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Synthesis of magnetite/non-oxidative graphene composites and their application for arsenic removal

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ABSTRACT

Since graphene-based materials have been investigated to adsorb many kinds of contaminants such as heavy metals especially arsenic, the fabrication costs of them are critically important for their application to the practical adsorption process. Here, we fabricate a non-oxidative graphene with mass production and synthesis magnetite/non-oxidative graphene (M-nOG) composites for arsenic removal. The M-nOG showed great capacity for adsorption of arsenic against its low material cost. We found that the arsenite was more influenced by surface complexation and the arsenate was favorable for intraparticle diffusion in the adsorption process using M-nOG. To confirm the feasibility of M-nOG as adsorbents for arsenic removal, the effect of various conditions such as pH, temperature, competing anions, and humic acid on the arsenic removal were evaluated. Moreover, the repetitive reuse and regeneration of M-nOG were performed. In conclusion, the M-nOG was cost-effective and feasible to use practically as adsorbents for arsenic removal.

1. Introduction

The occurrence of arsenic in groundwater has been issued around the world due to its toxicity and the potential for chronic exposure via drinking water [1–3]. Arsenic contamination affects millions of people especially in Bangladesh, Vietnam, Cambodia, India, southwest USA, Canada, Argentina, Chile, Mexico, and neighboring countries and results in long-term exposure to arsenic in drinking water that can cause skin, lungs, liver, kidney, and bladder cancer [4–6]. The World Health Organization and the United States Environmental Protection Agency have been adopted the guideline of 10 μg/L of arsenic as the drinking water standard [7,8]. Various studies have investigated arsenic remediation using different technologies, including co-precipitation/coagulation [9], ion exchange [10], adsorption [11], and membrane filtration [12,13]. Among these possible treatment processes, adsorption is considered to be easier and safer technology to handle as compared to the contaminated sludge produced by co-precipitation/coagulation, more versatile than ion exchange, and less expensive than membrane filtration [14].

Since graphene, a new generation of nano-carbon material, was discovered [15], the graphene-based material has recently been evaluated to remove arsenic from water in adsorption process [16–18]. Although those studies reported that the adsorption using the graphene-based material was considered as a promising technology for arsenic removal due to the outstanding removal efficiency, if the unit cost of adsorbent production is expensive, the advantages of adsorption process would be nonsensical. Mostly, graphene oxide (GO) and reduced graphene oxide (rGO) have been used to synthesize the graphene-based adsorbents for arsenic removal [16,17,19]. Even though the GO has a lot of oxygen-containing functional groups which can lead to synthesize with more arsenic adsorption supporting compounds such as iron oxides [19], the general fabrication method of GO, Hummers method [20], spend large amount of chemicals and long time of reactions. Moreover, the effort to fabricate a nearly pristine graphene such as rGO [21], the reduction product of GO, is not essential in terms of the adsorbent for water treatment process.

Thus, here, we report on the fabrication of non-oxidative graphene (nOG) which is a few-layer graphene for mass production at a lower cost and in a shorter time than GO and rGO. In this work,

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Nomenclature

As(III)	arsenite
As(V)	arsenate
q_t	amount of arsenic adsorbed at time t (mg/g)
q_e	equilibrium adsorption capacity (mg/g)
$q_{e(\exp)}$	experimental q_e value (mg/g)
$q_{e(\mathrm{cal})}$	calculated q_e value by the kinetic model (mg/g)
k_f	pseudo-first-order rate constant (min^{-1})
k_s	pseudo-second-order rate constant (g/mg min)
k_{id}	intraparticle diffusion rate constant (mg/g $min^{1/2}$)
C	intraparticle diffusion constant related to the thickness of the boundary layer.
R^2	correlation coefficient
Q_L	Langmuir constant reflecting the maximum adsorption capacity (mg/g)
b	Langmuir constant related to the free energy of adsorption (L/mg)
C_e	equilibrium arsenic concentration after adsorption (mg/L)
K_F	Freundlich constant related to the adsorption capacity ((mg/g)(L/mg)$^{1/n}$)
$1/n$	Freundlich isotherm exponent reflecting the adsorption intensity
Q_s	sips constant reflecting the maximum adsorption capacity (mg/g)
K_s	sips isotherm constant (L/mg)
s	sips isotherm exponent

the nOG has been used to synthesize magnetite/nOG composites (M-nOG) for application to the arsenic removal. The M-nOG has been characterized by several analytical techniques. The exploratory application of this reasonable graphene-based nanocomposites on the removal of arsenite [As(III)] and arsenate [As(V)] in aqueous solutions is investigated. The effects of the parameters including adsorption time, initial arsenic concentration, solution pH and temperature, and competing anions and humic acid on the arsenic removal properties are studied. Besides, repetitive reuse and regeneration of the M-nOG are performed. This study highlighted the facile applicability of this reasonable material in environmental pollution cleanup.

2. Experimental

2.1. Materials and chemicals

Natural graphite powder (99%) was obtained from Samjung CNG Co. Ltd. (Cheongdo, Korea, Rep.). Ammonium sulfate ($(NH_4)_2SO_4$), ammonium hydroxide (NH_4OH), sulfuric acid (H_2SO_4, 95%), iron(II) chloride tetrahydrate ($FeCl_2{\cdot}4H_2O$), and iron(III) chloride hexahydrate ($FeCl_3{\cdot}6H_2O$) were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, PR China). As(III) and As(V) solutions were prepared using $NaAsO_2$ (Fluka, Zwijndrecht, Netherlands) and $Na_2HAsO_4{\cdot}H_2O$ (Sigma-Aldrich, St. Louis, USA), respectively. In the experiment for an effect of coexisting anions and natural organic matter (NOM) on arsenic adsorption, chloride (Cl^-) nitrate (NO_3^-), bicarbonate (HCO_3^-), fluoride (F^-), sulfate (SO_4^{2-}), phosphate (PO_4^{3-}), and humic acid (IHSS Suwannee River humic acid standards) were used. These anions were purchased from Sigma-Aldrich (St. Louis, USA) and distilled-deionized (DDI) water was used in all experiments.

2.2. Preparation of nOG and M-nOG composite

nOG was synthesized from the natural graphite and there were no oxidation or reduction processes using chemicals. For a basic recipe for the nOG, 3 g of $(NH_4)_2SO_4$ were added to 100 mL of 95% H_2SO_4, and then 1 g of graphite was mixed and stirred with the solution at 50 °C for 30 min to expand the structure of graphite. The mixture was washed with DDI water for several times until to reach pH 7, and then it was dried at 100 °C for 24 h. Finally, nOG was obtained by physical exfoliation method using thermal treatment at 600 °C for 1 h. In the scale-up manufacturing process, 4 kg of nOG could be produced on one production line.

For M-nOG, 100 mg of nGO was dispersed in 100 mL of DDI water by ultrasonication for 1 h. A solution of melted 0.2 g of $FeCl_2{\cdot}4H_2O$ in 5 mL of 0.5 M HCl and melted 0.54 g of $FeCl_3{\cdot}6H_2O$ in 10 mL of DDI water was prepared and mixed. The mixed solution was slowly added to the nGO solution while stirring under a nitrogen atmosphere for 15 min. Then, 16 mL of 30% NH_4OH solution was quickly added to the solution to regulate the pH to 10. After stirring for 45 min, the solution was filtered and washed using ethanol and water several times. Finally, after the powder was dried in vacuum oven at 70 °C for 24 h, M-nOG was obtained.

To analyze the characteristics of the nOG and M-nOG, a field emission scanning electron microscope (FE-SEM, JSM-7600F, JEOL), Energy Dispersive X-ray Spectroscopy (EDS, JSM-7600F, JEOL), transmission electron microscopy (TEM, JEM-3010, JEOL), X-ray photoelectron spectroscopy (XPS, VG Microtech ESCA2000, JEOL), Raman (Bruker FRA 160/S, BRUKER), and X-ray diffraction (XRD, D8 ADVANCE, BRUKER) were used.

2.3. Adsorption studies

All of the adsorption experiments were performed in capped glass vials with 30 mL of arsenic solution and 3 mg of adsorbent (M-nOG). All of the samples were shaken for a specific contact time in a shaking incubator (SI-300, Lab Companion). The pH of the solutions was adjusted using 0.1 M NaOH or HCl to the desired initial pH values. All samples were filtered using 0.2 μm syringe filter (Chromafil CA-20, MACHEREY-NAGEL) after reaction, and the concentration of residual arsenic was analyzed using an inductively coupled plasma-atomic emission spectrometer (ICP/IRIS, Thermo Jarrell Ash Co., USA). The amount of arsenic adsorbed (q_e, mg/g) was calculated from the following Eq. (1)

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

where C_0 and C_e are the initial and equilibrium concentration of arsenic in solution (mg/L), V is the volume of solution (L), and m is the mass of the M-nOG composite (g).

3. Results and discussion

3.1. Characterization of M-nOG

Several characterization techniques were used to determine the properties of M-nOG and to confirm the proper synthesis of magnetite onto nOG. XPS spectra indicate the chemical states of elements, especially those of carbon (C1s), oxygen (O1s), and iron