

Graphene oxide/ferric hydroxide composites for efficient arsenate removal from drinking water

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ABSTRACT

A series of novel composites based on graphene oxide (GO) cross-linked with ferric hydroxide was developed for effective removal of arsenate from contaminated drinking water. GO, which was used as a supporting matrix here, was firstly treated with ferrous sulfate. Then, the ferrous compound cross-linked with GO was *in situ* oxidized to ferric compound by hydrogen peroxide, followed by treating with ammonium hydroxide. The morphology and composition of the composites were analyzed by X-ray diffraction, scanning electron microscopy and transmission electron microscopy. The ferric hydroxide was found to be homogeneously impregnated onto GO sheets in amorphous form. These composites were evaluated as adsorbents for arsenate removal from contaminated drinking water. For the water with arsenate concentration at 51.14 ppm, more than 95% of arsenate was absorbed by composite GO-Fe-5 with an adsorption capacity of 23.78 mg arsenate/g of composite. Effective arsenate removal occurred in a wide range of pH from 4 to 9. However, the efficiency of arsenate removal was decreased when pH was increased to higher than 8.

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1. Introduction

Graphene, a two-dimensional structure consisting of sp^2 -hybridized carbons with only one atomic thickness, is a rising star in the material science and technology [1–4]. Graphene is a giant aromatic macromolecule with several remarkable electronic and mechanical properties such as excellent electricity and heat conductivity in two dimensions [5], mechanical strength comparable to carbon nanotubes (CNTs) [6], etc. So far, numerous reports of different device applications of graphene have been reported, such as field-effect transistors [7], transparent electrodes [8], and organic photovoltaic devices [9]. However, large scale production of perfect graphene is still difficult, and multifunctional hybrid materials that take advantages of both the unique properties of graphene and the functional materials are highly desired. Usually, the synthesis of most graphene-based multifunctional hybrid materials begins with chemically oxidized graphene oxide (GO). The presence of copious oxygen-containing groups on GO, e.g. epoxides, alcohols, lactols, ketones, and carboxyl groups, can significantly affect the van der Waals interactions between the graphene layers and also render it strongly hydrophilic [10,11]. In addition, GO can be readily obtained from cheap natural graphite in large scale. Thus, hybrid multifunctional materials based on GO are much more applicable than those

based on the other more expensive nanomaterials such as functionalized CNTs. Recently, GO based composite materials, such as GO/bentonite [12], GO/aluminum polycation [13], GO/iron oxide [14], GO/iron acetate [15], have also been studied as the adsorbents for ammonia and nitrogen oxides.

Arsenic (atomic number 33, a metalloid element) is ubiquitous and ranks 20th in natural abundance. However, arsenic is infamous for its marked negative impacts on human health because of its chronic and carcinogenic effects as well as acute lethality [16–18]. Inorganic arsenic species, arsenate (As(V)) and arsenite (As(III)), are believed to be more toxic than the organic forms. As(V) is predominate in surface waters, while As(III) is dominant in groundwater systems [19,20]. Drinking water contamination by arsenic remains a major public health problem around the world, especially in Bangladesh, India, USA, China, Mexico, Chile, etc. [21,22]. The World Health Organization's (WHO) provisional guideline of 10 ppb (0.01 mg/L) for arsenic in drinking water has been adopted as the drinking water standard by most of the countries. Therefore, it is highly desired to develop eco-friendly, simple and economical techniques for arsenic removal. To date, arsenic removal techniques include coagulation [23], adsorption [24,25], ion exchange [26], membrane separation [27,28], etc. Generally, the adsorption and coagulation methods are more cost-effective, especially when the adsorbents are either cheap or re-generable. Several iron(III) oxides, such as amorphous hydrous ferric oxide [29], poorly crystalline hydrous ferric oxide [30], and goethite [31], are well-known for efficient removal of both As(V) and As(III) from

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aqueous solutions. Recently, several iron based granular materials have been developed [32–35]. Among them, granular ferric hydroxide is most effective with high treatment capacity although its robustness and mechanical strength need further improvement [36,37].

Ferric hydroxide was incorporated into matrix materials, such as sands [38] or activated carbon [39], to overcome its collapsing nature. Jang et al. incorporated hydrous ferric oxide into granular activated carbon via incipient wetness impregnation and cured at different temperature. High arsenic sorption capacity of 26 mg As/g absorbent was achieved in the column test [40]. Activated carbon bearing both iron complex and quaternary ammonium surfactants exhibited intriguing co-sorption of both arsenate and perchlorate via distinct mechanisms [41]. In the present work, a series of iron-decorated GO materials has been developed for effective removal of arsenate from contaminated drinking water. The theoretical specific surface area of individual graphene sheets is more than twice that of the finely developed activated carbon [42], which is widely used in water purification. Literatures have reported that treating activated carbon with various iron compounds can significantly increase the arsenic adsorption [43,44]. It is apparent that some iron compounds can cross-link to the oxygen groups on activated carbon, which can significantly enhance the arsenic sorption [43]. In this work, GO, which contains a wide range of oxygen functional groups, was firstly treated with ferrous sulfate followed by *in situ* oxidation to yield ferric compound functionalized GO. Then, ammonium hydroxide was added to the mixture to generate the nanocomposites of GO cross-linked with ferric hydroxide. The resultant absorbents should have the following advantages: (1) high efficiency in arsenate removal due to the impregnated ferric hydroxide; (2) improved chemical stability and mechanical strength by introducing GO sheets [45]; (3) more eco-friendly and economical absorbent based on cheap GO and ferric hydroxide.

2. Experimental

2.1. Materials

All chemicals were of reagent grade. All solutions were prepared using deionized (DI) water. Graphite powder and ferrous sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) were obtained from Alfa Aesar. Potassium arsenate monobasic (KH_2AsO_4) was obtained from Sigma.

2.2. Preparation of GO

GO was synthesized from natural graphite (crystalline, 300 mesh, Alfa Aesar) by a modified Hummers method [46]. Graphite (5.0 g) and NaNO_3 (2.5 g) were mixed with 120 mL of H_2SO_4 (95%) in a 500 mL flask. The mixture was stirred for 30 min in ice bath. While maintaining vigorous stirring, potassium permanganate (15.0 g) was added to the suspension. The rate of addition was carefully controlled to keep the reaction temperature lower than 20 °C. The ice bath was then removed and the mixture was stirred at room temperature overnight. As the reaction progressed, the mixture gradually became pasty and the color turned into light brownish. At the end, 150 mL of H_2O was slowly added to the paste with vigorous agitation. The reaction temperature was rapidly increased to 98 °C with effervescence, and the color changed into yellow. The diluted suspension was stirred at 98 °C for 1 day. Then, 50 mL of 30% H_2O_2 was added to the mixture. For purification, the mixture was washed by rinsing and centrifugation with 5% HCl then DI water several times. After filtration and drying under vacuum, GO was obtained as grey powder.

2.3. Preparation of GO/ferric hydroxide (GO-Fe) composites (GO-Fe-1, GO-Fe-2, GO-Fe-3, GO-Fe-4, GO-Fe-5)

Taking GO-Fe-1 as example: GO (345 mg) was dispersed into water (10 mL) by ultrasonication for 30 min. To this suspension, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (100 mg) was added. The mixture was stirred for 24 h at room temperature. During this procedure, H_2O_2 was added four times according to the ratio of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}/\text{H}_2\text{O}_2 = 1 \text{ g}/10 \text{ mL}$ at approximately 6 h interval. After 24 h, a small amount of ammonium hydroxide was added until the pH reached 8. Upon addition of ammonium hydroxide, the color of the mixture turned reddish and finally became a deep red color because of the formation of ferric hydroxide. The water in the reaction mixture was evaporated on a hot plate to give a solid black mass which was later washed with warm water and dried in a vacuum oven at 85 °C for overnight to yield 376 mg of GO-Fe-1 composite.

Following the same procedure, four more composites with different GO/ $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ratios were prepared, i.e. GO-Fe-2 (345 mg/300 mg) with a yield of 440 mg, GO-Fe-3 (345 mg/500 mg) with a yield of 503 mg, GO-Fe-4 (345 mg/750 mg) with a yield of 588 mg, and GO-Fe-5 (345 mg/1000 mg) with a yield of 659 mg.

2.4. General characterization

Transmission electron microscopy (TEM) measurements were conducted on a JEOL 2010 FEG microscope at 200 keV. The TEM sample was prepared by dispersing a small amount of dry powder in ethanol. Then, one drop of the suspension was dropped on 300 mesh copper TEM grids covered with thin amorphous carbon film. Scanning electron microscopy (SEM) measurements were carried out using a field emission scanning electron microanalyzer (JEOL-6300F) at 5 kV. The SEM sample was prepared by placing a drop of dilute ethanol dispersion of the composites onto a copper plate attached to an aluminum sample holder and the solvent was allowed to evaporate at room temperature. X-ray diffraction (XRD) patterns of the composites were measured using a Bruker-AXS D8 DISCOVER with GADDS Powder X-ray diffractometer. Copper K_α line was used as radiation source with $\lambda = 1.5406 \text{ \AA}$. Thermogravimetric analysis (TGA) was carried out on a TA instrument 2960 from room temperature to 1000 °C at a heating rate of 5 °C/min under air flow.

2.5. Chemical analysis

The arsenate concentration in the solution was analyzed by inductively coupled plasma (ICP), which determines metals in solution for identification and differentiation of elemental metals down to ppb levels. Analysis includes sample preparation by open/close digestion. Instrumentation includes PerkinElmer Dual-View Optima 5300 DV ICP-OES system. Sample was prepared by Milestone microwave laboratory system.

The ability of various GO-Fe composites for arsenate removal was assessed in a batch system using KH_2AsO_4 solution in DI water. The arsenate removal performances of these absorbents were assessed on the basis of iron impregnated, the arsenate adsorption isotherm, and pH edge. In each test, 42.0 mg of the absorbent was weighted into a 15 mL bottle, followed by adding 14 mL of the arsenate solution. The final absorbent dosage was 3.00 g/L. The mixture was mixed on a shaker (150 rpm) for 24 h at room temperature. Upon completion of the experiment, each sample was filtered through a 0.45 μm membrane. And the arsenate concentration of each filtrate was analyzed by ICP. An adsorption isotherm was obtained by changing the initial arsenate concentration from 20.00 to 0.50 mg/L at different pH, namely 4, 5, 6, 7, 8, and 9. The pH was adjusted using either NaOH or HNO_3 .

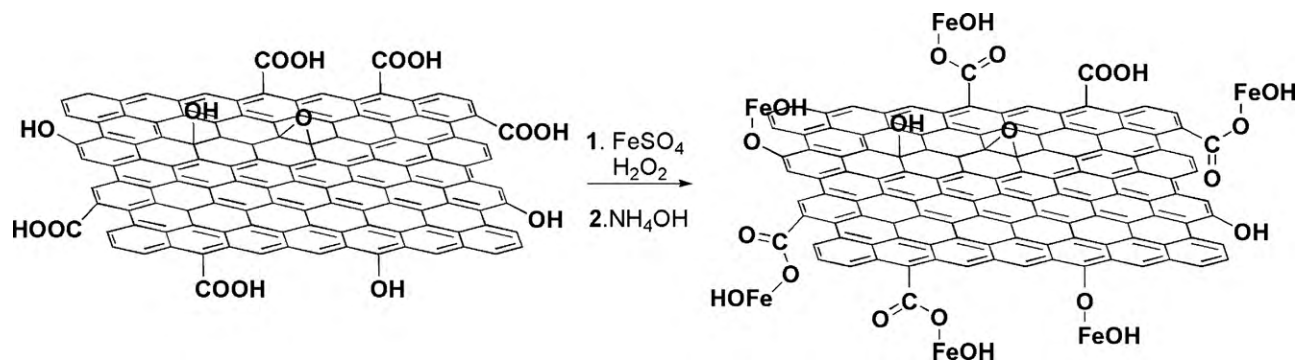


Fig. 1. Illustration of the process for preparation of GO-Fe composites.

3. Results and discussion

3.1. Preparation of composites

The preparation method of absorbents is illustrated in Fig. 1. GO was prepared according to a modified Hummers method [46]. It is known that GO is a compound composed of carbon, oxygen, and hydrogen in variable ratios. The maximally oxidized bulk product is brownish-gray color solid with C:O ratio between 2.1 and 2.9. It consists of loosely-bound layers, each being a two-dimensional arrangement of carbon atoms in the graphene pattern with thickness of around 1.1 nm. The edges of each layer are terminated with carboxyl, hydroxyl, etc. Thus, GO powder readily forms a stable aqueous suspension upon ultrasonication and stirring. As reported before, the oxygen groups on carbon materials can cross-link with iron compounds [43]. Thus, treating GO aqueous suspension with ferrous sulfate heptahydrate followed by *in situ* oxidation using H_2O_2 would generate a composite with ferric compounds linked on the edge or surface of GO sheets. Although Fe(III) in general has stronger complexation with oxygen groups than Fe(II), directly treating GO with $FeCl_3$, however, is not effective. Fe(III) salts are easily hydrolyzed and precipitated out when pH is higher than 3.0, while protons in strong acidic solution would suppress Fe(III) absorption on GO. The mixture was further treated with ammonium hydroxide to yield GO-Fe nanocomposite. After that, water was evaporated from the mixture by heating in air and the residue was washed with copious DI water followed by filtration. Finally, the obtained powder was dried thoroughly in a vacuum oven upon heating. As shown in Table 1, the actual ferric hydroxide contents in these composites, which could be estimated according to TGA analysis (Fig. S1), were 8.17% for GO-Fe-1, 19.62% for GO-Fe-2, 28.22% for GO-Fe-3, 42.26% for GO-Fe-4 and 54.12% for GO-Fe-5, respectively.

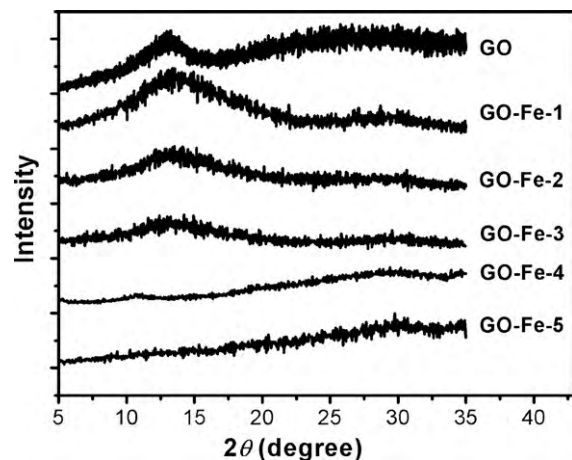


Fig. 2. X-ray diffraction patterns of GO and composites.

3.2. Characterizations of composites

As shown in Fig. 2, GO exhibits a weak peak around 12.2° , corresponding to the (001) diffraction peak, which indicates a typical loose layer-like structure. The 2θ value corresponds to an interlayer spacing (l_c) of about 0.63 nm, which might depend on the method of preparation and on the number of layers of water in the gallery space of the material [47]. In the composites, there are no additional diffraction peaks for crystalline ferric hydroxide, suggesting that the ferric hydroxide in the composites exists in an amorphous state. However, it is observed that with the increase of the Fe/GO ratio, the intensity of the peak at 12.2° gradually decreases, indicating that at a higher iron/GO ratio, amorphous ferric hydroxide mate-

Table 1
Effects of impregnated iron amount on arsenate removal.

	Fe(OH) ₃ content (%) ^a	C _{As} (ppm) ^b	C _{As} (ppm) ^c	R _{As} (%) ^d	q _{As} (mg/g) ^e	L _{Fe} (ppm) ^f
GO-Fe-1	8.17	19.32	3.77	80.4	4.91	2.97
GO-Fe-2	19.62	19.32	0.36	98.1	5.98	7.74
GO-Fe-3	28.22	19.32	0.15	99.2	6.04	3.22
GO-Fe-4	42.26	19.32	Nd ^g	100	6.10	0.64
GO-Fe-5	54.12	19.32	Nd ^g	100	6.10	0.25
GO-Fe-5	54.12	39.73	1.7	95.7	18.55	15.82
GO-Fe-5	54.12	51.14	2.4	95.3	23.78	14.93

^a Calculated from TGA tested in air.

^b Arsenate concentration of initial solution.

^c Arsenate concentration of the filtrate.

^d Percentage of arsenate removed.

^e Arsenate absorbed by absorbents.

^f Iron concentration of the filtrate.

^g Non-detectable.

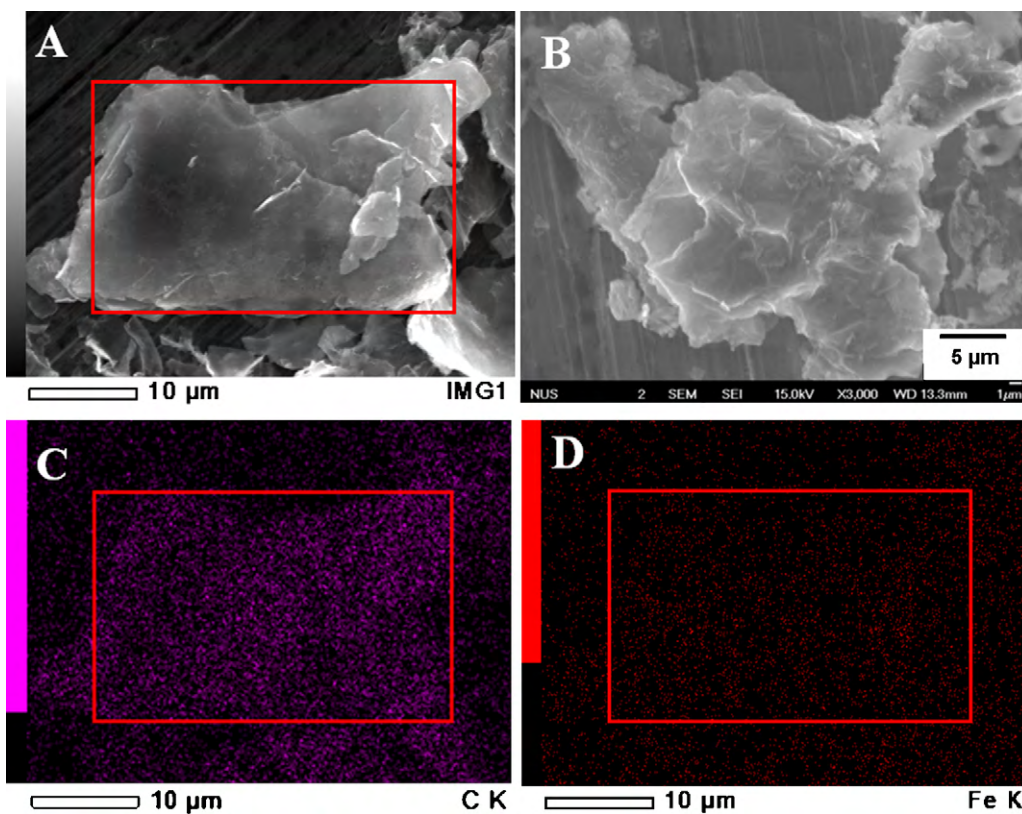


Fig. 3. SEM micrographs of GO and GO-Fe-5, and energy dispersive X-ray spectroscopy (EDS) of GO-Fe-5. (A) SEM image of GO-Fe-5, (B) SEM image of GO, (C) carbon mapping of GO-Fe-5, and (D) iron mapping of GO-Fe-5.

rials are intercalated between the GO sheets and a homogeneous, amorphous composite is formed. At a lower Fe/GO ratio, we still can observe this weak peak, implying that the GO in the composite still has a layer-like structure with the ferric oxide mainly adsorbed on the surface of the GO sheets. It is well known that amorphous ferric hydroxides can gradually transfer to crystalline iron(III) oxide form, but this did not happen for the present absorbents [48]. This is quite interesting while the preparation procedure involved drying at 85 °C overnight. It could be attributed to that most of the impregnated iron was in a coordination form with copious oxygen groups on the GO rather than in the free polymeric iron hydroxide form.

The morphology and structure of the GO and all of the composites were further studied by SEM and TEM. As representative

example, the SEM and TEM micrographs of the GO and GO-Fe-5 are shown in Figs. 3 and 4, respectively. Both the pristine GO and ferric hydroxide impregnated GO-Fe-5 prepared here exhibit a typically wrinkled, sheet-like structure with the size of tens micrometers. In addition, the morphological structure of the GO-Fe-5 shows no difference from the pristine GO. However, from the EDS of GO-Fe-5, one can clearly see that iron is homogeneously distributed onto GO sheets. In agreement with XRD patterns and SEM morphology, no big ferric hydroxide nanoparticles can be seen from the whole range of the TEM image of GO-Fe-5, which illustrates that ferric hydroxide is distributed onto GO layers in a typical amorphous form. As shown in Figs. S2–S5, the SEM and TEM images of GO-Fe-1, GO-Fe-2, GO-Fe-3 and GO-Fe-4 exhibited similar features as those of GO-Fe-5. After arsenate absorption, the morphology and compo-

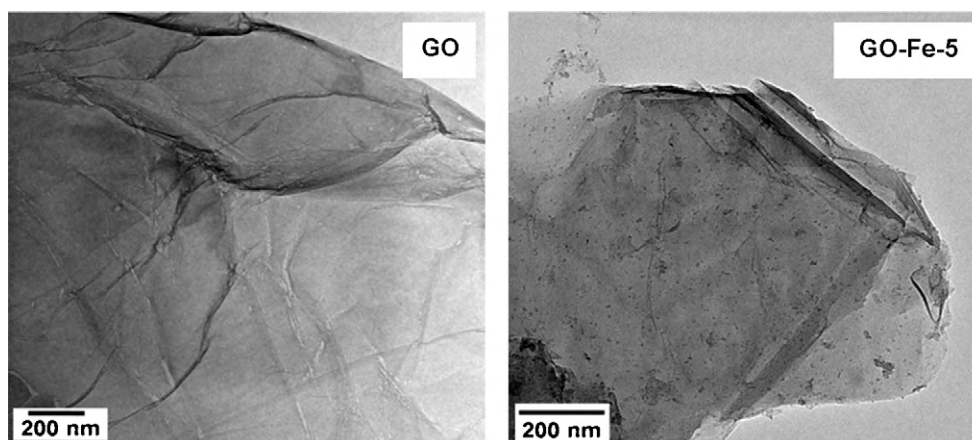


Fig. 4. TEM micrographs of GO and GO-Fe-5.

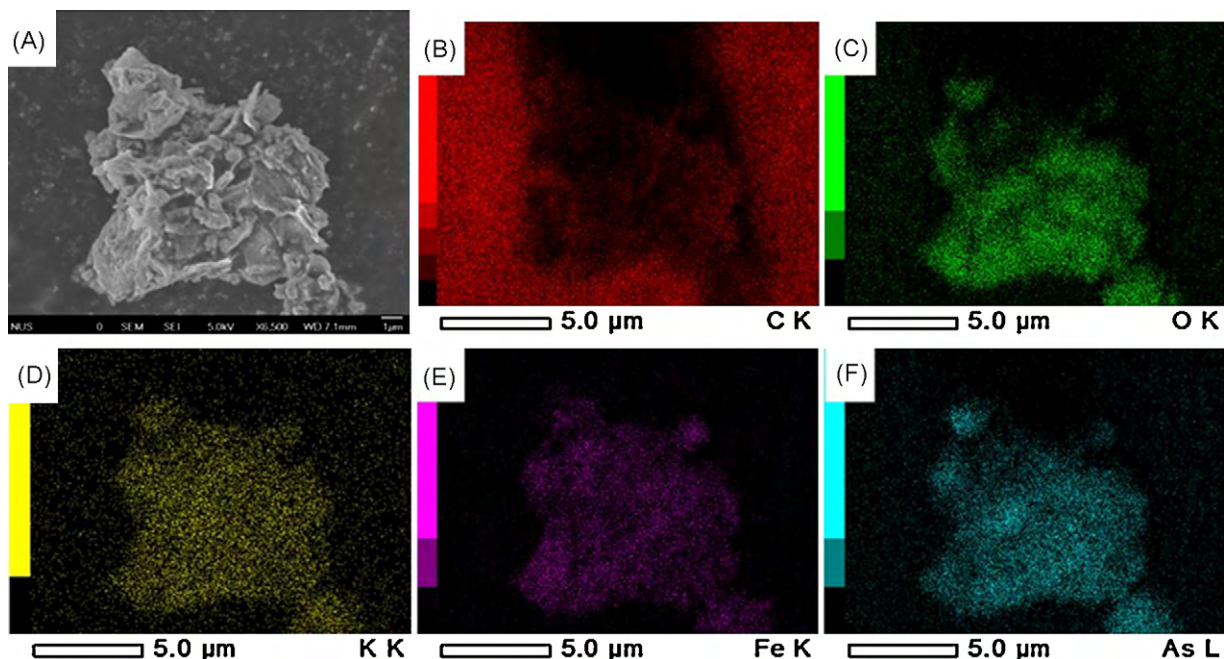


Fig. 5. SEM micrographs and energy dispersive X-ray spectroscopy (EDS) of GO-Fe-5 after arsenic removal: (A) SEM image, (B) carbon mapping, (C) oxygen mapping, (D) potassium mapping, (E) iron mapping, and (F) arsenic mapping.

sition of GO-Fe-5 were also investigated by SEM (Fig. 5) and TEM (Fig. S6). The SEM and TEM images are identical to those of the pristine GO-Fe-5. The element mapping images of SEM clearly illustrate that the arsenate was absorbed by GO-Fe-5, and distributed homogeneously on the surface of GO-Fe-5 in consistent with iron.

3.3. Selection of iron impregnation

As illustrated in Table 1, the weight ratio of iron to GO was increased stepwise in order to find the most efficient absorbent. Because of the high adsorption capacity of the absorbents, relatively high concentration of arsenate at 19.32 ppm, 39.73 ppm and 51.14 ppm had to be used to compare the relative efficiency of the different materials. Arsenate contaminated drinking water was prepared by dissolving KH_2AsO_4 into DI water. The composite/solution ratio for each test was 95 mg solid/30.0 mL solution. All the tests were undertaken at room temperature (25 °C) with absorption time of 24 h. As shown in Table 1, the percentage removal of arsenate increased with the amount of iron complex impregnated while fixing the starting arsenate concentration at 19.32 ppm. 100% removal of arsenate from the contaminated solutions was achieved by using GO-Fe-4 and GO-Fe-5 as absorbent. Even GO-Fe-1 was able to absorb 80.4% of arsenate from the solution. However, when using the pristine GO as absorbent, no effect for arsenate removal was observed. This means that the incorporated ferric hydroxide compounds contribute to the arsenate absorption solely. For GO-Fe-4 and GO-Fe-5, the adsorption of arsenate on these composites reached up to 6.10 mg/g, which is comparable to the best performance of iron-impregnated granular activated carbon (As-GAC) [49]. Meanwhile, the ferric ion concentrations in the resultant clean water were also concerned. The concentrations of ferric ion in the filtrates of GO-Fe-4 and GO-Fe-5 due to possible leakage of absorbents were kept at a rather low level (<1.00 ppm), indicating that such composites with ferric hydroxide cross-linked on GO sheets were very stable during the arsenate absorption process. Moreover, counting on the outstanding mechanical nature of graphene sheets, incorporating GO sheets into ferric hydroxide may also dramatically enhance the

mechanical strength of these composites. While the arsenate concentrations were further increased to 39.73 ppm and 51.14 ppm, GO-Fe-5 showed an arsenate sorption capacity of 18.55 mg/g and 23.78 mg/g, respectively. Such a high arsenate sorption capacity was comparable to HFO loaded GAC reported by Jang et al. [40]. However, in this case, the iron concentrations in the filtrate were increased to 15.82 ppm and 14.93 ppm, respectively, which was unwanted secondary pollution for water purification. Finally, GO-Fe-5 was chosen for further research, e.g. arsenate concentration and pH dependent absorption behavior.

3.4. Effect of pH on arsenate removal

The effect of pH on arsenate removal was examined using GO-Fe-5 at four different initial arsenate concentrations, i.e. 20.00, 8.93, 1.07 ppm (Fig. 6), as well as 0.50 ppm (Supporting Information Table S1). The percentage removal of arsenate measured at different concentrations indicated that pH had negligible effect on arsenate removal with pH 4–7. The arsenate removal efficiency using

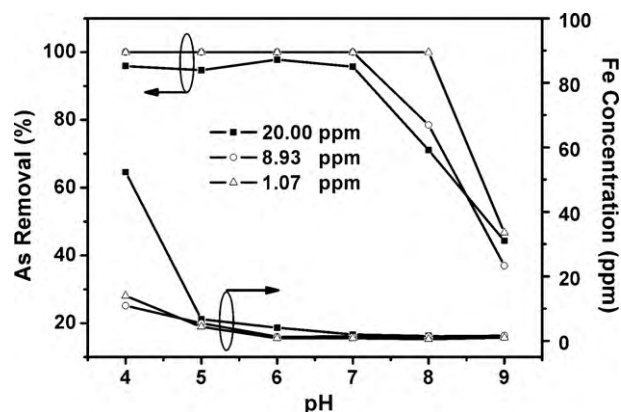


Fig. 6. Effects of pH on arsenate removal at different initial arsenate concentration (square: 20.00 ppm, circle: 8.93 ppm, triangle: 1.07 ppm) and the ferric concentration in the filtrate.

GO–Fe-5 as absorbent was always higher than 95% with arsenate concentration at 20.00 or 8.93 ppm. However, when pH of these two solutions were further increased, the percentage of arsenate removed by GO–Fe-5 decreased to 70% at pH 8, and further lowered to about 40% at pH 9. When the arsenate concentration was diluted to 1.07 ppm, the arsenate could still be completely removed by GO–Fe-5 with pH from 4 to 8. However, when the pH of this solution reached 9, the arsenate removal efficiency decreased to 46.7%. It has been well documented that increasing pH would decrease arsenate adsorption on iron-containing adsorbents [50]. The adsorption of an anion depends on acid/base properties of the adsorbents surfaces, and the specific interactions between the adsorbate and the surface functional groups on the adsorbents. It was noteworthy that even the arsenate concentration was controlled as low as 0.50 ppm, the arsenate in GO–Fe-5 treated contaminated drinking water was non-detectable (<0.01 ppm) by ICP. Considering that the maximum contaminant level of arsenic in drinking water adopted by many countries was 50 µg/L, the adsorbents prepared here could be used for efficient arsenate removal from drinking water.

4. Conclusions

In conclusion, a series of composites based on GO cross-linked with ferric hydroxide was developed for effective arsenate removal from contaminated drinking water. GO was used as a supporting matrix due to several intriguing properties, such as high mechanical strength, high theoretical surface area and facile preparation from cheap graphite. Ferric hydroxide was cross-linked on GO sheets to enhance the efficiency and capacity of arsenate removal. The morphology studies indicated that ferric hydroxide was homogeneously impregnated among the GO sheets. Efficient arsenate absorption using GO–Fe-5 as absorbent was observed over a wide range of pH from 4 to 9 and arsenate concentration from 20.00 ppm to 0.50 ppm, but the efficiency decreased when pH was higher than 8. The iron concentration in the treated water was detected to be at a rather low level (<1.00 ppm). Thus, GO stands for a new type of material as an excellent carrier matrix of ferric hydroxide for arsenate removal. Further studies including chemical condition dependence and ionic strength dependence as well as column evaluation are in progress.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2010.06.010.

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