

Characteristics of Thiol-Functionalized Mesoporous Silica and Its Application to Silver and Cadmium Ion Removal

Jayhyun Park, Hyunjung Kim, and Jaikoo Park

Abstract—An uptake of silver and cadmium from aqueous solutions by ion exchange on functionalized large pore mesoporous silica has been studied. Mesoporous silica with large pore (about 6nm) was synthesized by condensation of siliceous solution using nonionic oligomeric polyethylene glycol block copolymer (P123) as surfactant in acidic medium and was functionalized by 3-mercaptopropyltrimetoxysilane (MPTMS) on surface of silica for good selectivity and high adsorption capacity. The result of nitrogen gas adsorption (BET) and transition electron microscopy (TEM) show that silica adsorbate have ordered mesoporous structure with uniform pore size distribution. ^{29}Si MAS NMR, TG and FT-IR confirm the functionalization of MPTMS on the surface of mesoporous silica. 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.

Index Terms—Silver, adsorption, mesoporous, thiol.

I. INTRODUCTION

The optimization of wastewater treatment process requires a development of new operations based on low cost materials with high pollutant-removal efficiency [1]. The removal of toxic heavy metals for purification of water and wastewater, and the recovery of heavy valuable metals in the wastewater process can often result in cost saving [2]. Numerous processes such as ion exchange, precipitation, adsorption, ultrafiltration or reverse osmosis have been used for removing heavy metal ions [3-6]. These techniques have been successful, but they offer the disadvantages related to removal efficiency and in the majority of the cases, the process is not a recovery but really an elimination of metal. 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. These limitations ruled out the possibility of heavy metal recovery or recycle in wastewater solution because of the economical efficiency.

The use of functionalized mesoporous silica (FMS) materials as potential sorbents for the removal of heavy metal has been investigated recently [6-10]. Since the first report of the mesoporous materials surface modified with functional group [11], their synthesis and applications have attracted great interest because of the combined advantages of inorganic-organic composites and the mesoporous structure [12]. The uniformly distributed functional group in the mesoporous framework will impart the mesoporous materials with unique properties. 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 [13-16]. Wang and Stein reported that mesoporous silica (MCM-41) was functionalized with mercaptopropyl groups and its mercury loading was of 2.5 mmol g^{-1} [16,17]. After that, a number of FMS for heavy metal loading were synthesized with pore sizes less than 3nm though Yang reported that FMS with pore size larger than 3nm also has good selectivity of Hg and Cd [10]. Furthermore, main targeted metal ions onto FMS were mercury, cadmium, lead and zinc [18-20] and most of these investigations focus on the metal loading amount, selectivity and the distribution coefficient of heavy metal (K_d) but not adsorption isotherm.

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 chromate. And 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 (about 6nm) by condensation of siliceous solution in acidic medium using nonionic oligomeric polyethylene glycol block copolymer (P123) as surfactant and the functionalization of 3-mercaptopropyl trimetoxysilane (MPTMS) on the surface of mesoporous silica. The synthesized FMS materials were used as silver and cadmium ion adsorbents for application to aqueous solutions. 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.

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Jayhyun Park is with the R&D Team, Institute of Mine Reclamation Corporation, Coal Center, 30 Chungjin-dong, Jongno-gu, Seoul 110-727, Republic of Korea (e-mail: jayhp@mireco.or.kr).

Hyunjung Kim is with Department of Mineral Resources and Energy Engineering, Chonbuk National University, 664-14 Duckjin-Dong 1Ga, Duckjin-Gu, Jeonju, Jeonbuk 561-756, Republic of Korea (e-mail: kshjkim@jbnu.ac.kr, corresponding author).

Jaikoo Park is with the Department of Natural Resources and Environmental Engineering, Hanyang University, #17 Heangdang-dong, Seongdong-gu, Seoul 133-791, Republic of Korea (e-mail: jkpark@hanyang.ac.kr, corresponding author).

II. MATERIALS AND METHODS

A. Absorbent Synthesis Procedure

Zhao et al. [21] 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.

B. 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.

C. Characterization

The images of the IR transmission spectra were determined in transmission mode using potassium bromide based disk pellets prepared by mixing KBr powder with sample powder. The spectra were measured in the range of 4000cm⁻¹–400cm⁻¹, with a resolution of 2 cm⁻¹, using a Fourier transform infrared spectrometer (Nicolet, Omnic 405 Model). Thermogravimetric analyses of the samples were performed with a TA Instruments SDT2960. The sample for TG was not calcined to avoid the other thermal effect. The extraction with ethanol took the place of the calcination for removal of surfactant. In order to remove the surfactant, 3 g of solid was treated with 500 mL of ethanol at room temperature for 16h, then filtered, washed and dried. The sample powders were heated in flowing air from ambient temperature to 400 °C at a rate of 5 °C min⁻¹. 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.

III. RESULTS AND DISCUSSION

A. Adsorbent Structural Characterization

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).

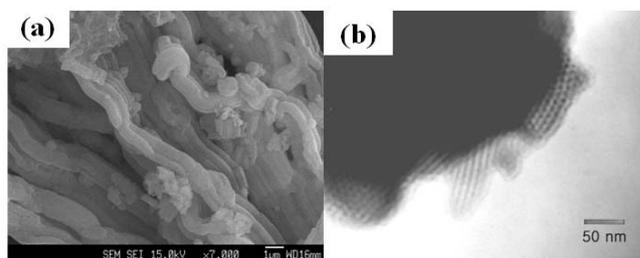


Fig. 1. (a)SEM and (b)TEM images of synthesized mesoporous silica material

The nitrogen adsorption-desorption isotherms and the pore size distribution of the synthesized material and functionalized materials are shown in Fig. 2.

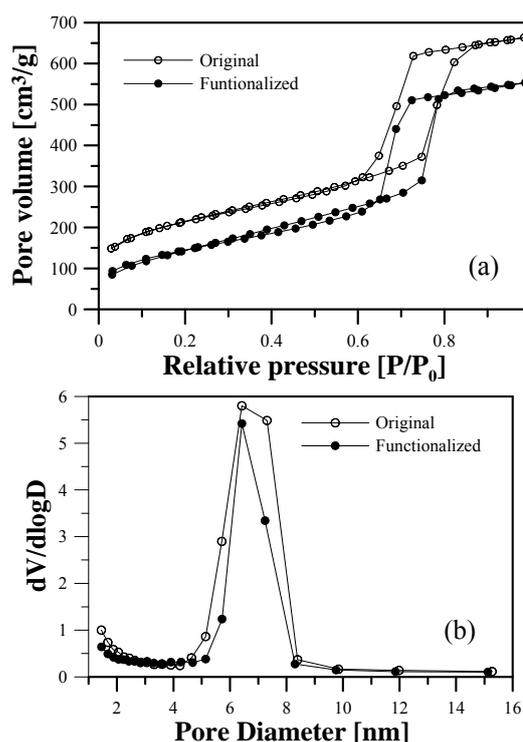


Fig. 2. (a) Nitrogen isotherms of samples and their (b) pore size distributions by BJH method

TABLE I: 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

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/P₀ 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 [22]. 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 brought about a decrease in the nitrogen adsorption capacity, reflected in a decrease in the specific surface area and pore volume of the sample. However, the mesopore diameter and the height of hysteresis which is in proportion to the mesopore volume don't reduce at all after functionalization. The specific surface area and pore volume of the original mesoporous sample were about 768 m²/g and 1.03 cm³/g respectively. These results indicate that MPTMS functionalization have an effect on the reduction of micro-pore volume without any remarkable change on the structural ordering of mesopore and narrow meso-pore size distributions of silica mesoporous materials.

B. Adsorbent Compositional Characterization

The surfaces of the mesoporous silica before and after the functionalization were characterized by FT-IR (Fig. 3).

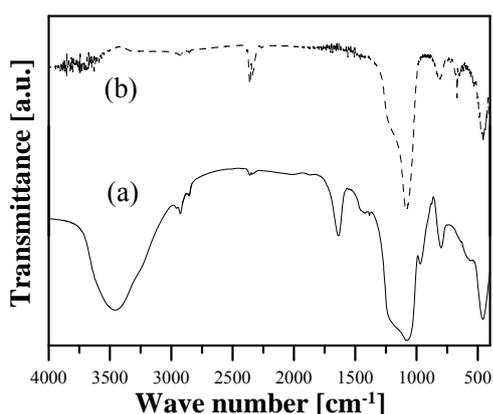


Fig. 3. FT-IR results of surfactant free mesoporous materials: (a) original and (b) functionalized.

The spectrum of the original mesoporous material was similar to that of amorphous silica. The bands at 798 cm⁻¹ and 450 cm⁻¹ were due to Si-O-Si symmetric stretching and bending vibrations, respectively. The band at 950 cm⁻¹ and 570 cm⁻¹ was due to Si-OH stretching and Si-OH vibration [23]. The sharp band at 1635 cm⁻¹ attributed to deformed water that interacted through hydrogen bonds with silanol groups was disappeared for the MPTMS functionalized samples. After functionalization, the Si-OH related peaks which were at 570 cm⁻¹ and 950 cm⁻¹ disappeared. But the siloxane (Si-O-Si) peaks which appeared at 450 cm⁻¹, 798 cm⁻¹ and 1070 cm⁻¹ had been kept after functionalization. The broad band in range of 3000-3750 cm⁻¹ was associated with the silanol stretching of surface and vibrational structure of siloxane by water molecule adsorption on silica surface. This broad band for MPTMS modified samples almost disappeared comparing to that of the original sample. It indicates that the surface of thiol modified samples, comparing to the original sample, is so hydrophobic that it significantly inhibit water molecule adsorption. After

surfactant removal process by washing with ethanol, the surfactant in unfunctionalized sample was remained as evidenced by appearing the C-H vibrations in the range of 2920–2875 cm⁻¹ and at 1375 cm⁻¹. It is hard to comment that the small peaks in the range of 2920–2875 cm⁻¹ in the functionalized silica may be due to the functionalization of mercaptopropyl group. Because the C-H vibrations of the mercaptopropyl group of functionalized sample in the range of 2926–2880 cm⁻¹ are overlapped with the C-H vibrations due to the remained surfactant. But, the CH₂ rocking vibration of Si-CH₂R appeared at 690 cm⁻¹ in the functionalized silica. Therefore, these C-H vibrations of the mercaptopropyl groups and the disappearance of silanol groups for material modified with MPTMS suggest that MPTMS is anchored well on the surface of silica.

²⁹Si-MAS-NMR technique was also used employed to investigate the surface information on functionalized silica (Fig. 4). The ²⁹Si NMR spectra for original sample shows that the Q₂ signal derived from silandiol (Si(OH)₂) group exists a little and that the silanol group (Si-OH, Q₃) is more than the siloxane (Si-O-Si, Q₄) group on silica surface. The Si-NMR signals of functionalized sample display higher Q₄ signal than Q₃ signal and disappearance of Q₂ signal. These results mean that MPTMS react with the active silanol and the silandiol groups.

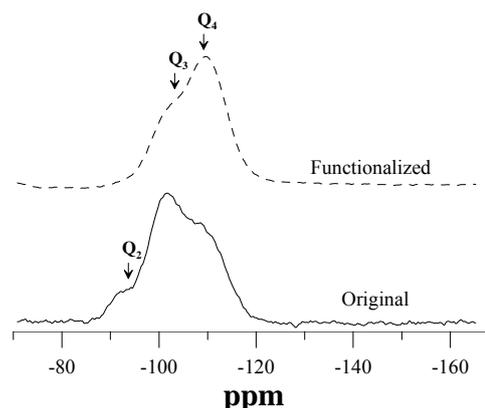


Fig. 4. ²⁹Si-MAS-NMR of surfactant free mesoporous silica absorbents

C. Thermogravimetric Analysis

Thermogravimetric analysis of the samples before and after functionalization was conducted. The weight loss below 70 °C in Fig. 5a is due to the removal of physisorbed water. There are rarely weight loss of this temperature part for the functionalized sample, indicating that the surface of silica come to be hydrophobic by functionalization. The original mesoporous material rapidly lost weight at between 230 °C and 280 °C (Fig. 5a). Weight loss in this range may be due to the removal of surfactant. It was considered that surfactant was still remained in the pore structure of mesoporous silica, though surfactant had been washed out with ethanol several times. Fig. 5 show that the weight loss of the MPTMS modified sample is different from that of the original material. The functionalized sample showed broader weight losses than that of the original mesoporous silica through the temperature range from 230 to 350 °C (Fig. 5b). Its weight loss could be assigned to the decomposition of unwashed surfactant and attached propylthiol group on silica surface.

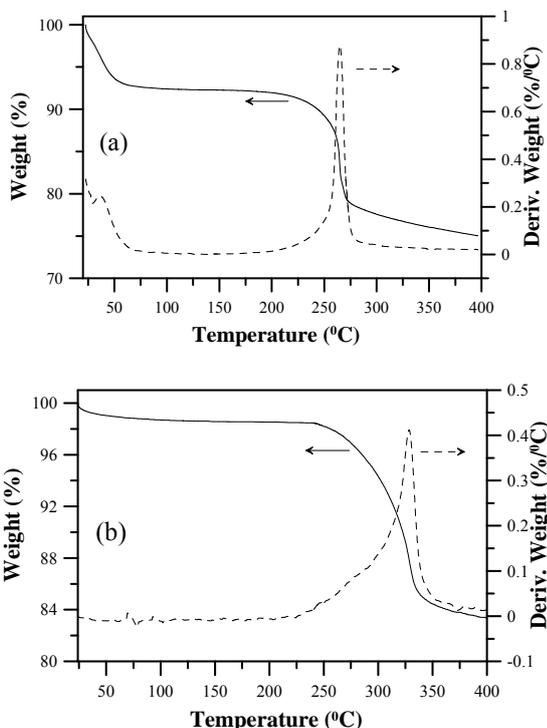


Fig. 5. Thermogravimetric analysis of (a) original and (b) thiol functionalized mesoporous silica.

D. Adsorption of Cations on Mesoporous Silica

Silver and cadmium ions adsorption capacities of functional 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. 6. The removal efficiencies in Fig. 6 were calculated using the following equations (1).

$$\text{Removal efficiency (\%)} = (C_i - C_f)/C_i \times 100 \quad (1)$$

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

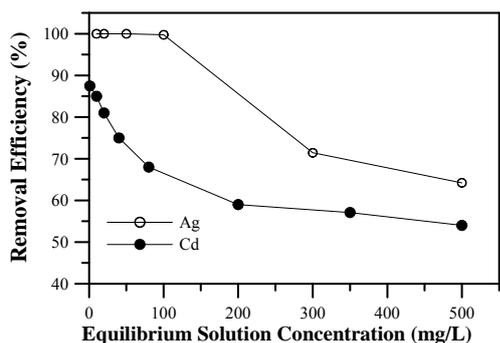


Fig. 6. Removal efficiency of Ag and Cd ions according to initial concentration.

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

The isotherms of adsorption of metal ions on the thiol modified mesoporous silica are shown in Fig. 7. Silver and cadmium adsorption capacity continued to increase with the rise in the influent concentration, indicating that strong interaction took place between the ion exchangeable thiol surface and the added metal cations. The relationships 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 cations over the concentration range from 10 to 500 mg/L at 30 °C have been correlated with Henry equation (2) [24].

$$C_{ads} = K_h C_e \quad (2)$$

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 .

The Freundlich adsorption isotherm, one of the most widely used isotherms, has 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 Freundlich adsorption model was also applied to the removal on the silver and cadmium cations (Fig. 7). The constant of Freundlich can be evaluated by linearization of (3) [25,26].

$$\ln C_{ads} = \ln K_f + 1/n \ln C_e \quad (3)$$

The constants K_f and $1/n$ were calculated and the obtained parameters 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 [24,25].

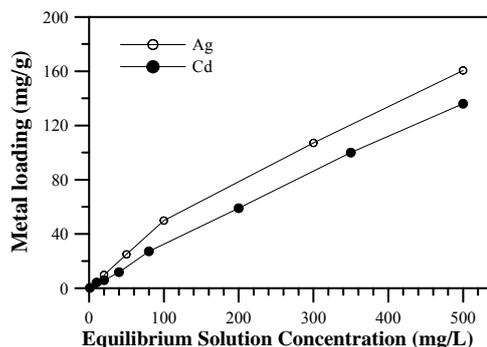


Fig. 7. Ag and Cd loading as a function of solution concentration

TABLE II: 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 model as well as the Henry model effectively described the adsorption data with almost value of $R^2 > 0.99$. Moreover, the higher values of K_f of adsorbed sample for Ag than that for Cd confirm the great affinity of the ions of silver towards the functionalized silica surface. This isotherm does not predict mathematically any saturation of the adsorbent surface; infinite surface coverage is plotted against $\ln C_e$, yielding a straight line indicating multilayer adsorption on the surface [27,28]. 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.

IV. CONCLUSIONS

Thiol functional porous silica with pore size of 6nm 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 FT-IR, Si MAS NMR and TG results showed that hydrophilic mesoporous silica surface (Si-OH) was replaced by hydrophobic MPTMS.

The removal efficiencies of Ag and Cd ions decrease with increasing metal ion concentration in aqueous solutions and it is concluded that FMS is efficient adsorbent of Ag than Cd. 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 isotherms of adsorption 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.

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