



Cu²⁺ sequestration by amine-functionalized silica nanotubes



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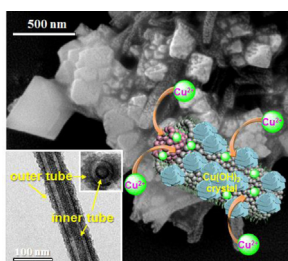
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HIGHLIGHTS

- Fabrication of nanotubular adsorbent for Cu²⁺ sequestration.
- High amount of Cu²⁺ sequestration using the nanotubular adsorbent.
- Combined technique of precipitation and adsorption for the enhancement of Cu²⁺ sequestration.

GRAPHICAL ABSTRACT



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ABSTRACT

A novel method for Cu²⁺ sequestration in Cu²⁺ aqueous solution has been demonstrated using amine-functionalized double-walled silica nanotubes (DWSNTs). Herein, the precipitation method and the adsorption method are combined to remove Cu²⁺ in the Cu²⁺ aqueous solution. Primary (1°), secondary (2°), tertiary (3°), di-, tri- amines are immobilized on the surface of DWSNT as the adsorption site. The results show that the Cu²⁺ adsorption amount on the amine-functionalized DWSNTs is in the following order: tri-amine > di-amine > 1° amine > 2° amine > 3° amine. The complexed Cu²⁺s with the amine-functionalized DWSNTs become Cu(OH)₂ crystals due to the reaction with OH⁻s dissociated from water. Thus, the amine-functionalized DWSNTs show the superior sequestration capacity of Cu²⁺ in the Cu²⁺ aqueous solution owing to the Cu(OH)₂ crystals growth on them. FT-IR, FEG-SEM, HR-TEM, and XRD studies demonstrate the mechanism of the Cu²⁺ adsorption and the Cu(OH)₂ crystals growth. The crystallization-technique of the heavy metal ion on the amine-functionalized DWSNTs is also expected to have potential applications such as the facile synthesis of nano- and microparticles, and the metal catalyst supporter.

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1. Introduction

Because of the rapid development of the modern industry, toxic heavy metal ions have become major contributors to pollution of the biosphere [1]. These heavy metal ions enter water through discharge from various industrial activities such as mining, batteries, metal plating, alloy making, fertilizer, pesticide industries [2]. Copper ions are also one of the toxic heavy metals. Cu occurs in 0, +1 and +2 oxidation states. In these oxidation states of Cu, the cupric

ion (Cu²⁺) is the most toxic species [3]. Cu²⁺ is an indispensable micronutrient, but the World Health Organization (WHO) recommended a maximum acceptable concentration of Cu²⁺ in drinking water of 2 mg/L [4]. Presence of higher concentrations (>5 mg/L) in the body has been linkage many of health problems such as kidney damage, high fever, hemolysis and vomiting [5]. As a result, it is essential to remove Cu²⁺ from wastewater before disposal.

A wide variety of techniques such as precipitation [6], coagulation/co-precipitation [7], ion exchange [8,9], cementation [10], electro dialysis [11,12], electrowinning [13], electrocoagulation [14,15], nanofiltration [16,17], adsorption [18–22], and reverse osmosis [23] are available for removal of heavy metals from liquid effluents. In these techniques, the adsorption method has

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received a great deal of attention due to low cost of the materials, relative simple process, and reusability [24–31]. Despite these advantages, the sequestration efficiency of the heavy metal ion in water is restricted from the amount of the adsorption active sites. Therefore, almost researches have been concentrated on enlarging the surface area of the adsorbent for the immobilization of large amounts of adsorption sites [32–35].

Herein, a different approach is taken to fabricate a high performance adsorbent. The precipitation method and the adsorption method are combined to remove Cu^{2+} in Cu^{2+} aqueous solution. We synthesize new tubular silica as a support material to immobilize the adsorption sites for Cu^{2+} sequestration. Although the tubular silica support has good pores for mass transfer, its specific surface area is relatively lower than the SBA-15, SBA-16, MCM-41, MCM-48, or KIT-6. This disadvantage causes the low Cu^{2+} removal capacity. Therefore, we design and synthesize the double-walled silica nanotube (DWSNT) to solve its shortcoming. We also report on the effects of amine types (primary, secondary, and tertiary) and amine numbers (mono, di, and tri) as the adsorption sites for Cu^{2+} sequestration. In this study, the adsorbed Cu^{2+} s on the surface of the amine-functionalized DWSNTs crystallized because of the high amount of OH⁻s near the surface which are dissociated from H_2O molecules. As the result of crystallization of Cu^{2+} on the amine-functionalized DWSNT, the modified DWSNT showed the high sequestration amount of Cu^{2+} in the aqueous solution. Therefore, in this study, the Cu^{2+} s adsorption amount on the amine-functionalized DWSNTs is not restricted to the amount of the complexed Cu^{2+} s with amines. It contains both amounts of complexed Cu^{2+} and Cu^{2+} in the crystallized Cu compound, and is the Cu^{2+} sequestration amount in the Cu^{2+} aqueous solution. In addition, the chemical state of the adsorbed Cu^{2+} on the amine-functionalized DWSNT and the crystallized Cu compound have been demonstrated using Fourier transform infrared spectroscopy (FT-IR) and X-ray diffraction (XRD). Our adsorption-crystallization method using amine-functionalized DWSNTs to remove Cu^{2+} in aqueous solution has been first reported, and showed superior adsorption to other adsorbents.

2. Materials and methods

2.1. Preparation of amine-functionalized DWSNTs

DWSNT was synthesized using a tubular template composed of 2-amino-*N*-dodecylacetamide (ADAA, $\text{H}_2\text{N}-\text{CH}_2-\text{CONH}-(\text{CH}_2)_{11}-\text{CH}_3$, Thermolon Korea Co., Busan, Korea). A 1 mmol of ADAA was dissolved in the mixture solution consisted of 20 mL of deionized water (DI water, obtained from a Milli-Q water system as 18.2 M Ω cm, Millipore, USA) and 2 mL of ethanol (Sigma–Aldrich Chemical Co., Milwaukee, USA) solution, and the ADAA dissolved solution was well stirred for 2 h at 60 °C. Then, 4 mmol of tetraethyl orthosilicate (TEOS, Aldrich Chemical Co., Milwaukee, USA) was added into the solution with stirring, and then resulting mixture was kept at room temperature for 72 h. The solid product was filtered, washed with ethanol and DI water, and dried in an oven at 50 °C for 24 h followed by calcination in air at 550 °C for 5 h to completely remove the ADAA. The calcined DWSNT was subsequently dried at 200 °C under vacuum for 3 h. The synthesized DWSNT was treated using a nochromix solution consisted of 3 g of nochromix (Godax Laboratories, Inc., Cabin John, USA) and 280 g of 98% sulfuric acid (Aldrich Chemical Co., Milwaukee, USA) for 30 min at ambient temperature. Subsequently, it was rinsed several times with DI water and ethanol (Sigma–Aldrich Chemical Co., Milwaukee, USA). And then the DWSNT was dried at 100 °C under vacuum for 2 days. 25 mmol of (3-aminopropyl) trimethoxysilane (APTMS, Aldrich Chemical Co., Milwaukee, USA) and 2 g of nochromix-treated

DWSNT were added to anhydrous toluene (150 mL, Sigma–Aldrich Chemical Co., Milwaukee, USA). The coupling reaction was allowed to proceed for 24 h at 30 °C with a gentle stirring under a nitrogen atmosphere. After reaction, the amine-functionalized DWSNT was rinsed with ethanol (Sigma–Aldrich Chemical Co., Milwaukee, USA). The modified DWSNT was dried in an oven at 120 °C for 2 h. After drying, it was rinsed three times with toluene (Sigma–Aldrich Chemical Co., Milwaukee, USA), a mixed solution of toluene and ethanol (1:1), and ethanol, in that order. To increase of amount of coupled APTMS on DWSNT, the above procedure was repeated three times. Finally, amine-functionalized DWSNT was freeze-dried under vacuum (pressure lower than 5 mTorr) for 1 week after washing with DI water. The immobilization of [3-(methylamino) propyl] trimethoxysilane (MAPTMS, Aldrich Chemical Co., Milwaukee, USA), [3-(diethylamino) propyl] trimethoxysilane (DEAPTMS, Aldrich Chemical Co., Milwaukee, USA), [3-(2-aminoethyl) amino-propyl] trimethoxysilane (AEAPTMS, Pittsburgh, Acros Organics Co., USA), and 3-[2-(2-aminoethylamino) ethylamino] propyl-trimethoxysilane (AEAEAPTMS, Acros Organics Co., Pittsburgh, USA) on the DWSNT was carried out by the same procedure with the above APTMS-immobilization method.

2.2. Characterization

The morphologies of the DWSNT, the amine-functionalized DWSNTs, and the Cu^{2+} -adsorbed amine-functionalized DWSNTs were examined using a field emission gun scanning electron microscopy (FEG-SEM) (Inspect F50, FEI, Hillsboro, USA) at 15 kV. The samples for FEG-SEM were prepared by dropping a large number of the modified DWSNTs onto a double-sided adhesive carbon disk and sputter-coated with a thin layer of Pt/Pd (E-1010, Hitachi, Japan) to prevent sample charging problems. High-resolution transmission electron microscopy (HR-TEM) images were obtained with a FEI Technai F20 (Hillsboro, USA) operating at 200 kV. The samples for HR-TEM were prepared by dispersing a large number of particles of the products through a slurry in ethanol onto a nickel grid, followed by evaporation. Nitrogen adsorption and desorption isotherms were measured at 77.3 K on an ASAP2420 (Micromeritics, Norcross, USA) having an accelerated surface area and porosimetry system. Prior to the determination of adsorption isotherm, the sample was evacuated at 1.333 Pa and 423.15 K for 2 h to remove all physisorbed species from the surface of the adsorbent. Surface area was determined by the Brunauer–Emmett–Teller (BET) method, and the pore size distributions were calculated by Barrett–Joyner–Halenda (BJH) method from the isotherm of adsorption branch. The nitrogen amount of amine-functionalized DWSNTs was obtained using an elemental analyzer (EA 1108, FISON Instruments, Parkton, USA). Fourier transform infrared (FT-IR) spectroscopy (Frontier, PerkinElmer, Waltham, USA) was used to confirm the synthesis of amine-functionalized DWSNTs and analyze the Cu^{2+} -adsorbed amine-functionalized DWSNTs. Samples were blended with KBr, and then pressed into disks for analysis. X-ray diffraction (XRD) patterns were recorded on a Rigaku ATX-G diffractometer (Tokyo, Japan) with a high-power Cu K α source operating at 60 kV and 300 mA.

2.3. Quantitative analysis of adsorbed Cu^{2+} on the amine-functionalized DWSNT

To analyze the Cu^{2+} adsorption capacity of the amine-functionalized DWSNT, CuCl_2 aqueous solution was prepared. pH-adjusted solution (100 mL, pH: 1.7–4.9) of 10 mM Cu^{2+} ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, Aldrich Chemical Co., Milwaukee, USA) and the amine-functionalized DWSNT (0.1 g) were placed in Erlenmeyer flasks and shaken for 24 h (200 rpm). After removing Cu^{2+} -adsorbed amine-functionalized DWSNT, the Cu^{2+} concentration in the

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