver than that for cadmium confirm that the great affinity of the silver ions towards the functionalized silica surface.

4. Conclusions

Thiol-functionalized porous silica with pore size of 6 nm was synthesized for use as heavy metal cation adsorbent, and the silver and cadmium heavy metal loading capacities of this material were examined. After the functionalization of MPTMS, the specific surface area and pore volume of mesoporous silica decreased about 30% and 18%, respectively. The removal efficiencies of silver and cadmium ions decreased with increasing metal ion concentration in aqueous solutions, and it is concluded that FMS is efficient adsorbent of silver than cadmium. The metal adsorption is also improved by increasing metal ion concentration in aqueous solutions. The Freundlich and Henry equations were used to describe the adsorption isotherms of single-solute system. The adsorption isotherms obtained are in agreement with the models of Freundlich and Henry in the whole range of the concentrations studied. It is considered that multilayer adsorption of metal ions in uniform pore takes place as increasing of the metal concentration of solution, from this isotherm results.

5. Acknowledgements

This work was supported by the National Research Foundation of Korea Grant funded by the Korean Government (MEST) (NRF-2010-0023782 and NRF-2011-0014627).

6. References

- [1] J. Perić, M. Trgo, N. V. Medvidović. Removal of zinc, copper and lead by natural zeolite—a comparison of adsorption isotherms. *Water Res.* 2004, 9: 1893-1899.
- [2] B. Bournonville, A. Nzihou, P. Sharrock, G. Depelsenaire. Stabilisation of heavy metal containing dusts by reaction with phosphoric acid: study of the reactivity of fly ash. *J. Hazardous Mater.* 2004, **116**(1-2): 65-74.
- [3] H. A. Qdais, and H. Moussa. Removal of heavy metals from wastewater by membrane processes: a comparative study. *Desalination* 2004, **164**(2): 105-110.
- [4] N. Chiron, R. Guilet, E. Deydier. Adsorption of Cu(II) and Pb(II) onto a grafted silica: isotherm and kinetic models. *Water Res.* 2003, **37**: 3079-3086.
- [5] L. Mercier, and T. J. Pinnavaia. A functionalized porous clay heterostructure for heavy metal ion (Hg^{2+}) trapping. *Micropo. & Mesopo. Mater.* 1998, **20**(1-3): 101-106.
- [6] A. Sayari, S. Hamoudi, Y. Yang, I. L. Moudrakovski, J. R. Ripmeester. New Insights into the synthesis, morphology, and growth of periodic mesoporous organosilicas. *Chem. Mater.* 2000, **12**(12): 3857-3863.
- [7] L. Mercier, and T.J. Pinnavaia. Access in mesoporous materials: Advantages of a uniform pore structure in the design of a heavy metal ion adsorbent for environmental remediation. *Adv. Mater.* 1997, **9**(6): 500-503.
- [8] Q. Yang, J. Liu, J. Yang, L. Zhang, Z. Feng, J. Zhang, C. Li. Acid catalyzed synthesis of ordered bifunctionalized mesoporous organosilicas with large pore. *Micropo. & Mesopo. Mater.* 2005, **77**(2-3): 257-264.
- [9] J. Brown, L. Mercier, T.J. Pinnavaia. Selective adsorption of Hg^{2+} by thiol-functionalized nanoporous silica. *Chem. Commun.* 1999, 69-70.
- [10] L. Mercier, and T. J. Pinnavaia. Heavy metal ion adsorbents formed by the grafting of a thiol functionality to mesoporous silica molecular sieves: factors affecting Hg(II) uptake. *Environ. Sci. Tech.* 1998, **32**: 2749-2754.
- [11] D. Zhao, Q. Huo, J. Feng, B. F. Chmelka, G. D. Stucky. Nonionic triblock and star diblock copolymer and oligomeric surfactant syntheses of highly ordered, hydrothermally stable, mesoporous silica structures. *J. Am. Chem. Soc.* 1998, **120**: 6024-6036.
- [12] S. Lowell, and J. E. Shields. *Powder Surface Area and Porosity*. 3rd ed. Chapman & Hall, London, 1991.
- [13] K. Kibe, M. Takahashi, T. Kameya, K. Urano. Adsorption equilibriums of principal herbicides on paddy soils in Japan. *Sci. Total Environ.* 2000, **263**: 115-125.
- [14] E. Erdem, N. Karapinar, R. Donat. The Removal of heavy metal cations by natural zeolites. *J. Colloid & Interface Sci.* 2004, **280**: 309-314.
- [15] H. Hadjar, B. Hamdi, Z. Kessaissia. Adsorption of heavy metal ions on composite materials prepared by modification of natural silica. *Desalination* 2004, **167**: 165-174.