Aminated glycidyl methacrylates as a support media for goethite nanoparticle enabled hybrid sorbents for arsenic removal: From copolymer synthesis to full-scale system modeling

Khaled Taleb [a], Jasmina Markovski [b,c,]*, Kiril D. Hristovski [c], Vladana N. Rajaković-Ognjanović [d], Antonije Onjia [b], Aleksandar Marinković [a]

[a] Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11120 Belgrade, Serbia
[b] Vinča Institute, University of Belgrade, PO Box 522, 11000 Belgrade, Serbia
[c] The Polytechnic School, Ira A. Fulton Schools of Engineering, Arizona State University, 7171 E. Sonoran Arroyo Mall, Mesa, AZ 85212, USA
[d] Faculty of Civil Engineering, University of Belgrade, Bulevar kralja Aleksandra 73, 11000 Belgrade, Serbia

Abstract

To achieve short mass transfer zones that enable arsenic removal under high hydraulic loading rates and short empty bed contact times needed for small point-of-use packed bed applications, hybrid media was developed and tested. Cross-linked macroporous glycidyl methacrylate copolymer support media was synthetized, amino modified and in-situ impregnated by goethite nanoparticles via an oxidative deposition in a hydrophilic/hydrophobic (water/xylene) system. The media properties were characterized via scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDS), X-ray diffraction (XRD), and surface area analysis. Arsenic removal capabilities of the hybrid goethite impregnated media were evaluated by conducting batch sorption tests, developing isotherms and simulating the breakthrough curve with a pore surface diffusion model (PSDM), after being verified by a short bed column (SBC) test. The high porous media ($e_p \approx 0.7$) contained ~16% of iron and exhibited Freundlich adsorption capacity parameter of $K \approx 369$ ($\mu g\ g^{-1}$)(L $\mu g^{-1})^{1/n}$ and Freundlich intensity parameter of $1/n \approx 0.54$. Without engaging in taxing pilot scale testing, the PSDM was able to provide a good prediction of the media's capacity and intraparticle mass transport properties under high hydraulic loading rates.

1. Introduction

Stemming from their rapid population growth, economic development, and climate change, many developing and developed countries are concerned with increasing demands for potable water [1,2]. Although available, potable water is often contaminated with a number of contaminants that prevent its direct use without any treatment [3]. Many of these contaminants are present in an inorganic form in the potable water sources, and disinfection, granular activated carbon or other inexpensive small system water treatment technologies are not capable of removing them to innocuous level [1,4]. Since the inorganic substances are the major chemical contaminants of potable water, its adverse effects to human populations are of growing concern [5]. For example, more than 70 countries contain high levels of arsenic and endanger lives of several hundred million people [1]. Considering its potential carcinogenicity and toxicity health risks, WHO and US EPA promulgated $10\ \mu g\ L^{-1}$ as a maximum contaminant level (MCL) of arsenic in a drinking water [6–8]. Latest toxicological research, however, suggests that the MCL should be further lowered to address the newest acceptable health risks associated with arsenic in drinking water [9]. Consequently, this new regulatory and scientific pressure creates a drive to develop novel technologies capable of addressing the low arsenic MCL challenge.

* Corresponding author. The Polytechnic School, Ira A. Fulton Schools of Engineering, Arizona State University, 7171 E. Sonoran Arroyo Mall, Mesa, AZ 85212, USA. Tel.: +1 (480) 727 1617; fax: +1 (480) 727 1549.
    E-mail address: jmarkov2@asu.edu (J. Markovski).

Nanomaterials, which could be tailored to exhibit large specific surface area and specific functionality, offer a promise that could help resolve some of the challenges associated with novel small systems arsenic treatment technologies [10–12]. Such systems are probably the only viable water treatment approach capable of addressing the needs of many small communities, which do not have the technological expertise, resources, or infrastructure to employ conventional and energy intensive water treatment systems [3,13]. In the past 15 years, there has been a growing interest in harvesting the unique properties of metal (hydr)oxide nanomaterials for developing adsorptive arsenic treatment technologies, considering that adsorption has been identified as one of the Best Available Technologies (BAT) for small systems' arsenic treatment [4,10,11,14–16]. Nano iron (hydr)oxides, like goethite (α-FeOOH), have been identified as one of the best candidates for developing nanomaterial based small arsenic treatment systems because of simple fabrication, low cost, high adsorption capacity and selectivity, and thermodynamic stability in naturally fluctuating water matrices [17–20].

When developing small systems for arsenic treatment, it is imperative to ensure simultaneous operational and technological simplicity and efficient performance on a large system scale. These technological targets are difficult to achieve with sorbent technologies that employ suspended nanomaterial reactors because nanomaterials would have to be removed from the treated water before the water is used [21]. This, of course, would necessitate employment of energy intensive membrane filtration technologies, which have their own set of operational challenges [22]. In contrast, fixed bed reactor configurations eliminate these operational challenges, but necessitate the use of either aggregated nanomaterial adsorbents or media composed of nanomaterial sorbent fixed to a macroscopic support platform i.e. hybrid media [10,15,21,23–27]. Aggregation of nanomaterials, especially iron (hydr)oxide based ones, often leads to problems related to adsorbent stability, attrition, surface area decrease, and porosity reduction, which consequently creates operational problems such as head loss, channeling, and nanomaterial release in the treated effluent. Iron (hydr)oxide nanomaterial hybrid sorbents have the potential to minimize these problems with a selection of adequate and mechanically strong and stable support platform. However, to fully utilize the potential offered by iron (hydr)oxide nanomaterials when developing these hybrid media for small treatment systems, the support material has to exhibit high macroporosity, which: (1) minimizes pore clogging during in-situ nanomaterial synthesis; (2) enables fast intraparticle mass transport at high hydraulic loading rates and empty bed contact times (EBCTs); (3) creates short mass transfer zones; and (4) allows for base material functionalization to obtain synergetic properties for simultaneous removal of other contaminants [15,23,25,26,28].

Glycidyl methacrylate based copolymers represent an ideal candidate for development of macroporous base media that fits the abovementioned criteria. These copolymers enable inexpensive controllable production of spherical nanoparticle support media with different geometries, and permits design of intraparticle properties via a number of versatile ring-opening reactions of the pendant epoxy groups [29]. Furthermore, the fabrication of these base support media could be optimized to maximize porosity while maintaining high mechanical strength and uniformity of the microscopic hybrid media.

The goal of this study was to evaluate the suitability of the developed goethite impregnated cross-linked macroporous copolymer media for removing arsenic from water. To achieve this goal, the following steps were undertaken: (1) fabricate macroporous copolymer support media using suspension polymerization followed by amino modification and in-situ impregnation by goethite nanoparticles; (2) characterize adsorbent media; (3) quantify the adsorption capacity by conducting pseudo-equilibrium tests under model conditions; (4) quantify the mass transport processes that control the rate of arsenic adsorption in a fixed bed column; (5) predict the performance of a full scale system using the pore surface diffusion model (PSDM).

2. Experimental and modeling approach

2.1. Fabrication of aminated glycidyl methacrylate support media

Macroporous glycidyl methacrylate copolymer was fabricated by dissolving 3.9 g of poly(*N*-vinyl pyrrolidone (PVP Kollidon 90, BASF) in 300 mL of deionized water (18 MΩ cm), and then mixed with oil phase consisting of monomer precursors, porogen and initiator as it is depicted in Fig. 1. The monomer precursor was composed of 30 mL glycidyl methacrylate (Merck) and 13 mL ethylene glycol dimethacrylate (Fluka), while 20 mL of 2-hexanone (Merck) was used as a porogen agent, and 1 g of 2,2′-azobis(2-methyl propionitrile) (Merck) as initiator. The two phases were vigorously stirred under inert atmosphere of nitrogen at 80 °C for a period of 2 h to facilitate a suspension polymerization process. The created copolymer was separated by filtration, washed firstly with ethanol (Sigma Aldrich) followed by deionized water, aged in ethanol for a period of 12 h, and then dried in a vacuum oven at 40 °C for 4 h. The porogen agent was removed from the copolymer by a 48 h continuous Soxlet extraction with chloroform (Sigma Aldrich). The obtained material was sieved and material consisted from the fraction in a range 150–600 μm was collected, and used in subsequent experiments.

Upon sieving, 10 g of glycidyl methacrylate copolymer was dispersed in 50 mL of dry tetrahydrofurane (Sigma Aldrich), and then 20 mL of diethylene triamine (Merck) was added drop-wise to initiate the amination reaction, which was conducted at 60 °C for a period of 6 h as it illustrated in Fig. 1. Introduction of terminal amino groups was conducted to demonstrate the possibility of functionalizing this base media and utilize the affinity of terminal amino groups to facilitate iron precursor diffusion. Modification of copolymer enriched by hydrophilic amino group helped surface wetting and more importantly the interaction of Lewis acid (ferric ions) with Lewis base site (surface amino groups) provides initial nucleation center for goethite precipitation. The aminated macroporous glycidyl methacrylate support media was then