Fabrication of a GNP/Fe–Mg Binary Oxide Composite for Effective Removal of Arsenic from Aqueous Solution

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ABSTRACT: Graphene nanoplates (GNPs) can be used as a platform for homogeneous distribution of adsorbent nanoparticles to improve electron exchange and ion transport for heavy-metal adsorption. In this study, we report a facile thermal decomposition route to fabricate a graphene-supported Fe–Mg oxide composite. The prepared composite was characterized using scanning electron microscopy, transmission electron microscopy, energy-dispersive spectrometry, X-ray diffraction, and X-ray photoelectron spectroscopy. Batch experiments were carried out to evaluate the arsenic adsorption behavior of the GNP/Fe–Mg oxide composite. Both the Langmuir and Freundlich models were employed to describe the adsorption isotherm, in which the sorption kinetics of the arsenic adsorption process by the composite was found to be pseudo-second-order. Furthermore, the reusability and regeneration of the adsorbent were investigated by an assembled-column filter test. The GNP/Fe–Mg oxide composite exhibited significant fast adsorption of arsenic over a wide range of solution pHs, with exceptional durability and recyclability, which could make this composite a very promising candidate for effective removal of arsenic from aqueous solutions.

INTRODUCTION

Contamination of water with toxic metals, such as arsenic (As), lead (Pb), and mercury (Hg), has significantly increased over the last few decades due to anthropogenic sources (industrialization and urbanization). Because of their toxicity and carcinogenicity to human beings, exposure to these elements poses a serious health risk. Among them, arsenic is one of the most toxic elements and is widely present in nature through leaching from soils, mining, fertilizers, industrial waste, biological activity, and As-containing minerals. As a consequence, the World Health Organization (WHO) has established a maximum recommended concentration of arsenic in water of 10 ppb. Long-term ingestion of food grown in arsenic-contaminated areas or directly drinking arsenic-contaminated water is linked to kidney, skin, and lung cancers. Therefore, it is urgent to remove arsenic from contaminated water to provide safe drinking water with arsenic levels below the limit recommended by the WHO. There are several approaches that have been used to remove arsenic from water, including adsorption, ion exchange, reverse osmosis, electrochemical treatment, membrane filtration, and co-precipitation. However, because of its simplicity, low cost, and high efficiency, adsorption is widely employed and studied as a promising technology for cost-effective arsenic removal.

Many materials have been employed as adsorbents for arsenic adsorption, such as agricultural and industrial wastes, surfactants, carbon-based materials, polymers, and metal oxides. Among these, metals and metal oxides, such as TiO2, Fe2O3, Fe3O4, CeO2, CuO, CaO, and ZrO2 have been extensively studied for arsenic treatment in aqueous solutions because of their high affinity to the arsenic species, low cost, and tunability of adsorption capacity. Recently, considerable attention has been focused on the development of adsorbent composites containing two or more metals and metal oxides to maximize arsenic adsorption. For example, Shan and Tong fabricated Fe–Mn binary oxides with a high adsorption capacity for arsenic. Also, super-paramagnetic Mg0.27Fe2.5O4, a novel arsenic adsorbent, was synthesized by Tang et al. In another report, Yu et al. presented Fe–Ti binary oxide magnetic nanoparticles, which combined the photocatalytic oxidation property of TiO2 with the high adsorption capacity and magnetic properties of γ-Fe2O3 for arsenic treatment. Xu et al. reported the synthesis and application of a CeO2–ZrO2 composite for the removal of arsenic from aqueous solutions. Basu and Ghosh found that Fe(III)–Al(III) mixed oxides and Fe(III)–Ce(IV) oxides have a high adsorption capacity toward arsenic.

Graphene, a two-dimensional material, has been attracting significant interest over the past decade due to its exceptional chemical and physical properties, which can be applied to many different areas, including but not limited to, electronic devices, energy storage and conversion, sensors, adsorption, and composites. Most recently, graphene has gained tremen-
dous interest as a supporting material for enhancement of the adsorption properties of adsorbents due to its large surface area, high conductivity, ionic mobility, and superior mechanical flexibility. For example, Gollavelli et al. reported a smart magnetic graphene that removed heavy metals from drinking water.\textsuperscript{38} A hybrid of monolithic Fe\textsubscript{3}O\textsubscript{4}/graphene was also fabricated and showed favorable properties for arsenic removal.\textsuperscript{39} Reduced graphene oxide-supported mesoporous Fe\textsubscript{2}O\textsubscript{3}/TiO\textsubscript{2} nanoparticles synthesized by a sol−gel route showed high adsorption toward arsenic.\textsuperscript{40} Kumar et al. synthesized single-layer graphene oxide with manganese ferrite magnetic nanoparticles for efficient removal of arsenic from contaminated water.\textsuperscript{41}

Herein, we report a simple one-pot hydrothermal method to prepare a GNP-supported Fe–Mg binary oxide (GNP/Fe–Mg oxide) composite. The obtained material was well characterized by transmission electron microscopy (TEM), scanning electron microscopy (SEM), energy-dispersive spectrometry (EDS), thermogravimetric analysis (TGA), X-ray photoelectron spectroscopy (XPS), and X-ray diffraction (XRD). Arsenic adsorption was employed to evaluate the adsorption capacity of the adsorbent. The effects of the parameters, including the Fe/Cu ratio, graphene loading, initial arsenic concentration, adsorption time, and solution pH, on arsenic adsorption were investigated through batch experiments, and a column test was also used to study the recyclability of the sorbent.

**RESULTS AND DISCUSSION**

The morphologies of the prepared graphene nanoplates (GNPs) and free-standing Fe–Mg oxide were studied by SEM, and the images are shown in Figure 1. It can be clearly seen in Figure 1A that the obtained GNPs have a crumpled, wrinkled morphology, with a diameter of tens of microns and thickness <20 nm.\textsuperscript{42} The SEM image of the as-prepared Fe–Mg binary oxide is shown in Figure 1B, which indicates that the Fe–Mg oxide consists of ultrafine nanocrystallites. The morphology of the Fe–Mg oxide is consistent with that in a previous study.\textsuperscript{27} We believe that the metal ions first physically adsorbed onto the GNPs and then

![Figure 1. SEM images of (A) GNPs and (B) free-standing Fe–Mg oxide.](image1)

![Figure 2. (A, B) SEM images and (C, D) TEM images of the GNP/Fe–Mg binary oxide composite.](image2)
reacted under hydrothermal conditions to form metal oxides on the GNPs.

SEM and TEM images of the GNP/Fe−Mg oxide composite are shown in Figure 2. In the low-magnification SEM and TEM images (Figure 2A–C), it is clear that Fe−Mg oxides are well formed and dispersed on the surface of GNPs. When the composite is viewed at higher SEM and TEM magnifications, as shown in Figure 2D and insets of Figure 2B,D, it can be seen that
Fe–Mg oxides on graphene are not well-defined nanocrystallites, with some agglomeration observed, which might be ascribed to the amorphous nature of Fe–Mg binary oxides on the GNPs. The amorphous nature of the Fe–Mg oxide formed on the GNPs is further confirmed by the XRD pattern of the composite (Figure S1). In the XRD pattern, apart from the peaks with an asterisk, which are attributed to the crystallites of GNPs, the presence of very weak and broad peaks in region of 30–80° indicates the amorphous nature of the Fe–Mg oxide.

EDS mapping was undertaken to study the elemental distribution in the GNP-supported Fe–Mg oxide composite, as exhibited in Figure 3. It can be clearly seen from the figure that the Mg–Fe oxide uniformly covers the entire GNP surface. To explore the chemical states of C, Fe, Mg, and O in the composite, the core-level XPS spectra of C 1s, Fe 2p, Mg 1s, and O 1s and their corresponding deconvolutions showing the contributions of the individual components are shown in Figure 4. The C 1s spectrum (Figure 4A) has two major peaks at 284.1 and 284.8 eV, which correspond to carbon in C=C (sp2) and C–C (sp3) bonds, respectively, of graphenic carbons. Deconvoluted core-level Fe 2p shows two dominant peaks at 711.4 and 724.5 eV, with satellites corresponding to Fe 2p3/2 and Fe 2p1/2 of the Fe3+ state, respectively. Figure 4C shows the binding energy and its deconvolution spectrum for core-level Mg 1s. There is only one peak observed at 1303.5 eV, which could be attributed to MgO. In the O 1s spectrum (Figure 4D), the peaks at 530.1 and 531.4 eV are due to the presence of O2− in FeO3 and MgO, respectively.39,47 Interestingly, the appearance and binding energy of the Fe oxide uniformly covers the entire GNP surface. The amorphous nature of the Fe oxide is further confirmed by the XRD pattern of the composite (Figure S1). In the XRD pattern, apart from the peaks with an asterisk, which are attributed to the crystallites of GNPs, the presence of very weak and broad peaks in region of 30–80° indicates the amorphous nature of the Fe–Mg oxide.

The thermal properties of the prepared GNP-supported Fe–Mg oxide composite were investigated by TGA, as presented in Figure 5. The TGA curve shows a two-step decomposition process. The first weight loss in the range of 30–150 °C is 0.52%, which can be attributed to the removal of adsorbed and trapped water in the composite. The weight loss of 0.93% in the second step (300–550 °C) is due to the decomposition of Fe(OH)3 to α-Fe2O3.

Figure 6A shows the effect of various Mg/Fe weight ratios on arsenic adsorption, with an initial As(V) concentration of 10 mg/L, an adsorbent dose of 200 mg/L, a pH of 7, and at room temperature. The results indicate that As(V) sorption by GNP-supported Fe–Mg oxide significantly increases with a decrease in the Mg/Fe weight ratio, and it reaches a maximum equilibrium adsorption capacity of 40.3 mg/g when the Mg/Fe ratio is 5:5. Then, As(V) adsorption slowly declines with a further decrease in the Mg/Fe weight ratio. It is also of note that As(V) sorption by GNP–Fe2O3 (31 mg/L) is somewhat higher than that by GNP–MgO (2 mg/L). The effect of the GNP load on the As(V) sorption capacity by the composite was also investigated, with an initial As(V) concentration of 9.5 mg/L, as shown in Figure 6B. It is obvious that when the GNP loading increases the As(V) sorption increases, and it reaches a maximum of approximately 37.5 mg/g at the GNP/Mg–Fe oxide weight ratio of 2:1. When the GNP load is further increased, the sorption capacity significantly decreases, and without Fe–Mg oxide, the As(V) sorption capacity by pure GNPs is only 2.38 mg/g. These results suggest that the combination of GNPs and Fe–Mg oxide significantly improves As(V) adsorption.

The adsorption isotherm was obtained to assess the arsenic adsorption and determine the maximum As(V) adsorption capacity of the GNP/Fe–Mg oxide composite. The amount of arsenic adsorbed onto the composite at equilibrium (qe) was calculated from the As(V) concentration difference, with the following equation

$$q_e = \frac{(C_0 - C_e) \times V}{m}$$  \hspace{1cm} (1)

where C0 (mg/L) is the initial concentration, Ce (mg/L) is the equilibrium concentration, V (L) is the solution volume, and m (g) is the mass of the GNP/Fe–Mg oxide adsorbent.

Figure 7 shows the arsenic adsorption capacity of the composite at equilibrium at various As(V) concentrations, in range of 5–90 mg/L; an adsorbent dose of 200 mg/g; pH 7; and at room temperature. The Langmuir and Freundlich adsorption isotherm models were employed to fit the data, as expressed in eqs 2 and 3, respectively

$$q_e = \frac{q_{\text{max}} \times K_L \times C_e}{1 + K_L \times C_e}$$  \hspace{1cm} (2)

$$q_e = \frac{K_F \times C_e^n}{1 + K_F \times C_e^n}$$  \hspace{1cm} (3)

where qe is the amount of arsenic adsorbed onto the solid phase at equilibrium (mg/g), qmax (mg/g) is the maximum arsenic adsorption capacity per unit weight of adsorbent, Ce is the equilibrium arsenic concentration (mg/L), KL is the equilibrium adsorption constant representing the affinity of binding sites (L/mg), KF is the Freundlich constant, and n is the heterogeneity factor.

The obtained adsorption constants are presented in Table 1. The higher correlation coefficient (0.985) value of the fitted Freundlich plot compared to that of the Langmuir plot (0.935) suggests that the Freundlich model is more suitable for representing the adsorption behavior of As(V) by the GNP/Fe–Mg oxide composite than the Langmuir model. The low calculated heterogeneity factor (n = 0.4) also suggests that the Freundlich model is the more favorable model to describe arsenic adsorption by GNP/Fe–Mg oxide. These results indicate that As(V) is heterogeneously adsorbed onto the composite surface, which could be attributed to the simultaneous existence of...
graphene, iron, and magnesium oxides in the solid phase. The maximum As(V)-adsorption capacity of GNP/Fe−Mg oxide determined from the Langmuir model is 103.9 mg/g, which indicates that the composite is very effective for arsenic removal.

Illustrated in Table 2 is a comparison of the As(V) adsorption capacity of the GNP/Fe−Mg oxide composite with that of other adsorbents. It is obvious from the comparison that the adsorption capacity of GNP/Fe−Mg oxide outperforms that of the majority of other adsorbents, which could make this material a promising sorbent for arsenic removal.

The adsorption kinetics of As(V) was obtained to further understand the adsorption behavior of As(V) on the GNP/Fe−Mg oxide surface. Figure 8 shows the adsorption data with an initial As(V) concentration of 5 mg/L at different time intervals. The adsorption process reaches equilibrium within 3 h. The pseudo-second-order model was applied to describe the kinetic data, as expressed in eq 4.

Table 1. Langmuir and Freundlich Isotherm Parameters for As(V) Adsorption on the GNP/Fe−Mg Binary Oxide Composite

| adsorbates                              | pH | \( q_{\text{max}} \) (mg/g) | \( K_L \) (L/mg) | \( R^2 \) | \( K_F \) (L/mg) | \( n \) | \( \tilde{R}^2 \) |
|-----------------------------------------|----|----------------------------|------------------|---------|-----------------|------|-------------|
| superparamagnetic \( \text{Mg}_{0.27}\text{Fe}_{2.5}\text{O}_4 \) | 7  | 83.2                       | 0.05             | 0.935   | 13.57           | 0.4  | 0.985       |
| \( \text{Fe}_3\text{O}_4 \)−GO (MGO) | 6.5| 59.6                       | 0.05             | 0.950   | 22.22           | 0.4  | 0.995       |
| \( \text{FeMnO}_x \)−RGO             | 4  | 1.019                      | 0.05             | 0.950   | 1.019           | 0.4  | 0.995       |
| \( \text{CeO}_2 \)−graphene composite | 4  | 1.019                      | 0.05             | 0.950   | 1.019           | 0.4  | 0.995       |
| \( \text{GO}−\text{ZrO(OH)}_2 \) nanocomposites | 5−11| 84.89                      | 0.05             | 0.935   | 13.57           | 0.4  | 0.985       |
| nZVI/graphene                          | 7  | 29                         | 0.05             | 0.950   | 13.57           | 0.4  | 0.985       |
| magnetic graphene                      | 4  | 3.26                       | 0.05             | 0.950   | 13.57           | 0.4  | 0.985       |
| \( \text{Fe}_3\text{O}_4 \)−graphene/LDH | 6  | 73.1                       | 0.05             | 0.950   | 22.22           | 0.4  | 0.995       |
| magnetic-GO                            | 4  | 38                         | 0.05             | 0.950   | 13.57           | 0.4  | 0.985       |
| magnetic-rGO                           | 4  | 12                         | 0.05             | 0.950   | 13.57           | 0.4  | 0.985       |
| \( \text{MnFe}_2\text{O}_4 \)        | 3  | 90                         | 0.05             | 0.950   | 13.57           | 0.4  | 0.985       |
| \( \text{CeFe}_2\text{O}_3 \)        | 3  | 74                         | 0.05             | 0.950   | 13.57           | 0.4  | 0.985       |
| \( \text{GO/}\text{MnFe}_2\text{O}_4 \)| 4  | 207                        | 0.05             | 0.950   | 13.57           | 0.4  | 0.985       |
| GNP/Fe−Mg oxide                        | 7  | 103.9                      | 0.05             | 0.935   | 13.57           | 0.4  | 0.985       |

Figure 6. Effect of (A) the Mg/Fe weight ratio and (B) GNP loading on As(V) adsorption by GNP/Fe−Mg oxide composites.

Figure 7. Adsorption isotherm for As(V) adsorption by the GNP/Fe−Mg binary oxide composite.

Figure 8. Adsorption kinetics of As(V) on the GNP/Fe−Mg binary oxide composite.
where \( q_e \) (mg/g) is the amount of arsenic adsorbed on the solid phase at time \( t \) (h), \( q_t \) (mg/g) is the amount of arsenic adsorbed on the solid phase at equilibrium, and \( K \) is the adsorption rate constant (g mg h). According to the adsorption kinetic values listed in Table 3, the experimental data are relatively well fitted, with a correlation coefficient of 0.957. This result implies that the adsorption process might be chemical adsorption accompanied by electron exchange between the composite and arsenic. Furthermore, the experimental adsorption capacity at equilibrium of the composite (22.4 mg/g) with an initial As(V) concentration of 5 mg/L is close to the calculated value from the pseudo-second-order model (25.5 mg/g).

The effect of solution pH on arsenic adsorption by the GNP/Fe−Mg oxide composite was determined with an initial As(V) concentration of 10 mg/L, as shown in Figure 9. It can be clearly seen that As(V) sorption is significantly dependent upon the pH. Under acidic conditions, arsenic adsorption slowly increases with an increase in solution pH, and it reaches a maximum capacity under neutral conditions (pH 7). The adsorption capacity significantly decreases under mild basic conditions (pH 8–9) before greatly declining when the solution pH further increases. This phenomenon may be attributed to the dependence of the adsorption of strong acid anions by metal oxides and hydroxides on solution pH. The dissolution of Fe and Mg in the GNP/Fe−Mg oxide composite at pH 7 was also recorded, as shown in Figure S2. It is obvious that the release of Fe and Mg is minimal compared with As(V) adsorption, which indicates that the GNP/Fe−Mg binary oxide composite is a stable and effective adsorbent for arsenic. As the source of GNPs in this study does not contain −COOH or −OH groups, the adsorption of arsenic on GNPs is mostly physical adsorption. However, when Mg−Fe oxide is loaded onto GNPs, there exists −OH groups on the surface of the metal oxide in aqueous solution (especially under the optimum pH condition). These −OH groups are responsible for the dramatic increase in arsenic adsorption due to electrostatic attraction.

As electrostatic attraction is a main force, which is responsible for the adsorption of As(V) on graphene−metal oxide composites, the change in the electrostatic force between As(V) and the GNP/Fe−Mg binary oxide composite may explain the effect of pH on As(V) adsorption. At a low pH, the adsorbent of GNP/Fe−Mg oxide has a net positive charge due to protonation of the −OH groups in the Fe−Mg binary oxide. As a result, they attract negatively charged As(V) anions, which leads to greater adsorption. When the pH increases, the positive charge decreases, resulting in a decrease in As(V) adsorption.

The selectivity of the GNP/Fe−Mg binary oxide adsorbent toward arsenic in the presence of common metal ions that exist in drinking water, such as Na⁺, K⁺, Ca²⁺, and Mg²⁺, was studied (Figure S3). It can be seen that whereas more than 95% of the arsenic was adsorbed there was an insignificant amount of Na⁺, K⁺, and Ca²⁺ ions adsorbed onto the GNP/Fe−Mg oxide composite. Interestingly, the concentration of Mg²⁺ in the tested solution increased by 10% after adsorption due to the release of Mg from the adsorbent.

To evaluate the recyclability, a filter column with a diameter of 2 cm and height of 10 cm was assembled, as shown in Figure 10. The mass of the GNP/Fe−Mg oxide composite used was 200 mg. The adsorption process was carried out with 10 mL of flow solution (pH 7) of 3 mg/L As(V). After adsorption, the filter column was washed with 20 mL of 2 M NaOH solution to regenerate the adsorbent before the next test cycle. The adsorption−regeneration process was repeated for five cycles. An insignificant decrease in the removal efficiency (less than 2%) after five cycles suggests that the GNP/Fe−Mg oxide composite has a high durability for arsenic removal.

## EXPERIMENTAL SECTION

### Materials.
Natural graphite flakes were supplied from Pressol Gmbh, with particle size >100 mesh. Chemicals, such as dry acetone, ethanol, concentrated sulfuric acid (98%), sodium hydroxide (NaOH), potassium hydroxide (KOH), ethanol, sodium persulfate (Na₂S₂O₈), MgCl₂·6H₂O, and anhydrous FeCl₃, were purchased from Ajax Finechem. All chemicals were used as received.

### Synthesis of GNPs.
Preparation of GNPs was undertaken according to previous methods. Typically, 1 g of natural graphite flakes was dispersed in 80 mL of sulfuric acid (98%), with swirling for 10 min, in a 250 mL reactor. Thereafter, 10 g of sodium persulfate (Na₂S₂O₈) was gradually added and the reaction mixture was gently stirred for 3 h at room temperature. The mixture was then filtered with a sintered glass filter (Durian sintered with a disc filter funnel of capacity 50 mL; maximum pore size, 4–5 μm) without quenching. The filtrate solution was separated and used for graphene exfoliation. The GNPs thus obtained were rinsed with dry acetone (3 × 10 mL) followed by 5 mL of water to remove any residual acid on the GNPs and dried at 60 °C in open air.

### Synthesis of the GNP/Fe−Mg Binary Oxide Composite.
GNP/Fe−Mg binary oxide composites were fabricated by a simple one-pot hydrothermal strategy. First, MgCl₂·6H₂O and FeCl₃ with various Mg/Fe weight ratios, 10:0, 9:1, 7:3, 5:5, 3:7, 1:9, and 0:10, were dissolved in 50 mL of ethanol. Then, GNPs
with different loadings were dispersed in the solution mixture by sonication for 10 min and stirring for 1 h. Subsequently, a 2 M NaOH solution was added dropwise into the solution under vigorous stirring until a pH of ~8 or 9 was reached. After 1 h of further stirring, the reaction solution was transferred and sealed in a Teflon-lined autoclave and placed in an oven preheated to 150 °C for 2 h. Then, the solution was cooled to room temperature and the precipitate was filtered and washed three times each with ethanol and distilled water. The sample was dried overnight at a temperature of 60 °C in air to obtain the GNP/Fe−Mg oxide composites.

Characterization. The structures and mapping elemental compositions of the samples were studied by EDS-equipped scanning electron microscopy (SEM), using an FEI Nova NanoSEM (Hillsboro) operating under high-vacuum conditions, with an accelerating voltage of 30 keV and an Everhart-Thornley detector. TEM images were obtained on a JEOL 1010 TEM instrument, operated at an accelerating voltage of 100 kV. Thermal analysis was performed on a TGA instrument from Perkin-Elmer, with a furnace, a microbalance, an operating temperature from 35 to 800 °C, and a heating rate of 20 °C/min. A BrukerAXS D8 Discover instrument with a general area detector diffraction system using a Cu Kα source was utilized to obtain XRD patterns. XPS spectra were obtained on a K-Alpha XPS instrument using monochromated aluminum as the X-ray source. C 1s, Fe 2p, Mg 1s, and O 1s core-level spectra were recorded with an overall resolution of 0.1 eV. The core-level spectra were background-corrected using the Shirley algorithm, and chemically distinct species were resolved using a nonlinear least-squares fitting procedure.

Adsorption Studies. A stock solution of 1000 ppm As(V) was prepared by dissolving As2O5 in water. The arsenic concentration was determined using an Agilent 4200 microwave plasma-atomic emission spectrometer (MP-AES). All samples were analyzed within 24 h after filtration.

Effects of the Mg/Fe Weight Ratio and GNP Loading on Arsenic Sorption. Adsorption experiments were carried out in closed glass vessels. Typically, 10 mg of each adsorbent, prepared from different Mg/Fe weight ratios and various GNP loadings, was added into glass vessels containing 50 mL of 10 mg/L arsenic solution at pH 7. The solution was kept shaking at 200 rpm at room temperature for 24 h. Then, all samples were filtered to remove the adsorbent and the concentration of arsenic in the residual solutions was analyzed.

Adsorption Isotherm. In glass vessels, 10 mg of the optimally fabricated adsorbent was added to 50 mL of arsenic solution, with initial concentrations ranging from 5 to 90 mg/L. Adsorption was carried out at a solution pH of 7 at room temperature, stirring at a speed of 200 rpm for 24 h. The mixtures were then filtered and analyzed for residual arsenic by MP-AES.

Adsorption Kinetics. In a typical experiment, 40 mg of the GNP/Fe−Mg binary oxide was mixed with 200 mL of 5 mg/L arsenic in a glass vessel. The mixed solution was shaken at 200 rpm on an orbital shaker, at room temperature and pH 7. At certain time intervals, 10 mL of the mixture was taken, filtered, and analyzed for arsenic.

Effect of Solution pH. The GNP/Fe−Mg oxide composite (10 mg) was added to 50 mL of 10 mg/L arsenic at various solution pH values, ranging from 4 to 11 (the pH values were adjusted with dilute HCl and NaOH solutions). The suspensions were shaken at a speed of 200 rpm at room temperature for 24 h. Then, all samples were filtered and the residual arsenic concentrations were determined.

Recyclability Test. The reusability of the prepared adsorbent was studied by a column test. The GNP/Fe−Mg oxide composite was assembled as a part of a filter column. Other parts included a glass tube with both ends wrapped with a few layers of filter paper and cotton. After each arsenic adsorption cycle, the filter column was regenerated by washing it several times with 2 M NaOH before implementing the next experiment.

■ ASSOCIATED CONTENT

* Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.6b00304.

XRD patterns of the prepared GNP/Fe−Mg binary oxide (Figures S1−S3) (PDF)
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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Hu, H. Human Health and Heavy Metals. In Life Support: the Environment and Human Health; MIT Press, 2002; pp 65–77.

(2) Kitchin, K. T.; Conolly, R.Arsenic-Induced Carcinogenesis Oxidative Stress as a Possible Mode of Action and Future Research Needs for More Biologically Based Risk Assessment. Chem. Res. Toxicol. 2010, 23, 327–335.

(3) Erdogan, H.; Yalcinkaya, O.; Türeker, A. R. Determination of inorganic arsenic species by hydride generation atomic adsorption spectrometry in water samples after preconcentration/separation on nano ZrO2/B 2 O 3 by solid phase extraction. Desalination 2011, 280, 391–396.

(4) Tuzen, M.; Çitak, D.; Mendil, D.; Soylık, M. Arsenic speciation in natural water samples by coprecipitation-hydride generation atomic absorption spectrometry combination. Talanta 2009, 78, 52–56.

(5) Bissen, M.; Frimmel, F. H. Arsenic—a review. Part I: occurrence, toxicity, speciation, mobility. Acta Hydrochim. Hydrobiol. 2003, 31, 9–118.

(6) Mohan, D.; Pittman, C. U. Arsenic removal from water/wastewater using adsorbents—a critical review. J. Hazard. Mater. 2007, 142, 1–53.

(7) JadHAV, S. V.; Bringas, E.; Yadav, G. D.; Rathod, V. K.; Ortiz, I.; Marathe, K. V. Arsenic and fluoride contaminated groundwaters: a review of current technologies for contaminants removal. J. Environ. Manage. 2015, 138, 306–325.

(8) Singh, R.; Singh, S.; Parihar, P.; Singh, V. P.; Prasad, S. M. Arsenic contamination, consequences and remediation techniques: a review. Ecotox. Environ. Saf. 2015, 112, 247–270.

(9) Kurniawan, T. A.; Sillanpää, M. E.; Sillanpää, M. Nanoadsorbents for remediation of aquatic environment: local and practical solutions for global water pollution problems. Crit. Rev. Environ. Sci. Technol. 2012, 42, 1233–1295.

(10) Ray, P. Z.; Shipley, H. J. Inorganic nano-adsorbents for the removal of heavy metals and arsenic: a review. RSC Adv. 2015, 5, 29885–29907.

(11) Jézéquel, H.; Chu, K. H. Enhanced adsorption of arsenate on titanium dioxide using Ca and Mg ions. Environ. Chem. Lett. 2005, 3, 132–135.

(12) Nabi, D.; Aslam, J.; Qazi, I. A. Evaluation of the adsorption potential of titanium dioxide nanoparticles for arsenic removal. J. Environ. Sci. 2009, 21, 402–408.

(13) Xu, Z.; Li, Q.; Gao, S.; Shang, J. K. As (III) removal by hydrous titanium dioxide prepared from one-step hydrolysis of aqueous TiCl 4 solution. Water Res. 2010, 44, 5713–5721.

(14) Blomvick, S.; Chakraborty, S.; Mondal, P.; Van Renterghem, W.; Van den Bergh, S.; Roman-Ross, G.; Chatterjee, D.; Iglesias, M. Montmorillonite-supported nanoscale zero-valent iron for removal of arsenic from aqueous solution: kinetics and mechanism. Chem. Eng. J. 2014, 243, 14–23.

(15) Dong, H.; Guan, X.; Lo, I. M. Fate of Au(3)-treated nano zero-valent iron: determination of arsenic desorption potential under varying environmental conditions by phosphate extraction. Water Res. 2012, 46, 4071–4080.

(16) Tang, W.; Li, Q.; Gao, S.; Shang, J. K. Arsenic (III, V) removal from aqueous solution by ultrathin α-Fe 2 O 3 nanoparticles synthesized from solvent thermal method. J. Hazard. Mater. 2011, 192, 131–138.

(17) Tang, W.; Li, Q.; Li, C.; Gao, S.; Shang, J. K. Ultrafine α-Fe2O3 nanoparticles grown in confinement of in situ self-formed “cage” and their superior arsenic sorption performance on arsenic (III). J. Nanopart. Res. 2011, 13, 2641–2651.

(18) Akin, I.; Arslan, G.; Tor, A.; Ersoz, M.; Cengeloglu, Y. Arsenic (V) removal from underground water by magnetic nanoparticles synthesized from waste red mud. J. Hazard. Mater. 2012, 235–236, 62–68.

(19) Feng, Q.; Zhang, Z.; Ma, Y.; He, X.; Zhao, Y.; Chai, Z. Adsorption and desorption characteristics of arsenic onto terra cotta nanoparticles. Nanoscale Res. Lett. 2012, 7, No. 84, DOI: 10.1186/1556-276X-7-84.

(20) Reddy, K. J.; McDonald, K. J.; King, H. A novel arsenic removal process for water using cupric oxide nanoparticles. J. Colloid Interface Sci. 2013, 397, 96–102.

(21) Goswami, A.; Raul, P.; Purkait, M. Arsenic adsorption using copper (II) oxide nanoparticles. Chem. Eng. Res. Des. 2012, 90, 1387–1396.

(22) Olyaie, E.; Banejad, H.; Afkhami, A.; Rahmani, A.; Khodaveisi, J. Development of a cost-effective technique to remove the arsenic contamination from aqueous solutions by calcium peroxide nanoparticles. Sep. Purif. Technol. 2012, 95, 10–15.

(23) Cui, H.; Su, Y.; Li, Q.; Gao, S.; Shang, J. K. Exceptional arsenic (III, V) removal performance of highly porous, nanostructured ZrO 2 spheres for fixed bed reactors and the full-scale system modeling. Water Res. 2013, 47, 6258–6268.

(24) Cui, H.; Li, Q.; Gao, S.; Shang, J. K. Strong adsorption of arsenic species by amorphous zirconium oxide nanoparticles. J. Ind. Environ. Chem. 2012, 18, 1418–1427.

(25) Habuda-Stanić, M.; Nujić, M. Arsenic removal by nanoparticles: a review. Environ. Sci. Pollut. Res. 2015, 22, 8094–8123.

(26) Shan, C.; Tong, M. Efficient removal of trace arsenite through oxidation and adsorption by magnetic nanoparticles modified with Fe–Mn binary oxide. Water Res. 2013, 47, 3411–3421.

(27) Tang, W.; Su, Y.; Li, Q.; Gao, S.; Shang, J. K. Superparamagnetic manganese ferrite nanoadsorbent for effective arsenic (III, V) removal and easy magnetic separation. Water Res. 2013, 47, 3624–3634.

(28) Yu, L.; Peng, X.; Ni, F.; Li, J.; Wang, D.; Luan, Z. Arsenite removal from aqueous solutions by γ-Fe 2 O 3−3 TiO 2 magnetic nanoparticles through simultaneous photocatalytic oxidation and adsorption. J. Hazard. Mater. 2013, 246–247, 10–17.

(29) Xu, W.; Wang, J.; Wang, L.; Sheng, G.; Liu, J.; Yu, H.; Huang, X.-J. Enhanced arsenic removal from water by hierarchically porous CeO 2–ZrO 2 nanospheres: role of surface- and structure-dependent properties. J. Hazard. Mater. 2013, 260, 498–507.

(30) Basu, T.; Ghosh, U. C. Arsenic (III) removal performances in the absence/presence of groundwater occurring ions of agglomerated Fe(III)–Al (III) mixed oxide nanoparticles. J. Ind. Eng. Chem. 2011, 17, 834–844.

(31) Basu, T.; Ghosh, U. C. Nano-structured iron (III)–cerium (IV) mixed oxide: Synthesis, characterization and arsenic sorption kinetics in the presence of co-existing ions aiming to apply for high arsenic groundwater treatment. Appl. Surf. Sci. 2013, 283, 471–487.

(32) Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Zhang, Y.; Dubonos, S. V.; Grigorieva, I. V.; Firsov, A. A. Electric field effect in graphene. Science 2004, 306, 666–669.

(33) Bunch, J. S.; Van Der Zande, A. M.; Verbridge, S. S.; Frank, I. W.; Tanenbaum, D. M.; Parpia, J. M.; Craighead, H. G.; McEuen, P. L.
Electromechanical resonators from graphene sheets. *Science* 2007, 315, 490–493.

(34) Katsnelson, M. I. Graphene: carbon in two dimensions. *Mater. Today* 2007, 10, 20–27.

(35) Kopelevich, Y.; Esquinazi, P. Graphene physics in graphite. *Adv. Mater.* 2007, 19, 4559–4563.

(36) Morozov, S. V.; Novoselov, K. S.; Katsnelson, M. I.; Schedin, F.; Elias, D. C.; Jaszczak, J. A.; Geim, A. K. Giant intrinsic carrier mobilities in graphene and its bilayer. *Phys. Rev. Lett.* 2008, 100, No. 016602, DOI: 10.1103/PhysRevLett.100.016602.

(37) Becerril, H. A.; Mao, J.; Liu, Z.; Stoltenberg, R. M.; Bao, Z.; Chen, Y. Evaluation of solution-processed reduced graphene oxide films as transparent conductors. *ACS Nano* 2008, 2, 463–470.

(38) Gollavelli, G.; Chang, C.-C.; Ling, Y.-C. Facile synthesis of smart magnetic graphene for safe drinking water: heavy metal removal and disinfection control. *ACS Sustainable Chem. Eng.* 2013, 1, 462–472.

(39) Li, L.; Zhou, G.; Weng, Z.; Shan, X.-Y.; Li, F.; Cheng, H.-M. Monolithic Fe₂O₃/graphene hybrid for highly efficient lithium storage and arsenic removal. *Carbon* 2014, 67, 500–507.

(40) Babu, C. M.; Vinodh, R.; Sundaravel, B.; Abidov, A.; Peng, M. M.; Cha, W. S.; Jang, H.-T. Characterization of reduced graphene oxide supported mesoporous Fe₂O₃/TiO₂ 2 nanoparticles and adsorption of As(III) and As(V) from potable water. *J. Taiwan Inst. Chem. Eng.* 2016, 62, 199–208.

(41) Kumar, S.; Nair, R. R.; Pillai, P. B.; Gupta, S. N.; Iyengar, M.; Sood, A. Graphene oxide–MnFe₂O₄ magnetic nano-hybrids for efficient removal of lead and arsenic from water. *ACS Appl. Mater. Interfaces* 2014, 6, 17426–17436.

(42) La, D. D.; Bhargava, S.; Bhosale, S. V. Improved and A Simple Approach For Mass Production of Graphene Nanoplatelets Material. *ChemistrySelect* 2016, 1, 949–952.

(43) Zhu, J.; Sadu, R.; Wei, S.; Chen, D. H.; Haldolaarachchige, N.; Luo, Z.; Gomes, J.; Young, D. P.; Guo, Z. Magnetic graphene nanoplatelet composites toward arsenic removal. *ECS J. Solid State Sci. Technol.* 2012, 1, M1–M5.

(44) Mateo, D.; Esteve-Adell, I.; Albero, J.; Royo, J. F. S.; Primo, A.; Garcia, H. 111 oriented gold nanoplatelets on multilayer graphene as visible light photocatalyst for overall water splitting. *Nat. Commun.* 2016, 7, No. 11819, DOI: 10.1038/ncomms11819.

(45) Langevoort, J.; Sutherland, I.; Gellings, P. On the oxide formation on stainless steels AISI 304 and incoloy 800H investigated with XPS. *Appl. Surf. Sci.* 1987, 28, 167–179.

(46) Seyama, H.; Soma, M. X-ray photoelectron spectroscopic study of montmorillonite containing exchangeable divalent cations. *J. Chem. Soc., Faraday Trans. 1* 1984, 80, 237–248.

(47) Nelin, C. J.; Uhl, F.; Staemmler, V.; Bagus, P. S.; Fujimori, Y.; Sterrer, M.; Kuhlenbeck, H.; Freund, H.-J. Surface core-level binding energy shifts for MgO (100). *Phys. Chem. Chem. Phys.* 2014, 16, 21953–21956.

(48) Katsoyiannis, I. A.; Zouboulis, A. I. Removal of arsenic from contaminated water sources by sorption onto iron-oxide-coated polymeric materials. *Water Res.* 2002, 36, 5141–5155.

(49) Song, Y.; Qin, S.; Zhang, Y.; Gao, W.; Liu, J. Large-scale porous hematite nanorod arrays: direct growth on titanium foil and reversible lithium storage. *J. Phys. Chem. C.* 2010, 114, 21158–21164.

(50) Sheng, G.; Li, Y.; Yang, X.; Ren, X.; Yang, S.; Hu, J.; Wang, X. Efficient removal of arsenate by versatile magnetic graphene oxide composites. *RSC Adv.* 2012, 2, 12400–12407.

(51) Zhu, J.; Lou, Z.; Liu, Y.; Fu, R.; Baig, S. A.; Xu, X. Adsorption behavior and removal mechanism of arsenic on graphene modified by iron–manganese binary oxide (FeMnOₓ/RGO) from aqueous solutions. *RSC Adv.* 2015, 5, 67951–67961.

(52) Luo, X.; Wang, C.; Wang, L.; Deng, F.; Luo, S.; Tu, X.; Au, C. Nanocomposites of graphene oxide-hydrated zirconium oxide for simultaneous removal of As(III) and As(V) from water. *Chem. Eng. J.* 2013, 220, 98–106.

(53) Wang, C.; Luo, H.; Zhang, Z.; Wu, Y.; Zhang, J.; Chen, S. Removal of As(III) and As(V) from aqueous solutions using nanoscale zero