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Comparison of adsorptive features between silver ion and silver nanoparticles on nanoporous materials

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ABSTRACT

The removal of Ag^+ or AgNPs released from nano-products or effluent of WTP is important to reduce the potential risk of AgNPs. In this work, we prepared bimodal nanoporous silica (BNS) to compare the removal efficiency of Ag^+ and AgNP with unimodal nanoporous silica (NS). To determine the adsorption capacity of Ag^+ and AgNPs on NS and BNS, isotherm and kinetics studies was carried out at different concentrations. The results showed BNS with a bimodal nanoporous structure and a large external surface showed a higher uptake capacity and faster adsorption rate.

1. Introduction

The rapidly increasing nanotechnology industry is producing nanomaterials that are being incorporated into nano-consumer products. Especially, the use of silver nanoparticles (AgNPs) in nano-consumer products is accelerating. Because AgNPs are one of the most promising nanoparticles for future applications due to their antimicrobial, antifungal, and partially antiviral properties [1–6], AgNPs are used in various fields of applications such as disinfecting sprays, cosmetics, fabrics, and household appliances [2–5]. However, such widespread use can lead to exposure of Ag^+ or AgNPs to the environment and to humans, and many studies of the toxic effects of AgNPs have been reported [6–8]. While Ag^+ released from AgNPs, AgNP surface-associated ionic Ag, and AgNPs are all likely to contribute to observed toxicity, ionic Ag generally exhibits the strongest toxic effect [6]. Namely, the ubiquitous use of commercial products containing AgNPs could potentially compromise the health of ecosystems [3].

A few studies are available on the leaching of silver from clothing into water [1–5,9,10]. For example, Benn and Westerhoff investigated the silver released from commercial socks into water, and they found socks that contained up to 1.36 mg-Ag/g-sock leached as much as 0.65 mg of silver in 0.5 L of distilled water [3]. Nowack and co-workers also determined the amount and form of silver released during washing from nine fabrics with different methods of silver incorporation into the fibers [1]. Impellitter et al. have shown that bleach has strong effects on the speciation of silver in textiles and that significant transformation of elemental Ag to AgCl occurred in the presence of bleach [9]. Farkas et al. provided evidence that AgNPs of about 10 nm diameter are present in the effluent of washing machines that release Ag into the washwater [10].

The silver released into sewer systems can be partitioned onto wastewater biomass and be removed at the wastewater treatment plant (WTP). Based on the pilot scaled WTP, about 90–95% spiked AgNPs are efficiently reduced by biological treatment and accumulated in activated sludge or biosolids [11]. Namely, it is possible for 5–10% of silver to remain in the treated water. If the removal of silver in WTP is difficult, Ag^+ or AgNPs remaining in the treated effluent stream can enter surface water environments, potentially disrupting numerous biological ecosystems. Therefore, the removal of Ag^+ or AgNPs released from the nano-products or effluent of WTP is important to reduce the potential risk of AgNPs.

Although many studies on the removal of Ag^+ from aqueous solutions have been reported [12], few studies have been carried out on the elimination of AgNPs using adsorbents or resins. Khan et al. reported the adsorptive removal of AgNPs by resistant bacteria to AgNP, isolated from the sewage environment [13]. The removal feature of AgNPs might differ from that of Ag^+ of aqueous

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solutions. Therefore, in this work, we investigated the adsorptive features of different sizes of Ag^+ ion and AgNP.

Porous materials with a controlled nanostructure are of fundamental importance in science and engineering and have continued to attract considerable interest in a variety of applications, including organic or metal ion adsorbents [14,15]. Intensive research has been conducted relative to the design of a variety of nanoporous materials using chemical templates such as surfactants, porogens, and polymers. In addition, hierarchical channels or well-connected small and large pore networks show multiple advantages for application in adsorbent in aqueous conditions [16]. Micropores and mesopores provide size or shape selectivity for a guest molecule, while additional macropores reduce transport limitations. In this work, we prepared a bimodal nanoporous adsorbent to compare the removal efficiency of Ag^+ and AgNP with unimodal nanoporous adsorbent. For the removal of target materials, the surface of adsorbents should be functionalized with thiol, carboxyl, or amine groups. Therefore, amine-functionalized (bimodal) nanoporous adsorbents are finally prepared to investigate the different adsorptive features between Ag^+ and AgNP from aqueous solutions.

2. Experimental

2.1. Preparation of nanoporous silica (NS)

Nanoporous silica (NS) was synthesized by dissolving 2 g of cetyltrimethylammonium bromide (CTAB) in 120 mL of deionized water (DW) and stirring until the solution was homogeneous and clear. After adding 8 mL of ammonium hydroxide, the mixture was stirred for 5 min, after which 10 mL of tetraethoxylorthosilane (TEOS) was added. After drying the resulting material, calcination was performed at 550 °C for 5 h to remove CTAB [17].

2.2. Preparation of bimodal nanoporous silica (BNS)

To prepare the bimodal nanoporous silica (BNS), polystyrene (PS) beads are used as a physical template. An emulsifier-free emulsion polymerization method was used for the synthesis of nearly monodisperse latex beads of PS at a size of ca. 100 nm [16]. The PS beads were prepared using 700 mL of degassed water, 54 ml of styrene monomer, 0.65 g of potassium persulfate (Aldrich) as the initiator, and 20 mL of divinylbenzene as a cross-linking agent. The PS beads were prepared at 70 °C and 350 rpm, and dried under ambient conditions. They were then added to the NS solution before drying, and the remaining process was the same at the preparation of NS.

2.3. Functionalization of porous silicas

The amine functionalized porous adsorbents were prepared as follows: A 1 g sample of calcined porous silica was heated under reflux in 25 mL of anhydrous ethanol containing 50 mM aminopropyltriethoxy silane (APTES) for 24 h. The products were recovered by filtration and washed several times with acetone and ethanol.

2.4. Adsorption test for isotherm and kinetics

The equilibrium concentrations for Ag^+ and three different AgNPs were controlled at 5–200 ppm. Approximately 0.1 g of dried porous adsorbents were added to 20 mL of a solution prepared at a predetermined Ag^+ and AgNPs concentration using DW, followed by shaking at room temperature for 24 h. The samples were separated by filtration, and the adsorption capacities were calculated from the difference between the initial and the final concentrations. A kinetic study was carried out at different intervals of time according to the above procedure to determine the rate of Ag^+ and AgNPs removal by porous silica at a concentration of 200 ppm. The rate constants were calculated using the conventional rate expression.

2.5. Characterizations

The morphology of the prepared materials was observed using both TEM (JEM-200CX, Jeol) and SEM (XL-20, Philips). Nitrogen sorption isotherms were examined at 77 K using a Micromeritics ASAP-2010 sorptometer (Buruker). The adsorption capacities were measured by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, Shimadzu ICPQ 1000). Particle size distribution was analyzed by dynamic light scattering spectroscopy (DLS, ELS-Z Photal).

3. Results and discussion

3.1. Characterization of porous adsorbents and AgNPs

Nanoporous silica (NS) and bimodal nanoporous silica (BNS) are prepared using the templating method, and CTAB and PS beads are used as chemical and physical templates, respectively. In general, NS prepared by CTAB as a chemical template showed a diameter of 2–10 nm and surface area of 600–1200 m^2/g [14,17]. The high surface area and uniform pore structure of NS were helpful for applying catalysts and adsorbents as physical supports. In metal ion adsorption, Ag^+ with 129 pm of ionic radius could be easily adsorbed onto the inner surface of the nanopore of NS and thus all internal surface areas were utilized by ion adsorption. However, AgNP with a larger diameter than ionic state cannot penetrate into the inner pore and stays only on the outer surface of NS. Therefore, all internal surface areas are useless for adsorbing AgNP using NS.

To enhance the adsorption capacity for AgNP, the width of the external surface area should be increased. Tanev and Pinnavaia defined and classified two terms: framework porosity and textural porosity [18]. Framework porosity represents the porosity contained within the uniform channels of a templated framework, while textural porosity represents porosity arising from non-crystalline intra-aggregate voids and spaces formed as a result of interparticle contact. NS with well-developed textural porosity shows a large external surface area.

In our previous report for the preparation of bimodal porous alumina using PS beads [16], the adsorbent showed 3.3 nm of nanopore and 5 μm of macropore. Their surfaces were 1.5 times larger than that of unimodal nanoporous alumina. Therefore, to enlarge the external surface, bimodal nanoporous silica was prepared using CTAB and PS bead, which formed a nanopore and submicron-pore in BNS. PS beads prepared using the emulsifier-free emulsion polymerization method showed nearly monodisperse latex beads of PS at a size of ca. 100 nm. When PS beads are added to the synthesizing solution of NS, the core-PS/shell-NS structure was formed. After the calcination step to remove the PS and CTAB, a hollow sphere can be obtained. The aggregation of spherical BNS formed the textural porosity and enlarged the external surface area.

As shown in Fig. 1, two adsorbents have different pore structures and external morphologies. NS has a sponge-like nanopore structure, indicating the advantage of a highly interconnected pore system, while BNS shows an aggregated form of hollow sphere. The inner pore and wall thickness of the nanopore were about 100–150 nm and 20 nm, respectively. Since the primary hollow sphere with 140–170 nm forms aggregates, the void fraction between the aggregates formed textural pores and a coarse surface. To define the pore sizes of NS and BNS, a N_2