Iron oxide-modified nanoporous geopolymers for arsenic removal from ground water

Dinesh Medpelli [a], Robert Sandoval [b], Laurie Sherrill [b], Kiril Hristovski [b], Dong-Kyun Seo [a,*]

[a] *Department of Chemistry and Biochemistry, Arizona State University, Tempe, AZ 85287, USA*
[b] *The Polytechnic School, Ira A. Fulton Schools of Engineering, Arizona State University, Mesa, AZ 85212, USA*

Abstract

Composite materials of hierarchically porous geopolymer and amorphous hydrous ferric oxide were produced and characterized as a new potentially cost-effective arsenic adsorbent. The arsenic removal capabilities of the iron (hydr)oxide (HFO) media were carried out using batch reactor experiments and laboratory scale continuous flow experiments. The Rapid Small-Scale Column Tests (RSSCT) were employed to mimic a scaled up packed bed reactor and the toxicity characteristic leaching procedure (TCLP) test of arsenic adsorbed solid material was carried out to investigate the mechanical robustness of the adsorbent. The best performing media which contained ~20 wt% Fe could remove over 95 µg of arsenic per gram of dry media from arsenic only water matric. The role of the high porosity in arsenic adsorption characteristics was further quantified in conjunction with accessibility of the adsorption sites. The new hierarchically porous geopolymer-based composites were shown to be a good candidate for cost-effective removal of arsenic from contaminated water under realistic conditions owing to their favorable adsorption capacity and very low leachability.

1. Introduction

Arsenic is one of the most frequently found contaminants found in many drinking water sources in small and rural communities all over the world. The largest population at risk among countries with known groundwater arsenic contamination is in Bangladesh, followed by the state of West Bengal in India [1–3]. Prolonged intake of arsenic contaminated drinking-water is known to cause dermal lesions such as hyper- and hypopigmentation, peripheral neuropathy, skin cancer, bladder and lung cancers and peripheral vascular disease [4]. Although arsenic can exist in (−3), (0), (+3) and (+5) oxidation states in the earth's crust, in natural waters, it is mostly present in the most oxidized (+5) state as arsenate (AsO_4^{3-}); however, under anaerobic conditions, it is likely to be present in the (+3) oxidation state as arsenite (AsO_3^{3-}) [5,6].

A number of technologies have been reported for treating arsenic from drinking water based on different treatment methods [5,7–9]. Among these technologies, the ones based on adsorption have demonstrated the greatest potential because of their cost effectiveness, versatility, and simplicity of operation and maintenance [10]. Adsorption based systems for treating arsenic from water typically employ metal (hydr)oxides such as ferrihydrite, iron (hydr)oxide (HFO), titanium dioxide, zirconium dioxide, hematite, and goethite because they have excellent selectivity for arsenic, which forms inner sphere complexes with the metal atoms in the sorbent through oxygen bridges [11,12].

The high adsorption capacity of the metal (hydro)oxides is directly related to available sorption sites with which arsenic can form these inner-sphere complexes. However, it is often misguidedly thought that high adsorption capacities and arsenic removal performance could only be achieved by increasing the available surface area without engineering the accessibility to the available sites. In this context, the porosity and pore size distribution of a media play even a more critical role in increasing the overall arsenic removal performance of the adsorbent [13–17]. The impact of media's pore related properties on its arsenic removal performance becomes

* Corresponding author. Department of Chemistry and Biochemistry, Arizona State University, Tempe, AZ 85287, USA. Tel.: +1-480-727-7789; fax: +1-480-965-2747.

E-mail address: dseo@asu.edu (D.-K. Seo).

especially significant in hybrid adsorbents. These hybrid media employ strong porous materials as a supporting platform for metal (hydr)oxide nanoparticles, which allow for high surface area, but cannot be utilized in pack bed configurations because of their size. In parallel, their aggregation leads to surface area reduction and structural instability, which consequently leads to operational problems because of attrition and nanomaterial leaching. To mitigate these problems, highly porous supporting materials such as mesoporous silica or granular activated carbon (GAC) have been proposed for metal (hydr)oxide nanoparticle impregnation [18–22]. However, no study has been conducted to clearly demonstrate that porosity and pore size distribution of the base media critically affect the metal (hydr)oxide nanoparticle hybridization process, and consequently the overall arsenic removal performance of metal (hydr)oxide hybrid media.

To address this knowledge gap, we report new highly efficient and yet potentially inexpensive class of arsenic adsorbents, which utilize porous geopolymer as a mechanically strong supporting material. Geopolymers are emerging class of ceramic-like materials that are gaining significant attention due to their unusual properties, such as high compressive strengths, good heat and chemical resistance, and low environmental impact during production. Beyond the conventional applications as building or refractory materials [23] or in immobilizing toxic wastes [24], new research efforts are being focused toward introducing porosity into the material and utilize them in catalysis [25] and drug delivery [26,27]. Recently, we introduced hierarchically meso/macroporous structure into the otherwise dense geopolymeric matrix following a simple and readily scalable synthetic methodology developed previously by some of the current authors [28,29]. A hierarchical pore structure is advantageous because the smaller mesopores can be easily accessed through the larger macropores, hence improving (1) accessibility of precursors used in in-situ metal (hydr)oxide nanoparticle synthesis; and (2) diffusion kinetics of contaminants to available sorption sites. Larger macro/meso-porosity allows for more uniform distribution of nanoparticles into the media with minimal reduction in effective pore volume, consequently leading to a greater number of available metal (hydr)oxide sorption sites for contaminants like arsenic [30]. Additionally, the larger porosity leads to smaller intraparticle mass transport limitations and improves the overall kinetic efficiency of the system [16].

In order to further quantify the role of the high porosity in arsenic adsorption characteristics, we (1) synthesized different nanoporous geopolymer base media by modifying synthesis conditions; (2) impregnated the geopolymer base media with HFO nanoparticles; (3) characterized the properties of both geopolymer base and HFO nanoparticle impregnated media; (4) conducted batch isotherm experiments to develop Freundlich isotherm parameters; (5) employed the pore surface diffusion model to screen the performance of the media in packed bed conditions; (6) conducted a Rapid Small Scale Column Test (RSSCT) with the best performing media to assess the effect of co-contaminant completion on arsenic removal capacity; and (7) conducted tests to assess the arsenic leaching potential of spent adsorbent media.

2. Experimental and modeling approach

2.1. Synthesis of nanoporous geopolymer material (base media)

In the first step of the synthesis, a potassium silicate solution was prepared by dissolving an appropriate amount of KOH pellets (Sigma Aldrich) in deionized water in a polypropylene cup placed in a water bath. A suitable amount of fumed silica (Cabot, CA-BO-SIL® EH-5) was then added into the KOH solution and the mixture was stirred with a Stir-Pak laboratory mixer for 30 minutes at 800 rpm to give a clear solution. The geopolymer resins were then prepared by mechanically mixing metakaolinite into the potassium silicate solution to form a homogenous fluidic liquid. The metakaolinite was produced in advance by calcining kaolinite ($Al_2Si_2O_7 \cdot H_2O$, Alfa Aesar) at 750 °C for 10 h. Eight different samples were prepared by varying the amounts of water, K/Al ratio and Si/Al ratio (Table 1). The pH of the resins was about 14 for all the compositions. Canola oil (The J.M. Smucker Company, Crisco®), paraffin oil (Alfa Aesar) or a mixture of both oils (Table 1) was then added to the resin at a 1:1 oil-to-water volume ratio and mixed for an additional 15 minutes to give a homogeneous but viscous emulsion. The emulsion was transferred to a polypropylene cup and cured in a laboratory oven at 60 °C for 24 h. The cured monolithic product was then broken into small pieces (approximately $1 \times 1 \times 1$ cm³) and subjected to Soxhlet extraction with n-butanol as a solvent. The resulting nanoporous geopolymer (base media) pieces free of organics were dried overnight in the lab oven maintained at 120 °C. Complete removal of organics was confirmed by CHN analysis and infrared spectroscopy (data not shown).

2.2. In-situ synthesis of iron (hydr)oxide (HFO) nanoparticles

The base media were ground and sieved into 30×40 US mesh particles sizes (425–600 µm). This media size range is reflective of typical particle sizes used in full scale packed bed configurations for water treatment applications [31]. Subsequently, the impregnation of the base media with iron (hydr)oxide nanoparticles was carried out through an incipient wetness impregnation technique in the steps: (i) base media was soaked in $FeCl_3 \cdot 6H_2O$ (Alfa Aesar) dissolved in methanol (2.0 M solution) for 24 h; (ii) the resulting particles were filtered and were heated at 85 °C in an ammonia/moisture saturated atmosphere

Table 1
Synthetic parameters of the base media.

Sample	Water content (mol%)	K:Al:Si	Oil used	Oil ratio
1	68	2:1:2	Canola/Paraffin	50%/50%
2	68	2:1:2	Paraffin	100%
3	73	3:1:2	Canola	100%
4	73	3:1:2	Canola/Paraffin	50%/50%
5	68	1:1:1.5	Canola	100%
6	68	1:1:1.5	Canola/Paraffin	50%/50%
7	68	1:1:1.5	Canola/Paraffin	33%/66%
8	68	1:1:1.5	Paraffin	100%