Removal of arsenic(V) by magnetic nanoparticle activated microfibrillated cellulose

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HIGHLIGHTS

- MFC/Fe$_2$O$_3$ has a relatively high adsorption capacity for As(V) from aqueous solutions.
- That adsorption capacity of Fe$_3$O$_4$/MFC was relatively higher than bare Fe$_3$O$_4$ nanoparticles.
- The adsorption rate is fast.
- The adsorption is dependent on the solution pH.

GRAPHICAL ABSTRACT
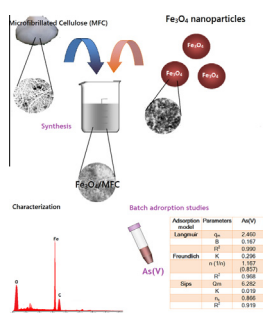
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ABSTRACT

In this study a novel adsorbent, magnetic iron nanoparticles modified microfibrillated cellulose (FeNP/MFC), was used for arsenate (As(V)) removal from aqueous solutions. The modified cellulose was characterized by FTIR, elemental analysis, zeta potential analyzer, SEM, and TEM. In order to demonstrate the adsorption performance of synthesized material, the effects of contact time, pH, initial As(V) concentration, and regeneration were investigated. The equilibrium adsorption data were fitted to Langmuir, Freundlich, and Sips adsorption models, and the model parameters were evaluated. The monolayer adsorption capacity of the adsorbent, as obtained from the Langmuir isotherm, is 2.460 mmol/g. The adsorption process could be described by pseudo-second-order kinetic model. Iron nanoparticle modified MFC was found to be an exceptional adsorbent material due to its magnetic properties, high surface area and a good adsorption capacity.

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1. Introduction

Arsenic is one of the most toxic elements in the world [1]. It is a metalloid, possessing thus both metallic and non-metallic properties, and is ubiquitously present in air, soil, natural water, mineral deposits and rocks and biota [2–4] in varying concentrations. Arsenic is present in water as a result of both natural and anthropogenic activities. Natural processes are volcanic emissions, biological activities, burning of fossil fuels and weathering of arsenic bearing rocks and minerals such as realgar (AsS), orpiment (As$_2$S$_3$), arsenopyrite (FeAsS), and lollingite (FeAs$_2$) [5]. Anthropogenic sources include applications of arsenical pesticides and insecticides [6,7], wood preservatives, paints, drugs, dyes, semiconductors, incineration of arsenic containing substances, industrial wastewater discharge, mine tailing/landfill leaching, and manufacturing of arsenic compounds [8,9]. Inorganic arsenic can occur in the environment in several forms depending on the ambient environment (i.e. pH, Eh) and microbial activity [10]. The most common valence states of arsenic in water are oxidized (+V oxidation state, (As(V)) and reduced (+III oxidation state, (III)) forms. As(V) is less toxic than As(III) and is a main species in natural waters [11].

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The arsenic contamination in groundwater is a major threat to human health in many regions of the world. Arsenic dissolved in water is acutely toxic, mutagenic and carcinogenic. Also Arsenicosis due to long-term arsenic exposure can lead to a number of health problems, such as pigmentation of the skin and the development of hard patches of skin on the palm of the hands and soles of the feet. Arsenic poisoning finally leads to skin, bladder, kidney, lung, liver and prostate cancers [12,13]. Due to its high toxicity to human health, USEPA and WHO established an international maximum contaminant level for arsenic in drinking water, which is 0.01 mg/L or 10 ppb [13–16].

Various technologies such as oxidation [15,17], precipitation/coprecipitation [18], coagulation [19,20], sorption [21,22], ion-exchange [23], reverse osmosis [24] and electrokinetic methods [25] have been studied for the removal of arsenic from water. These methods have been widely employed, but they have several drawbacks: high operating and waste treatment costs, high consumption of reagents and large volume of sludge formation [26]. Among all the treatment processes mentioned, adsorption is recognized as an effective approach due to the low cost, high concentration efficiency, and environmental friendliness.

Conventional adsorbents used in arsenic removal are activated carbons and alumina, soils, and resins, which can be coated with different materials like iron or alumina [27–31]. The major detriments of these techniques are difficult separation, waste formation and in many cases poor adsorption capacity [32]. However, because of the selectivity and affinity of Fe(III) toward inorganic arsenic species, Fe(III)-bearing materials are widely used in arsenic adsorption [33–36]. Though these materials are selective and efficient in removing arsenic, their applicability is often limited due to their cost [37].

Within recent decade iron-based nanoparticles have been widely applied for arsenic removal from soils and aqueous surroundings [27,38,39] The popularity of these nanosized particles arises from their unique characteristics such as high surface area, interfacial reactivity, and magnetic properties. However, applicability of the iron nanoparticles is shown to suffer from their poor chemical stability and mechanical strength and tendency to aggregate. Furthermore, these nanoparticles as such are not suitable for fixed-bed column or flow-through systems due to for instance mass transport problems and significant pressure drops. To overcome the above drawbacks different solid supports have been used in order to prepare composite materials without losing the beneficial properties of the nanoparticles. Especially, polymeric supports with proper functional groups despite offering the required stability may even enhance the adsorptive properties of the nanoparticles under study [40,41].

Due to intensified "green thinking" in process industry as well as environmental protection, adsorption of arsenic using natural products has emerged as a viable option. Cellulose is most widely available and renewable biopolymer in nature. It is a very promising raw material available at low cost for the preparation of various functional materials. Due to the presence of hydroxyl groups, cellulose is considered to be an excellent material for surface modification [42,43]. At the same time, a combination between bioadsorbents and iron oxide nanoparticles can pose an efficient biocomposite material, which could possibly show high adsorption capacity, intensified stability, and easy recovery from treated effluents by applying a magnet [27].

In the present study, a novel adsorbent, magnetic iron oxide modified microfibrillated cellulose, was synthesized for the selective removal of arsenic from aqueous solutions. The modified cellulose was characterized by FTIR, elemental analysis, zetasizer, SEM, and TEM. In adsorption studies, the effects of contact time, pH, initial arsenate concentration, and regeneration were investigated.

2. Materials and methods

2.1. Chemicals and materials

Microfibrillated cellulose (MFC) was obtained from the University of Oulu, Finland. Zero-valent iron nanoparticles in aqueous dispersion were supplied by the NANOIRON®. All solutions were prepared in Millipore milliQ high-purity water. All other chemicals used in this study were of analytical grade and supplied by Sigma–Aldrich (Germany). Stock solution of 1000 mg/L was prepared by dissolving appropriate amount of As(V) oxide at first in 25% NaOH following instant neutralization with 2 M HCl and dilution with deionized water. Adjustment of pH was accomplished using 0.1 M NaOH or 0.1 M HNO_3.

2.2. Preparation of FeNP modified MFC

Preparation of modified MFC was conducted according to Zhu et al. with some modifications [44]. 8.9 wt% NaOH/5.5 wt% sulfocarbamide/6.0 wt% urea mixed aqueous solution was pre-cooled to −4 °C in a refrigerator. MFC (2 g) was immediately dispersed into the mixed aqueous solution under vigorous stirring for 5 min at ambient temperature to obtain a transparent cellulose solution with 2% concentration. The resultant cellulose solution was centrifuged at 4000 rpm for 5 min at room temperature to eliminate insoluble components and air bubbles. 1 g of Fe^0 nanoparticles were added into cellulose solution under dynamoelectric stirring for 1 h. The resulting suspension was poured into a coagulation bath containing 10 wt% NaCl under vigorous stirring.

After aged for 12 h, 5 mL of epichlorohydrin was slowly added into the above mixture with stirring for 45 min and its temperature was raised to 75 °C with stirring for another 150 min to obtain wet FeNP/MFC. FeNP/MFC was washed with double distilled water and ethanol for three times.

2.3. Characterization of materials

Fourier transform infrared spectroscopy (FTIR) type Vertex 70 by B Bruker Optics (Germany) was used to identify the surface groups of the modified nanocellulose. The FTIR spectra were recorded at 4 cm^{-1} resolution from 400 to 4000 cm^{-1} and 100 scans per sample. The surface morphology and chemical composition of FeNP/MFC was examined using a Hitachi S-4100 scanning electron microscope (SEM) and energy dispersive analysis of X-rays (EDAX), respectively. Distribution of nanoparticles on the cellulose surface was further verified using transmission electron microscope (HT7700 120 kV High-Contrast/High-Resolution Digital TEM). TEM sample was prepared by dispersing a small amount of modified MFC in ethanol and placing a drop of this mixture on the carbon coated copper grid. The instrument used for C, H and N determination was Organic Elemental Analyzer Flash 2000 (Thermo Scientific, Germany). About 2.5 mg of the sample in a capsule made of tin (assay of C, H and N) or silver (assay of O) was burned at 920–1000 °C. The quantity of each element is expressed in percent of dry mass. Surface charge and point of zero charge of the modified and unmodified cellulose were determined by isoelectric point titration as a function of pH by using Zetasizer Nano ZS (ZEN3500, Malvern).

2.4. Batch adsorption studies

Applicability of FeNP/MFC for As(V) removal was studied using batch experiments in a reaction mixture of 0.100 g of adsorbent and 0.015 L of metal solution containing As(V) at concentrations ranging from 0.14 to 10.68 mmol/L. The effect of contact time