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Enhanced removal of trace arsenate by magnetic nanoparticles modified with arginine and lysine

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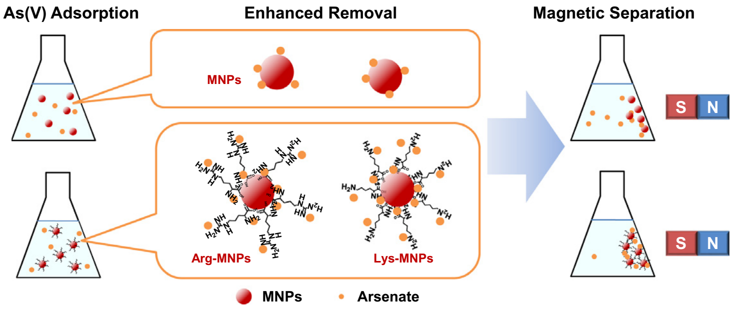
HIGHLIGHTS

- Arginine/lysine modified magnetic nanoparticles were synthesized.
- The modification greatly enhanced As(V) adsorption of MNPs.
- As(V) can be effectively removed by the modified adsorbents in a wide pH range.
- Phosphate did not significantly inhibit As(V) adsorption.
- Both modified adsorbents exhibited good potential for repeated use.

GRAPHICAL ABSTRACT



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ABSTRACT

Two types of adsorbents, arginine (Arg) and lysine (Lys) modified Fe_3O_4 magnetic nanoparticles (Arg-MNPs and Lys-MNPs), were synthesized by employing conventional co-precipitation process and used to remove trace arsenate [As(V)] from water. Various techniques including transmission electron microscopy (TEM), powder X-ray diffraction, Föurier transform infra-red spectroscopy, energy dispersive X-ray spectrometry, and thermogravimetric analysis were utilized to characterize the synthesized adsorbents. TEM images showed that both fabricated materials were spherical with diameter of approximately 10 nm. With saturation magnetization of around 73.0 emu/g, both adsorbents could be easily separated from water with a simple magnetic process in 5 min. The As(V) adsorption capacities of Arg-MNPs and Lys-MNPs were 29.14 and 23.86 mg/g, respectively, which were twice larger than that of bare MNPs (12.12 mg/g). Both adsorbents (0.1 g/L) could remove over 90% of As(V) (100 μg/L) from water over a wide pH range from 3 to 9. Moreover, natural organic matters (humic acid and alginate) and competitive anions including sulfate, bicarbonate, silicate, and phosphate did not obviously affect the adsorption of As(V) by the modified adsorbents. The removal of As(V) maintained above 83% even with extremely high concentration of phosphate (50 mg/L). As(V) could also be effectively removed from challenge water and real river water by the modified adsorbents. Both magnetic particles could be easily regenerated in alkali solutions and their adsorption capacities were still greater than 10 mg/g even in the fifth cycle.

1. Introduction

Arsenic could be introduced into water by both natural and anthropogenic activities such as dissolution of minerals, manufacturing and mining [1]. Arsenic contamination of water especially groundwater has become a major problem around the world. Long-term drinking of arsenic contaminated water could result in serious health risks due to its high toxicity and carcinogenicity

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[2,3]. Consequently, a maximum contaminant level (MCL) of 10 μg/L arsenic in drinking water has been adopted by US Environmental Protection Agency (EPA), European Union and many other countries such as China, to replace the old standard of 50 μg/L, which is prone to increase the incidence of lung and bladder cancer [4]. To meet the increasingly strict regulations, great efforts therefore have been devoted to develop more efficient technologies to remove arsenic from water in recent years.

A variety of techniques including coprecipitation, membrane filtration, iron exchange, reverse osmosis, electrocoagulation, and adsorption have been utilized to remove arsenic [5]. Due to easy operation, cost-effectiveness, and high efficiency, adsorption has been regarded as one of the most promising methods to remove low-concentration (100 μg/L) of arsenic from water [6]. Many metal oxides such as iron oxide [7], aluminum oxide [8,9], manganese oxide [10], titanium oxide [11], and bimetal oxides [12–16] have previously been used to remove arsenic from water. However, the applications of most of these metal oxides especially those in nanoscale have been inhibited by the difficulty in recovering adsorbents after adsorption applications. Herein, magnetic nanoparticles (MNPs) have recently gained considerable attention for arsenic removal due to their convenient separation from water by an external magnetic field [17]. For example, magnetite [18,19], magnetite-reduced graphene and graphite oxide composites [20,21], carbon fiber/iron oxide [22], and bimetal oxide magnetic nanomaterials [23] have been utilized to remove arsenic from water. To avoid the oxidation of magnetic nanoparticles, different chemicals have been employed to modify nanoparticles for arsenic removal [24–28]. For instance, Yantasee et al. [24] bonded dimercaptosuccinic acid onto surfaces of superparamagnetic iron oxide nanoparticles. Lim et al. [25] grafted alginate on the surfaces of magnetite. White et al. [26] immobilized cysteine onto the surface of commercially available magnetic γ-Fe_2O_3 nanoparticles. Sayin et al. [27] utilized calix[4]arene to modify magnetite nanoparticles. Jin et al. [28] recently employed cetyltrimethylammonium bromide (CTAB) to modify magnetic Fe_3O_4 nanoparticles.

L-Arginine (Arg) and L-lysine (Lys), the isoelectric points of which are the highest among the 20 natural amino acids (pI(Arg) = 10.76; pI(Lys) = 9.60), have been previously adopted to optimize magnetic nanoparticles for various applications in the fields of magnetic resonance imaging (MRI), drug delivery, immunoassays, and high density data storage [29,30]. Due to their strong positive charged side chains, both types of amino acids have good potential to bind with anions through electrostatic force over a wide pH range. Thereby, it can be expected that magnetic nanoparticles modified with Arg or Lys would have strong affinity with arsenate anion and can efficiently remove arsenic under a wide range of pH conditions. Moreover, Arg or Lys modified MNPs would be conveniently separated from solution by using magnetic force. However, to the best of our knowledge, the adsorption of arsenic on magnetite nanoparticles coated with either Arg or Lys has never been explored and thus requires systematical investigation.

Hence, the objective of this research was to fabricate Arg and Lys modified MNPs and to investigate the adsorption of As(V) on these two types of modified adsorbents. The characteristic of two types of modified MNPs, the adsorption capacity, and the adsorption kinetics of arsenic on both Arg-MNPs and Lys-MNPs were determined. The effects of solution pH, common coexisting anions, and natural organic matters (NOMs) on arsenate removal were concerned. In addition to the synthetic water, the feasibility of As(V) removal from challenge water and real river water was studied. Moreover, As(V) desorption and adsorbents regeneration/reuse studies were also conducted to evaluate the reusability of both Arg-MNPs and Lys-MNPs.

2. Materials & methods

2.1. Materials

L-arginine, L-lysine, $FeCl_3 \cdot 6H_2O$ and $FeCl_2 \cdot 4H_2O$ were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) and used as received. As(V) stock solutions were prepared by dissolving $Na_2HAsO_4 \cdot 7H_2O$ (Sigma–Aldrich, St. Louis, MO, USA) with ultrapure water (resistivity > 18.2 MΩ cm) from an integral water purification system (Milli-Q, Millipore, Billerica, MA, USA). Suwannee River humic acid (SRHA) (Cat#2S101H, Standard II, International Humic Substances Society) and sodium alginate (A2158, Sigma–Aldrich, St. Louis, MO, USA), which have been previously selected as model humic substances [31–33] and polysaccharides [34], were employed to represent typical NOMs in this study. All the other chemicals used were of analytical grade from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) and Xilong Chemical Group (Shantou, Guangdong, China). Standard solutions for analytical use were obtained from National Institute of Metrology of China and were diluted to desired concentrations with ultrapure water.

2.2. Preparation of adsorbents

The adsorbents were synthesized via a two-step process modified from a previous study [35], including the preparation of the magnetic nanoparticles (MNPs) and subsequent modification of MNPs with Arg and Lys, respectively. Specifically, 60 mL of 0.1 M $FeCl_3$ and 30 mL of 0.1 M $FeCl_2$ were mixed with a magnetic stirrer in a 200 mL flask containing 20 mL of deoxygenated water. Ultrapure nitrogen gas (99.999%, Beijing Special Gas Inc., China) was bubbled throughout the synthesis process to expel oxygen. The solution was heated to 80 °C with a digital heating circulating water bath (Kunshan Biotechnology Ltd., China). Then, ammonium hydroxide ($NH_3 \cdot H_2O$, 25–28 wt.%) was added dropwisely into the solution until the pH reached around 10, under which conditions the black precipitate was formed. After the mixture was stirred at 80 °C for another 20 min, the black precipitate was separated by magnetic decantation and washed with deionized water repeatedly until the supernatant reached neutral pH (7.0). The acquired black particles were then equally divided into two portions for further modification with Arg and Lys. For each portion, the black precipitate was re-dispersed into 100 mL of corresponding amino acid solution (Arg or Lys) under ultrasonication for 30 min. The weight ratios of both Arg and Lys to MNPs were controlled at 1:1. After the sonication treatment, the black precipitates were once again collected with magnetic decantation and washed with deionized water for three times. Arg-MNPs and Lys-MNPs were then obtained after dry process of the washed materials under vacuum at 80 °C for 12 h. The modified MNPs were stored in a stoppered bottle under vacuum for further use.

2.3. Adsorbents characterization

Powder X-ray diffraction (XRD) analysis was conducted by DMAX-2400 (Rigaku, Japan) at 40 kV and 100 mA to determine the constituents of Arg-MNPs and Lys-MNPs. The fabricated adsorbents were analyzed by Föurier transform infrared spectroscope (FT-IR, Tensor 27, Bruker Optics, Germany) and scanning electron microscope (SEM, S-360, Cambridge Scientific Instrument, UK) equipped with energy dispersive X-ray spectrometry (EDS). Moreover, the amounts of Arg and Lys loaded on MNPs were estimated by using thermogravimetric analysis (TGA, Q600 SDT, TA instruments, USA) from 20 to 800 °C with a heating rate of 10 °C/min. The morphology and size of the adsorbents were characterized