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Feasible water flow filter with facilely functionalized Fe_3O_4-non-oxidative graphene/CNT composites for arsenic removal

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ABSTRACT

Practical applications of carbon-based nanomaterials are important issues for water treatment technologies, especially for heavy metal adsorption. For the applications, a facile method to functionalize the carbon-based nanomaterials and a strategy for their typical uses are required. Here, we report a highly feasible water flow filter filled with Fe_3O_4-functionalized non-oxidative graphene/CNT prepared via facile functionalization in a Couette-Taylor flow reactor for arsenic removal. Fe_3O_4 was uniformly functionalized on the CNTs and the non-oxidative graphene using the Couette-Taylor flow method, which allows fast production of a large number of filters. The hybrid composite of Fe_3O_4-functionalized non-oxidative graphene/CNT demonstrated an improvement in the arsenic removal efficiency when it served as a flow filter rather than when used in the batch method because its 3D structure enhanced both the water flow pathway and the contact area with Fe_3O_4. Adaption for household use for continuous purification of water is simple for this proposed filter.

1. Introduction

The target heavy metal, arsenic, is one of the most toxic elements on earth and is widely present in the environment in rocks, soils, and groundwater [1–4]. Arsenic is primarily present in the groundwater as oxyanions of trivalent arsenite [As(III)] and pentavalent arsenate [As(V)] [5–7]. These chemical forms are regarded as highly toxic substances that can cause serious human health problems, such as skin lesions, hyperkeratosis, and cancer [8]. To reduce these health risks, several water treatment technologies to remove arsenic, such as co-precipitation [9,10], ion exchange [11], membrane filtration [12–14], and adsorption [15–17], have been studied. Of these technologies, adsorption is the most promising technique because of its cost-effectiveness, ease of operation, and consistent performance [18].

Recently, due to their large specific surface areas and ability to be combined with metal oxides, carbon nanotubes (CNTs), which are 1D substances, and graphene-based materials, which are 2D substances, have been functionalized with metal oxides for use in the water treatment process [19–22]. In addition, after combining CNTs and graphene-based materials to create 3D structures with large specific surface areas these carbon-based nanomaterials can more efficiently remove heavy metals, such as arsenic, through functionalization with larger amounts of metal oxides [23,24]. Functionalizing the surfaces of these carbon-based 3D structures with metal oxides can create an attractive adsorbent for water purification. Many technologies for the removal of arsenic from water that use carbon-based nanomaterials functionalized with the metal oxide magnetite (Fe_3O_4) have been reported [25–28].

However, despite the advantages of CNT- or graphene-based materials functionalized with Fe_3O_4, the general functionalization method such as hydrothermal synthesis is not feasible to functionalize the materials uniformly. Besides, as shown in Table 1, the general Fe_3O_4 composites have a very low adsorption capacity for arsenic. Furthermore, batch studies of the Fe_3O_4-functionalized carbon-based nanomaterials for arsenic removal were difficult to perform in practical situations.

Herein, we uniformly and rapidly functionalized Fe_3O_4 onto the CNTs and non-oxidative graphene using the Couette-Taylor flow

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Table 1
Previous relevant studies of arsenic removal using magnetite composites.

Adsorbents	Experimental Conditions				Adsorption capacity (mg/g)		Ref.
	pH	m/V (g/L)	Temp. (°C)	RT (h)	As(III)	As(V)	
Magnetite nanocrystal	8	500	25	24	0.992	0.984	[29,30]
Magnetite nanoparticles	8	0.1	20	1	0.512	0.485	[31]
Magnetic multi-granular nanoclusters	7	1	25	24	–	2.4	[32]
Hematite-coated magnetite	7	0.3	25	24	1.0	2.1	[33]
Commercial nanomagnetite	9	5	25	3	0.209	0.205	[34,35]

technique. We found that the toroidal motion of the fluids created in the Couette-Taylor reactor leads to highly efficient radial mixing between the Fe_3O_4 and the CNTs and/or the non-oxidative graphene in the system [36–38]. Additionally, the Fe_3O_4-functionalized carbon-based nanomaterials used in this study (Fe_3O_4-non-oxidative graphene (M-G), Fe_3O_4-CNT (M-C), and Fe_3O_4-non-oxidative graphene/CNT (M-G/C)) were tested in a water flow filter similar to those used at water treatment facilities. To investigate the removal efficiency of As(III) and As(V) in aqueous solution, the arsenic adsorption capacities of the flow filters fabricated using M-G, M-C, and M-G/C were compared with those prepared using the batch method.

2. Experimental details

2.1. Materials

Non-oxidative graphene powder (20–30 layers) and CNTs (multi-walled CNTs) were obtained from World Tube Co. Ltd. (South Korea). $FeCl_2 \bullet 4H_2O$, $FeCl_3 \bullet 6H_2O$, ammonium hydroxide (NH_4OH), and all other reagent grade chemicals were purchased from Sinopharm Chemical Reagent Co. Ltd. The As(III) and As(V) solutions used in the adsorption experiment were prepared using $NaAsO_2$ (Fluka) and $Na_2HAsO_4 \bullet H_2O$ (Sigma Aldrich), respectively. Distilled-deionized (DDI) water was used in all experiments.

2.2. Preparation of M-G, M-C, and M-G/C composite using Couette-Taylor flow

The non-oxidative graphene and CNTs were dispersed in water via ultrasonication. A solution of melted $FeCl_2 \bullet 4H_2O$ in 0.5 M HCl and melted $FeCl_3 \bullet 6H_2O$ in water was prepared and mixed. The mixed solution was slowly added to the non-oxidative graphene solution while stirring. The Couette-Taylor flow reactor (length: 400 mm) consists of two coaxial cylinders with a fixed outer cylinder (radius: 125 mm) and a rotating inner cylinder (radius: 25 mm). After the mixture was introduced into the gap between the two cylinders, the inner cylinder was rotated. The rotating speed of the inner cylinder was 600 rpm for a reaction time of 15 min. Then, 30% NH_4OH solution was quickly injected into the mixed solution in the gap between the two cylinders to maintain a pH of 10 (Fig. 1). For purification, the solution was filtered and washed several times using ethanol and water. Finally, the solution was vacuum- or freeze-dried to produce M-G/C. The above process was also used to produce M-G and M-C.

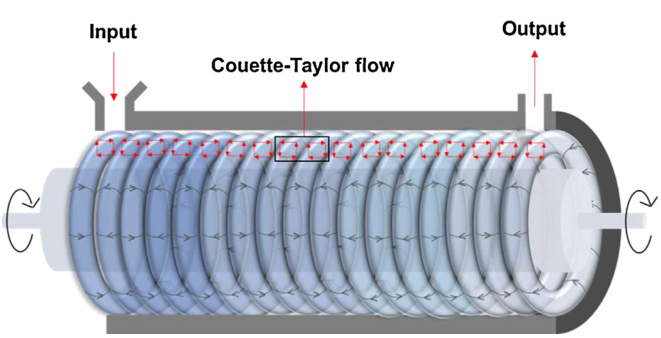

Fig. 1. Scheme of the functionalization of Fe_3O_4-carbon-based nanomaterials (M-G, M-C, and M-G/C) via a Couette-Taylor flow reactor.

2.3. Adsorption study: batch

For the batch method, 3 mg of the adsorbent compound (M-G, M-C, or M-G/C) was added to a capped glass vial containing 30 mL of arsenic solution at a fixed pH 7. The initial concentrations of As (III) and As(V) were 1, 3, and 5 mg/L. All of the samples were shaken for a specific contact time in a shaking incubator at 25 °C and 200 rpm. After reaction, samples were filtered using 0.2 μm syringe filter and analyzed to detect the residual arsenic concentration. The arsenic adsorption capacity of three different compounds in the batch test was calculated from Eq. (1):

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

where q_e is the amount of arsenic adsorbed (mg/g), C_0 is the initial concentration of arsenic in the solution (mg/L), C_e is the equilibrium concentration of arsenic after adsorption (mg/L), V is the volume of solution (L), and m is the mass of the adsorbents (g).

2.4. Adsorption study: flow filter

For the water flow filter, M-G, M-C, and M-G/C were assembled as part of a fixed-bed filter column. The other parts of the column included a Teflon tube sealed at both ends and wrapped with a few

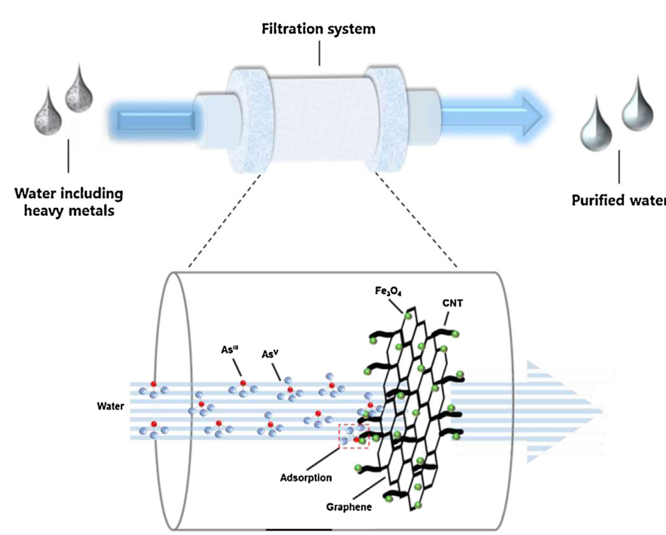

Fig. 2. Scheme of the water flow filter for removal of arsenic with a conceptual image of the filter containing M-G/C.