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Facile synthesis and characterization of γ-AlOOH/PVA composite granules for Cr(VI) adsorption

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ABSTRACT

γ-AlOOH(boehmite)/PVA composite granules with high adsorption performance towards Cr(VI) were successfully synthesized by combining sol–gel and oil-drop methods. The γ-AlOOH/PVA sample with 35 wt% PVA showed the highest Cr(IV) adsorption capacity of 35.91 mg/g, which was much higher than that of the pure γ-AlOOH sample (17.08 mg/g). The adsorption behaviors of Cr(VI) ions onto the γ-AlOOH and γ-AlOOH/PVA granules were well described by the pseudo-second-order kinetic model, and the adsorption mechanisms included electrostatic attraction, ligand exchange and redox reaction. The recovery of Cr(VI) under basic conditions was conducted to evaluate the practical utility of the synthesized composite granules.
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Introduction

Cr(VI) is well known as being carcinogenic and having high mobility in the environment, and it is therefore classified as a serious environmental pollutant [1–4]. In aqueous solutions, Cr(VI) can exist in several forms that are difficult to eliminate through conventional means including CrO_4^{2-}, $HCrO_4^-$, and $Cr_2O_7^{2-}$ (depending on the solution pH and concentration) [1]. The removal of Cr(VI) from industrial effluent typically involves the reduction of Cr(VI) to Cr(III), followed by either precipitation or adsorption [5]. The synthesis of inexpensive adsorbents for the removal of Cr(VI) from wastewater has been attracting attention in recent years, and many kinds of adsorbent materials have been investigated [1,2,4–7]. Among them, aluminum oxide, aluminum hydroxide and oxyhydroxide showed excellent physicochemical properties for Cr(VI) removal [8]. Alternatively, biochar [7], activated carbon [9,10], hollow carbon nanofibers (CNFs) [11], SiO_2@γ-AlOOH [12], rice husk derived magnetic absorbent [13], and Fe_2O_3@AlOOH [14], poly(ether sulfone) nanofiber [15] showed good adsorption of Cr(VI). However, it is still a challenge to prepare adsorbents with high Cr adsorption capacity in a simple and easy way.

Boehmite (AlOOH) is known as an important precursor material for transition aluminas, and it has been extensively used as a catalyst support, in adsorbents and as a membrane material [8,16]. Boehmite exists in two distinct forms: well-crystallized boehmite and pseudo-boehmite, and these have significantly different morphologies, porosities and surface areas [17]. Due to the high surface area and well-defined pore structures, boehmite is considered to be a potential adsorbent for chromium ions [16]. Very recently, Luo et al. [8] prepared AlOOH/PVA composite membranes for Cr(VI) adsorption with the assistance of glacial acetic acid. They reported that a AlOOH/PVA composite membrane showed much better adsorption performance compared to pure boehmite and commercial boehmite [8]. PVA has been extensively used as a surfactant for synthesis of nanomaterials [18], in nanofiltration [19] and biomedical applications [20] due to its low toxicity, unique mechanical strength, biocompatibility, and toughness. Film-forming characteristics of PVA were utilized for preparing free-standing AlOOH/PVA membranes, which have great potential to remove pollutants due to their easy separation from aqueous media. However, it is more desirable to prepare this material to millimeter-scale spheres for versatile applications as adsorbents.

In this study, a facile and scalable synthesis of spherical γ-AlOOH/PVA granules for Cr(VI) removal from aqueous solution was conducted by combining the sol–gel and oil-drop methods. As the product granular adsorbents are spherical (in millimeter scale), they can be easily packed in a fixed-bed reactor and separated from

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aqueous solution after adsorption compared to the powder-type adsorbents. The effects of PVA concentration and solution pH on the adsorption behaviors of γ-AlOOH/PVA granules were systematically investigated. Also, the adsorption mechanism of Cr(VI) onto γ-AlOOH/PVA granules was studied. The product γ-AlOOH/PVA composite granules were characterized by N_2 porosimetry, XRD, FT-IR, SEM and XPS.

Experimental

Preparation procedures

Boehmite sol (2 M) was prepared by a modified Yoldas process using aluminum isopropoxide ($Al(OC_3H_7)_3$, 98%, Aldrich) as a precursor. The details are given elsewhere [21,22]. Briefly, 102.2 g of aluminum isopropoxide was first hydrolyzed in 250 ml deionized water at 80 °C for 1 h. The resulting slurry (with AlOOH precipitates) was peptized by adding 1 M HNO_3 to the $[H^+]/[Al^{3+}]$ ratio of 0.07 and refluxed overnight for 12 h at 95 °C. The remnant alcohol was evaporated by refluxing the sol exposed to air for 2 h at 95 °C. The PVA solution was prepared by dissolving of 22.0 g of poly (vinyl alcohol) in 200 ml deionized water at 90 °C for 3 h. The boehmite sol and PVA solution were mixed at a desired ratio and stirred for 6 h at room temperature. After sealing the mixture was aged at 80 °C for 12 h. Then, it was further aged without sealing for 1–2 h until reaching the gelation point. The partially gelled sol was transferred into a dropper for the generation of sol droplets about 5 mm in size. The sol droplets fell through a glass tube (length: 1 m), which consisted of a hot paraffin oil layer (mineral oil, from Yakuri Pure Chemicals Co., Ltd.) and a 10 wt% ammonia solution layer. After aging the granules in the ammonia solution for 2 h, the granules were collected and washed several times with ethanol and distilled water, followed by drying at 75 °C for 12 h [22]. The prepared samples were denoted as AlOOH, AlOOH/PVA-5, AlOOH/PVA-15, AlOOH/PVA-35 and AlOOH/PVA-50, corresponding to PVA concentrations of 0.0, 5.0, 15.0, 35.0 and 50.0 wt%.

Characterization

The shape and size of the boehmite/PVA composite granules were observed using an optical microscope (Microscope System STVMS 305R, Sometech Co., Korea). The specific surface area, pore volume and pore size distribution of the prepared granules were determined using N_2 porosimetry (ASAP 2020, Micromeritics Instrument Co., USA) at 77 K. Before analysis, the samples were degassed at 300 °C in flowing N_2 for 6 h. The crystallographic structures of the samples were determined by powder X-ray diffraction (XRD) using an X-ray diffractometer (MAC-18XHF, Rigaku, Japan) equipped with a CuKα radiation source (λ = 1.54 Å) operated at a scanning rate of 5°/min from 10° to 80°. The morphologies of the granules were analyzed using field-emission scanning electron microscopy (FE-SEM; Leo-Supra 55, Carl Zeiss STM, Germany). The FT-IR absorption spectra were obtained with a Bruker model Tensor 27 in the range of 4000–400 cm^{-1} using KBr powder. An X-ray photoelectron spectrometer (XPS) was used to identify the state of Cr species by using a Thermo Scientific K-Alpha spectrometer. The binding energies were corrected by setting the binding energy (BE) of the adventitious carbon (C 1s) peak to 284.6 eV.

Adsorption experiments

The Cr(VI) solution was prepared by dissolving the desired amount of $K_2Cr_2O_7$ in deionized water. In this study, the working concentration of Cr(VI) solution was fixed at 25 mg/L. The pH of the Cr(VI) solution was adjusted by using NaOH (0.01 M) or HNO_3 (0.01 M) solutions before adsorption. Adsorption experiments were carried out in a batch mode by mixing 0.1 g of adsorbent and the Cr(VI) solution in a rotary shaker at room temperature. At specified time intervals, the solution was analyzed using a UV–vis spectrophotometer (Optizen POP, Mecasys Co., Korea) at a maximum wavelength of 540 nm after complexation with 1,5-diphenylcarbazide, following the standard method [23]. The

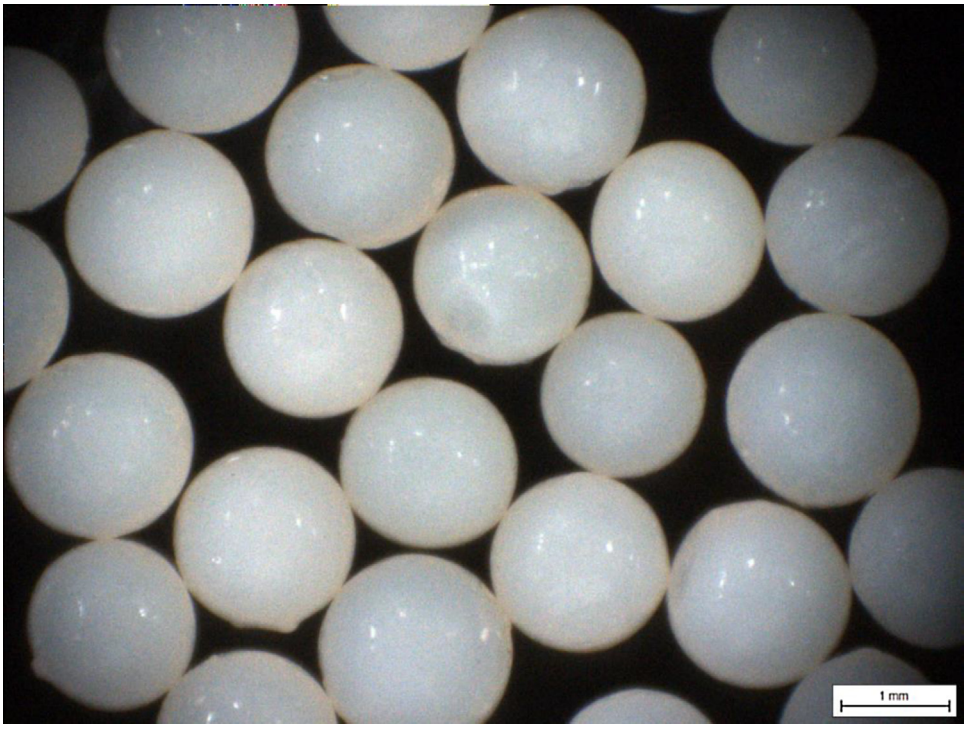

Fig. 1. Optical photograph of γ-AlOOH/PVA composite granules with 35 wt% PVA.

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