Colloids and Surfaces A: Physicochem. Eng. Aspects 522 (2017) 161–172

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

High-performance iron oxide–graphene oxide nanocomposite adsorbents for arsenic removal

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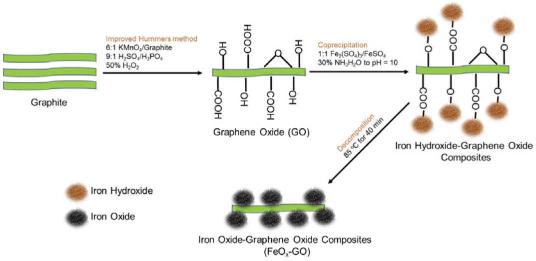
HIGHLIGHTS

- Cost-effective amorphous iron oxide–graphene oxide nanocomposite adsorbents.
- Arsenic concentration can be reduced efficiently from ∼110 to <0.02 ppb.
- High maximum adsorption capacity of 147 mg g^{-1} for As(III) and 113 mg g^{-1} for As(V).

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 16 December 2016
Received in revised form 22 February 2017
Accepted 23 February 2017
Available online 24 February 2017

Keywords:
Graphene oxide
Arsenic adsorption
Iron oxide
Nanocomposite
Adsorbent

ABSTRACT

We report the synthesis of a new range of iron oxide–graphene oxide (GO) nanocomposites having different iron oxide content (36–80 wt%) as high-performance adsorbents for arsenic removal. Synthesized by co-precipitation of iron oxide on GO sheets that are prepared by an improved Hummers method, the iron oxide in the nanocomposites is featured primarily in the desirable form of amorphous nanoparticles with an average size of ca. 5 nm. This unique amorphous nanoparticle morphology of the iron oxide beneficially endows the nanocomposites with high surface area (up to 341 m^2 g^{-1} for FeO$_x$–GO-80 having the iron oxide content of 80 wt%) and predominant mesopore structures, and consequently increased adsorption sites and enhanced arsenic adsorption capacity. FeO$_x$–GO-80 shows high maximum arsenic adsorption capacity (q_{max}) of 147 and 113 mg g^{-1} for As(III) and As(V), respectively. These values are the highest among all the iron oxide–GO/reduced GO composite adsorbents reported to date and are also comparable to the best values achieved with various sophisticatedly synthesized iron oxide nanostructures. More strikingly, FeO$_x$–GO-80 is also demonstrated to nearly completely (>99.98%) removes arsenic by reducing the concentration from 118 (for As(III)) or 108 (for As(V)) to <0.02 μg L^{-1}, which is far below the limit of 10 μg L^{-1} recommended by the World Health Organization (WHO) for drinking water. The excellent adsorption performance, along with their low cost and convenient synthesis, makes this range of adsorbents highly promising for commercial applications in drinking water purification and wastewater treatment.

1. Introduction

Arsenic is one of the most toxic and carcinogenic chemical elements. Arsenic contamination of natural water sources due to mineral leaching and/or anthropogenic activities has been considered as one of the most serious environmental problems worldwide

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http://dx.doi.org/10.1016/j.colsurfa.2017.02.065
0927-7757/

[1–3]. Inorganic arsenic species, primarily in the forms of arsenate (As(V)) and arsenite (As(III)), are believed to be more toxic than the organic forms. Both As(V) and As(III) exist in natural water, with the latter being more toxic and more difficult to remove than the former [1–3]. To date, a variety of techniques has been developed to remove arsenic from both natural and industrial water sources such as coagulation, adsorption, ion exchange, membrane filtration, biological remediation, etc. [3,4]. In particular, adsorption is considered to be most economical and efficient over other techniques, especially in the low concentration range. A wide range of adsorbents has been studied to remove arsenic from water and wastewater, including commercial activated carbons, metal oxides, soils and constituents, natural minerals, etc. [3,4].

Compared to other types of adsorbents, iron oxide-derived adsorbents have received enormous attention for arsenic removal due to their superior performance for arsenic adsorption [5]. In this regard, iron oxides in various forms have been studied and developed for arsenic removal, including amorphous iron oxide [6,7], goethite (α-FeOOH) [8], hematite (α-Fe_2O_3) [8,9], crystalline magnetic maghemite (γ-Fe_2O_3) and magnetite (Fe_3O_4) nanoparticles [10–12], as well as other iron oxide nanostructures [13–20]. Among them, amorphous iron oxides show the highest adsorption capacity (as high as 260 and 200 mg g^{-1} for As(III) and As(V), respectively) due to its highest specific surface area [8], but with the shortcomings of its difficulty (as fine powders) for separation following adsorption and its tendency to form low-surface-area crystalline iron oxides during preparation [4]. On the contrary, magnetic crystalline iron oxides [10–12] and the various iron oxide nanostructures [13–20] generally show lowered adsorption capacity due to their low specific surface area.

Iron oxide-derived nanocomposite adsorbents prepared by loading iron oxides onto various substrates have also been extensively developed and investigated for arsenic adsorption [3,4]. Typical substrates include low-cost abundant ones, such as naturally occurring minerals [21], activated carbons [22], graphene oxide (GO) [23–33], and cellulose [34], as well as some specially synthesized costly ones, such as mesoporous carbons [35,36], carbon nanotubes [37], macroporous silica [38], etc. Such nanocomposite adsorbents facilitate their more convenient separation following adsorption. However, their maximum arsenic adsorption capacity is often relatively low, except in one case with specially designed, costly macroporous silica as the substrate [38]. Due to its unique two-dimensional one-atom-thick sheet structure with high surface area and abundant oxygen-containing functionalities, GO prepared easily from abundant graphite by oxidization and reduced GO (RGO) prepared by subsequent reduction of GO have recently received enormous interest for environmental remediation applications [39–42]. Crystalline magnetic iron oxide nanoparticles have been loaded onto GO or RGO, rendering nanocomposite adsorbents for arsenic adsorption [23,33]. However, the arsenic adsorption capacity achieved thus far with the iron oxide-GO/RGO nanocomposite adsorbents is commonly very low [only up to 54 and 73 mg g^{-1} reported for As(III) and As(V), respectively], with significant room for further improvements.

Tackling the above issues, we report in this paper the synthesis of a range of cost-effective amorphous iron oxide-GO nanocomposite adsorbents of significantly improved arsenic adsorption capacity. The key to the enhanced adsorption capacity is the unique loading of primarily amorphous iron oxide nanoparticles of high specific surface area on GO. The composite adsorbents have been designed to contain different contents of the amorphous iron oxide, and have been thoroughly characterized for their compositional, structural, and textural properties. A systematic study on the performance of these composite adsorbents for the adsorption of As(III) and As(V) has been undertaken. Our results suggest their high potential as cost-effective adsorbents for arsenic removal from both drinking water and industrial wastewater.

2. Experimental

2.1. Materials

Natural graphite flake (+100 mesh: ≥75.5%, Aldrich), potassium permanganate (99.0+%, Sigma Aldrich), hydrogen peroxide (50%, Fisher Scientific), sulfuric acid (96.9 wt%, Fisher Scientific), phosphoric acid (85+%, Acros), ferrous sulfate heptahydrate (99+%, Sigma Aldrich), ferric sulfate hydrate (97%, Fe 21.6%, Sigma Aldrich), ammonium hydroxide solution (28–30%, Sigma Aldrich), hydrochloric acid (37%, Fisher Scientific), methanol (ACS reagent, Fisher Scientific), were used as received without any additional purification. Deionized water was purified by a Barnstead/Synbron Nanopure II purification system.

Sodium (meta) arsenite ($NaAsO_2$, ≥90%, Aldrich) and sodium arsenate dibasic heptahydrate ($Na_2HAsO_4 \cdot 7H_2O$, ≥98%, Aldrich) were selected as the source of As(III) and As(V), respectively. As(III) and As(V) stock solutions at the arsenic concentration of 2000 mg L^{-1} were prepared in deionized water. The standard arsenic solutions with different concentrations were diluted from the 2000 mg L^{-1} stock solutions with the pH adjusted to desired values with HNO_3 or NaOH.

2.2. Synthesis of graphene oxide (GO)

GO was synthesized by exfoliation of natural graphite flakes with the use of an improved Hummers method reported by Tour et al. [43] In a typical process, a mixture of concentrated H_2SO_4/H_3PO_4 (360:40 mL) was prepared in a round-bottom flask, then 3 g of graphite flakes were added to the mixture under vigorous mechanic stirring for 10 min to obtain a dark-colored suspension. Subsequently, 18 g of $KMnO_4$ were added slowly into the above suspension in an ice bath. The mixture was stirred vigorously for 36 h at 50 °C. A reddish brown viscous mixture was obtained. This mixture was cooled to room temperature, and then poured slowly into 400 mL of cold deionized water containing 3 mL of H_2O_2 (50%). Afterward, the suspension was centrifuged and washed sequentially with HCl, water, then methanol for several times, until pH reached 6. The solid material was collected after centrifugation and dispersed again in 1200 mL of water as the stock solution (GO concentration of 3.5 mg mL^{-1}; 4.2 g in total) for subsequent use.

2.3. Preparation of amorphous iron oxide–GO nanocomposites (FeO_x–GOs)

FeO_x–GO composites were synthesized by the co-precipitation method. The GO suspension (64 mL, containing 0.22 g of GO) was first diluted with 160 mL of water. An aqueous solution of $Fe_2(SO_4)_3$ and $FeSO_4$ at 1:1 molar ratio (or Fe^{3+}:Fe^{2+} = 2:1) was prepared. In the case for the preparation of the nanocomposite with 80 wt% of iron oxide (FeO_x–GO-80), the amounts of ferric sulfate hydrate and ferrous sulfate heptahydrate were 1.51 g and 0.81 g, respectively. The solutions of $Fe_2(SO_4)_3$ and $FeSO_4$ were added into the GO suspension slowly at room temperature. Subsequently, 30% ammonia solution was added under stirring to this suspension to make pH 10. The suspension was heated to 85 °C and was rapidly stirred for 40 min. It was then cooled down to room temperature. The resulting black suspension was filtered, washed with water and methanol several times, and finally dried overnight under vacuum at 60 °C, rendering 850 mg of FeO_x–GO-80. Two other nanocomposites (FeO_x–GO-36 and FeO_x–GO-60) containing different contents (36 and 60 wt%, respectively) of iron oxide were similarly prepared.