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A novel chitosan/clay/magnetite composite for adsorption of Cu(II) and As(V)

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HIGHLIGHTS

- A composite composed of chitosan, nano-magnetite, and heulandite was prepared.
- Properties of the composite were characterized using various instrumentation.
- The composite was applied as an adsorbent for removal of Cu(II) and As(V).
- The optimal mass ratio of chitosan, nano-magnetite, and heulandite was 1:1:2.
- We demonstrated potential utility of the material in environmental cleanup.

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ABSTRACT

A composite adsorbent was prepared by entrapping cross-linked chitosan and nano-magnetite (NMT) on heulandite (HE) surface to remove Cu(II) and As(V) in aqueous solution. The optimized mass ratio among chitosan, HE, and NMT was determined to be 1:1:2. Kinetics studies indicated the removal of both ions followed pseudo-second order kinetics, suggesting specific interaction with surface functional groups was the major route of the removal process. The composite gave the maximum equilibrium uptakes of Cu(II) and As(V) of 17.2 and 5.9 mg g^{-1} in initial concentration ranges of 16–656 and 17–336 mg L^{-1}, respectively. The thermodynamic data showed that both adsorption processes were thermodynamically favorable, spontaneous, and endothermic nature. The adsorption capacity for Cu(II) increased continuously with an increase in initial solution pH (3–9), but adsorption of As(V) showed an opposite trend. The overall results demonstrated the potential utility of the composite for Cu(II) and As(V) removal from aqueous solutions.

1. Introduction

Copper is one of the essential elements to human body in trace quantities, but elevated levels of copper may cause various health problems in liver, kidney, and the central nervous system [1]. Also, arsenic is a priority pollutant posing various health threats associated with lung, skin, bladder, liver, and other cancers, and high levels of arsenic in drinking water have affected millions of people across the world [2]. Arsenic in the environment is mostly of natural origin, occurring in minerals in conjunction with other metals and sulfide. The predominant arsenic form in oxidizing conditions is arsenate (As(V)), while it readily converts to arsenite (As(III)) in reducing conditions. High levels of As(V) are frequently found in geological regions rich in arseno-metal sulfide minerals [3]. Industrially, arsenic has been used a main ingredient of copper alloy metals for providing material strength, and therefore, both metals are likely to be found in a single water body if contamination originates from such sources.

Surface- and groundwaters contaminated with inorganic pollutants can be treated by various methods, including ion exchange, precipitation, adsorption, and membrane processes [4–8]. Adsorption is a relatively effective and economical method compared to other methods, which occasionally suffer from high operation cost and low treatment efficiency. During the past decade, there has been a great deal of growing interests and research advancement on the use of biomaterials for environmental clean-up. For example, chitosan-based materials have drawn significant attention for their favorable properties and versatility as a treatment medium for various contaminants [9,10].

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Chitosan is an alkaline deacetylated product of chitin, characterized by high hydrophilicity and large number of surface hydroxyl and amino groups, and is considered as an eco-friendly material with minial toxicity, biocompatibility, biodegradability, and great availability in nature [9,11]. Chitosan is soluble in acidic media and solidifies in alkaline media, with the latter offering compatibility with other supporting materials such as clay minerals, sand, activated carbon, and PVC bead [1,9,12,13]. The key technical issue in application of a chitosan-based adsorbent in aqueous media is prevention of chitosan dissolution in acidic pH conditions. Cross-linking agents such as epichlorohydrin, tripolyphosphate (TPP), and glutaraldehyde have been frequently employed for such a purpose of enhancing the physical stability of chitosan [14–16].

In addition, recent researches on chitosan application have focused on imparting magnetic property to chitosan-based adsorbents for facile recovery after treatment. Fan et al. [17,18] developed magnetic chitosan adsorbents by coating thiourea-chitosan with magnetic fluids and further enhanced adsorbent capacity with surface imprinting method. Klepka et al. [19] prepared Fe-crosslinked chitosan complex by co-precipitation technique. Yuwei and Jianlong [20] developed super-paramagnetic chitosan nanoparticles from mixture of chitosan and Fe(II)–Fe(III) ions under anaerobic condition. Zhang et al. [21] synthesized activated carbon fiber coated with nano-sized magnetite using chitosan as a film-forming material. Magnetic chitosan composite materials were alternatively prepared by micro-emulsion process using kaolin [16] and fly-ash [22] as a base material.

This study aimed to preparation of a novel magnetic composite material, composed of chitosan, nano-magnetite (NMT), and clay (heulandite) using TPP as a chitosan stabilizer, for removal of As(V) and Cu(II) in aqueous solution. Heulandite (HE) is a zeolite-type mineral possessing sheet-like structure, and therefore it is expected to provide good anchoring sites for NMT and chitosan as well as serving as a direct adsorbent for metal ions [23]. In other words, clay would offer a large surface area for incorporating NMT and chitosan while preventing particle agglomeration for better contaminant adsorption, and also provide additional adsorption sites. The characteristics of the composite material were examined with various instrumental analyses, and its performance for adsorption of Cu(II) and As(V) was evaluated under various experimental conditions to demonstrate adsorption kinetics, isotherms, thermodynamics, and effect of pH.

2. Experimental

2.1. Materials

Chitosan with 75–85% degree of deacetylation and 190,000–310,000 g mol^{-1} viscosity molecular weight was purchased from Sigma–Aldrich (USA). HE was obtained from Donghae Chemical Co., South Korea, and pulverized and sieved through a 100-mesh screen prior to use. NMT (<50 nm), sodium tripolyphosphate (STPP), copper chloride, sodium arsenate, acetic acid (99%), sodium hydroxide, hydrochloric acid were purchased from Sigma–Aldrich and were of ACS reagent grade.

2.2. Preparation of chitosan/heulandite/Fe_3O_4 composites

Chitosan (2 g) was dissolved in 100 mL acetic acid (2%) to prepare chitosan solution. STPP solution was prepared by dissolving 13.3 g of the solid in 1 L of distilled water and adjusted to pH 4 with 1 N HCl. Known amount of NMT and HE were added into the chitosan solution under ultrasonic stirring for 30 min. Then the mixture was added drop wise using 10 mL syringe into 100 mL STPP solution. The cross-linked adsorbents were formed by the interaction between phosphate groups of TPP and amino group of chitosan. The composites were kept in the solution for 12 h, washed several times with distilled water to remove the excess of TPP, and oven-dried for 24 h at 50 °C. After drying and grinding, the composites were milled through a 100-mesh screen. The adsorbent synthesized was referred to as chitosan/clay/Fe_3O_4 (CCM). A schematic plot of CCM preparation is shown in Fig. S1 in Supplementary Materials (SM).

X-ray diffractometer (D8 Advance, Bruker-AXS) analyses were performed for CCM, HE, NMT, and chitosan, using Cu Kα radiation and a LynxEye position sensitive detector. The diffraction pattern was collect from 5° to 65° 2θ, with a nominal step size of 0.01° and a time per step of 1 s, using a 0.3° divergence slit and 2.5° secondary Soller slit. The resulting peaks and intensities of each mineral were compared with the powder diffraction files published by the International Centre for Diffraciton Data. Field-emission scanning electron microscope coupled with energy dispersive spectroscopy (FE-SEM/EDS), zeta potential at solution pH 5, and BET surface area of HE and CCM were measured using a Sirion FE-SEM analyzer (Netherlands), Malvern Zetasizer nano-zs (UK), and Micromeritics ASAP 2020 (USA), respectively. Magnetic properties of HE and CCM were also analyzed using a Bartington magnetic susceptibility meter (UK) with 36 mm internal diameter calibration vol. 10 cc.

2.3. Adsorption experiments

Cu(II) and As(V) adsorption experiments were carried out 25 mL high density polyethylene vials (Fisher Scientific, USA). Standard solutions of desired Cu(II) and As(V) concentrations were obtained by diluting 1000 mg L^{-1} stock solution, followed by pH adjustment at pH 5 with 0.1 N HCl or NaOH. Adsorption kinetics experiments were performed by equilibrating 0.1 g adsorbent with 20 mL adsorbate solutions of 45.1 mg L^{-1} Cu(II) and 39.5 mg L^{-1} As(V) in the vials. Each mixture was shaken at 23 ± 2 °C and 150 rpm for 600 min. At specified intervals, the samples were collected and filtered with 0.45 μm filter (Whatman, USA) to determine the concentration of Cu(II) and As(V). Adsorption isotherm experiments were carried out by varying the concentrations of Cu(II) and As(V) solution from 16 and 17 to 656 and 336 mg L^{-1}, respectively, under the same conditions as the adsorption kinetics experiments. The experiments were performed in duplicate and the amount of Cu(II) and As(V) ions adsorbed per unit mass of CCM (q_e) was calculated as follows:

$$q_e(\text{mg g}^{-1}) = \frac{(C_o - C_e)V}{W} \quad (1)$$

where C_o and C_e are initial and equilibrium concentrations of adsorbate (mg L^{-1}), respectively, W is the dry mass of the adsorbent (g), and V is volume of the solution (L). The concentration of Cu(II) and As(V) in aqueous solution was determined by ICP-OES (Ultima 2C, Horiba-Yuvon, France). The pH of solution was measured using a pH meter (Horiba, Ltd. Kyoto, Japan).

2.4. Effect of temperature and pH

Adsorption experiments were conducted at different constant temperatures in the range of 25–45 °C under the same condition as adsorption isotherm experiments to investigate the effect of temperature on adsorption of Cu(II) and As(V) onto CCM. The effect of pH on Cu(II) and As(V) adsorption by CCM was also investigated in the initial pH ranges between 3 and 9. The reactors received 20 mL of 68.7 mg L^{-1} Cu(II) or 66.9 mg L^{-1} As(V), and solution pH was adjusted with 0.1 N NaOH and 0.1 N HCl. Adsorbent (0.1 g) was added in each reactor and reacted for 24 h at 25 °C.