ADSORPTION OF ARSENATE ON Fe$_3$O$_4$/REDUCED GRAPHENE OXIDE NANO COMPOSITE

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Abstract: In the present paper, the synthesis of reduced graphene oxide modified by magnetic iron oxide (Fe$_3$O$_4$/rGO) and its application for arsenate (As(V)) removal were demonstrated. The obtained samples were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS) and magnetic measurement. The results showed that the obtained graphene oxide (GO) consisted of a small part of initial graphite as well as reduced graphene oxide (rGO). The iron oxide in magnetic iron oxide was dispersed successfully over rGO. Fe$_3$O$_4$/rGO exhibited super-paramagnetic properties at room temperature. The formal kinetics and adsorption isotherms of As(V) over obtained Fe$_3$O$_4$/GO have been investigated. Fe$_3$O$_4$/rGO exhibits excellent As(V) adsorption, and it is a potential adsorbent for water sources contaminated with arsenic.

Keywords: graphene oxide, reduced graphene oxide, adsorption, As(V), removal

1 Introduction

Arsenic is one of the most harmful and toxic elements found in nature. It is a slow poisoning element, severely affecting the human health and other living organisms. In natural water, inorganic arsenic is mostly found as trivalent arsenite or pentavalent arsenate. In surface water under oxidizing conditions, arsenate predominates, while in anoxic water under reducing conditions, arsenite becomes stable. Arsenic is introduced into aquatic environment from both natural and man-made sources. Typically, however, arsenic occurrence in groundwater is caused by the weathering and dissolution of arsenic-bearing rocks, minerals, and ores [16].

Thus far, a variety of remediation technologies, including nanofiltration, reverse osmosis, coagulation/coprecipitation, electrodialysis, ion exchange, adsorption, solvent extraction, foam flotation and bioremediation have been developed for As(V) removal [5].

As an efficient separation technique, adsorption has been in use for a long time to remove arsenic. Large scale wastewater treatment systems are presently using this practice as a cost-effective solution. Numerous materials from natural to specially designed ones have already been proposed for the adsorption of arsenic from water [13]. However, there are still several issues that limit the practical application of these adsorbents, for example, the adsorption capacity of these materials is relatively low, and it is difficult to separate the adsorbents from aqueous solutions. Therefore, the exploration of new promising adsorbents is still desirable.

Graphene and reduced graphene oxide (rGO) are kinds of novel and interesting carbon materials and have attracted tremendous attentions from both the experimental and theoretical scientific communities in recent years [4, 15]. In addition to being a principal component of the
most carbon-based nano-materials, rGO also exhibits extraordinary properties such as excellent mechanical characteristics, electrical, thermal conductivity, and a very high specific surface area, it might also be a good candidate of adsorbents.

In the past few years, magnetic separation technology has been widely used in the fields of separations and adsorptions [1]. The introduction of magnetic properties into graphene or rGO will combine their high adsorption capacity and the separation convenience of the magnetic materials. The preparations of graphene-based magnetic nanocomposites and their applications in arsenic removal have been reported recently [3, 6].

In this work, a magnetic reduced graphene oxide nanocomposite (Fe₃O₄/rGO) has been synthesized using the direct method, and its practical application in the removal of arsenate from aqueous solutions has been investigated.

2 Experimental

2.1 Chemicals

Graphite powder, potassium permanganate (KMnO₄), iron(III) chloride hexahydrate (FeCl₃.6H₂O), iron (II) sulfate heptahydrate (FeSO₄.7H₂O), sodium nitrate (NaNO₃), sodium monohydrogen arsenate (Na₂HAsO₄.2H₂O), ethanol (C₂H₅OH) were purchased from Merck. Sulfuric acid (H₂SO₄), hydrogen peroxide (H₂O₂ 30 %), ammonia solution (NH₄OH, 25 %), hydrochloric acid (HCl) were purchased from Sigma-Aldrich. All chemicals are of analytical grade.

2.2 Preparation

*Graphene oxide (GO) and reduced graphene oxide (rGO):* Graphene oxide (GO) was synthesized from graphite powder using the modified Hummer’s method [7]. In a typical synthesis, 1.0 g of graphite powder was added to 2.5 g of NaNO₃ and 100 mL of concentrated H₂SO₄ under constant stirring. Then, 3.0 g of KMnO₄ was gradually added to this mixture at 10 °C under stirring during 2 h. 100 mL of distilled water was added, and the resulting mixture was heated to 98 °C, and further stirred for 2 h. After that, 10 mL of H₂O₂ 30 % was added to the mixture with stirring for 2 h. The colour of the mixture changed to bright-yellow. Finally, the mixture was filtered and washed with a 5 % HCl aqueous solution to remove metal ions and with distilled water to remove the acid residues. The resulting brown-black solid was separated in an ultrasonic treatment in water and dried at 60 °C under vacuum for 12 h.

To prepare reduced graphene oxide (rGO), the as-prepared GO (1 g) was ultrasonically dispersed into 300 mL of deionized water in a flask for 1h under a nitrogen atmosphere. The temperature of the mixture was then elevated to 80 °C, and 10 g of ascorbic acid was added under gradual stirring for 20 minutes. A brown solid was obtained by filtering and washing with ethanol and dried at 80 °C under vacuum for 10h.
Magnetic oxide/reduced graphene oxide (Fe₃O₄/rGO): The Fe₃O₄/rGO nanocomposite was prepared according to [8]. rGO (500 mg) was dispersed in deionized water under ultrasonication for 2 h. The rGO was anchored to Fe₃O₄ nanoparticles using the direct method. An FeSO₄·7H₂O (0.002 mol) and FeCl₃·6H₂O (0.004 mol) solution was added to rGO and further sonicated for 1 h. An NH₄OH solution (1.65 M) was added in dropping under vigorous stirring. The obtained black solution was filtered, washed with water and then with ethanol several times to remove the acid residues and dissociative Fe(II). In order to get Fe₃O₄/rGO, the yielded solid was soaked in anhydrous ethanol for 60 min. Finally, the obtained solid was dried under vacuum at 60 °C for 10 h.

Characterization of materials: The X-ray diffraction (XRD) analysis was carried using a D8 Advanced Bruker anode X-ray Diffractometer with CuKα (λ = 1.5406 Å) radiation. The Fourier transform infrared spectrum (FTIR) was recorded with an IR-Prestige-21 spectrometer (Shimadzu, Japan) within the wave range of 400-4000 cm⁻¹. The X-ray photoelectron spectrometry (XPS) was conducted with an ESCA Lab 250. The nitrogen physisorption measurements were conducted using a Micromeritics ASAP2020 volumetric adsorption analyzer system. The samples were pre-treated by heating under vacuum at 130 °C for 10h. The specific surface area of samples was calculated using the Brunauer–Emmett–Teller (BET) method. The transmission electron microscope (TEM) images were obtained using a JEOL JEM-2100F. The magnetic properties were analyzed using a vibrating sample magnetometer (VSM, Micro Sence Easy VSM 20130321-02) at room temperature.

2.3 Sorption experiments

Effects of pH: In the pH experiments, 50 mL (50 mg/L) of As(V) was put in a series of flasks. The pH of solutions was carefully adjusted from 2.2 to 12.4 by adding a small amount of a dilute HCl or NaOH solution. Then, 0.1 g of Fe₃O₄/rGO was put into each flask, and the mixtures were shaken for 24 hours. The arsenate ion concentration of the solutions was measured before and after adsorption using an AAS instrument. The amount of adsorbed arsenate ions is expressed in the form of adsorption capacity and calculated as follows:

$$q_t = \frac{V(C_0 - C_t)}{m}$$  \hspace{1cm} (1)

where \(C_0\) is the initial concentration (mg/L) of As(V); \(C_t\) is the concentration (mg/L) of As(V) in solution after adsorption; \(V\) is the volume of solution (mL), and \(m\) is the weight (g) of Fe₃O₄/rGO.

Adsorption kinetics: The kinetics study was conducted by varying the initial concentration of As(V). 100 mL of As(V) solution with pH = 5.5 – 6 was taken into a 500 mL conical flask placed in a thermostatically controlled water bath at 25 ± 1 °C and kept on a mechanical stirrer. 0.1 g of Fe₃O₄/rGO was added to the flask. During the experiment, small samples of the solution were taken for analysis at predetermined intervals. After magnetic separation, the As(V) concentration (C) of the sample was determined using AAS. The initial concentration of As(V) (C₀) varied from around 13.1 to 75.8 mg/L.
Adsorption isotherms: The equilibrium adsorption of As(V) on Fe₃O₄/rGO was carried out to find the adsorption capacity at pre-decided As(V) concentrations and pHs at 25 °C. A 250 mL solution of As(V) was put in a 500 mL conical flask, and the initial pH was adjusted to 5.5–6 using HCl/NaOH solutions. 0.1 gram of Fe₃O₄/rGO was added to seven flasks and kept in a shaking incubator at 25 °C for 24 h, which is more than the sufficient time to reach equilibrium. The flasks were sealed to minimize the As(V) concentration change due to water evaporation. The solutions were analyzed for As(V) concentration at equilibrium (Cₑ) using AAS. The amount of As(V) adsorbed on the adsorbent at equilibrium (qₑ) was calculated using Eq. (1).

Determination of the point of zero charge: The point of zero charge (pHₚZC) of Fe₃O₄/rGO was evaluated using the solid method [11]. 25 mL of 0.1 M KNO₃ solutions were put to a series of 250 mL conical flasks. The initial pH value (pHᵢ) of the solutions was adjusted from 2 to 10 by adding either a 0.1 M HCl or a 0.1 M NaOH solution. Then, 0.05 g of Fe₃O₄/rGO was added to each flask, and the mixtures were agitated. After 24 hours, the final pH (pH₇) of the solutions was measured. The difference between the initial and the final pH of the solutions (ΔpH = pHᵢ − pH₇) was plotted against the pHᵢ. The point of intersection of the curve with the abscissa, at which ΔpH is 0, provided the pHₚZC.

3 Results and discussion

3.1 Material characterization

The XRD measurements were employed to investigate the crystalline phase and structure of the synthesized samples. Figure 1 shows the XRD patterns of GO, rGO and Fe₃O₄/rGO. The pattern of GO exhibits a strong peak at 11.4°, corresponding to the (002) diffraction plane, indicating the presence of oxygen-containing functional groups formed during oxidation (that can be confirmed in FT-IR spectra) as reported in the literature [3, 6]. However, the small peak at around 26°, which can be ascribed to the natural graphite, is discernible indicating the incomplete oxidation of graphite. Similar results were also reported in other papers [6, 18]. After being reduced by ascorbic acid, the material does not show the peak at 11.4°, and a weak broad reflection peak at 25.8° corresponding to the relative short-range-order structures in the stacked disordered rGO appears, indicating that GO has been reduced to rGO [22]. The crystallinity of the Fe₃O₄/rGO nanocomposite is very similar to that of Fe₃O₄ nanoparticles, and all peaks are in good agreement with Fe₃O₄ face-centered cubic crystals (JCPDS File Card No.19-0629), implying the existence of magnetic oxide.

The FT-IR spectra of GO and Fe₃O₄/rGO are shown in Figure 2. It can be seen that upon oxidation of graphite to GO, the characteristic peaks representing the presence of oxygen in the carbon frameworks at 1730 cm⁻¹ (C=O stretching of carbonyl and carboxyl groups), 1412 cm⁻¹ (tertiary C-OH groups stretching), 1060 cm⁻¹ (C-O stretching vibration of epoxide) were observed. The band at around 578 cm⁻¹ was attributed to Fe-O, indicating the existence of Fe₃O₄ [2].
The wide-scan XPS spectrum of Fe$_3$O$_4$/rGO in Figure 3 (a) shows the photoelectron lines at binding energies of 285, 530 and 710 eV corresponding to carbon (C 1s), oxygen (O 1s) and Fe 2p, respectively. The high-resolution XPS for C 1s of GO and rGO are shown in Figure 3 (b) and (c), correspondingly. The deconvoluted C 1s spectrum lines (Fig. 3 (b)) imply that GO consists of functional groups, such as sp$^2$ (C=C, 284.8 eV), hydroxyl and epoxy (C-O, 286.8 eV), carbonyl (C=O, 287.9 eV) and carboxylates (O=C-O, 288.8 eV) [6]. The high-resolution XPS lines of C 1s for rGO (Fig. 3 (c)) show that the intensity of functional groups of rGO remarkably reduced in compared with those of GO, indicating an efficient deoxidization. As the XRD patterns of magnetite Fe$_3$O$_4$ and maghemite Fe$_2$O$_3$ are very similar, the XPS Fe2p core level has been conducted to confirm the presence of magnetite. Fig. 3 (d) shows the XPS Fe2p core level spectrum of Fe$_3$O$_4$/rGO. There are no satellite peaks at around 719 eV, which is characteristic for maghemite, and the broad peaks at around 710,9 and 724,5 eV are typical for magnetite, indicating a successful loading of Fe$_3$O$_4$ [6].

The VSM magnetic characterization of Fe$_3$O$_4$/rGO was determined at room temperature. The magnetization hysteresis is S-like, and the saturation magnetization is 59.4 emu as shown in Figure 4. This value is lower than that of pure nano-magnetic Fe$_3$O$_4$[2] but higher than that of
Fe\textsubscript{3}O\textsubscript{4}/rGO reported in [9, 21]. The difference of saturation magnetization between Fe\textsubscript{3}O\textsubscript{4}/rGO and pure magnetic Fe\textsubscript{3}O\textsubscript{4} may be attributed to the presence of reduced graphene oxide nanosheets and the relatively lower density of magnetic components in the nanocomposites. The magnetic coercivity was nearly zero, indicating no remaining magnetization upon the removal of the external magnetic field. Therefore, the superparamagnetic behaviour of Fe\textsubscript{3}O\textsubscript{4}/rGO nanocomposites was established.

![XPS spectrum of Fe\textsubscript{3}O\textsubscript{4}/rGO](image)

**Fig. 3.** XPS spectrum of Fe\textsubscript{3}O\textsubscript{4}/rGO (a); XPS C1s core level spectrum of GO (b); XPS C1s core level spectrum of rGO (c); XPS Fe2p core level spectrum of Fe\textsubscript{3}O\textsubscript{4}/rGO (d)

![Magnetization curve](image)

**Fig. 4.** Magnetization curve of Fe\textsubscript{3}O\textsubscript{4}/rGO
3.2 Effect of pH on As (V) adsorption

The point of zero charge of Fe₃O₄/rGO determined using the solid addition method is around 6.3. The solution pH has a significant influence on the adsorption process because it can affect the degree of ionization of pollutants as well as the ionic state of the functional groups on the sorbent surface. To investigate the effect of pH on As(V) adsorption, a series of solutions with pH ranging from 2 to 12 was prepared and adjusted with HCl and NaOH solutions. As it can be seen in Figure 5, the adsorbed amount of As(V) increased up to pH = 6.2 and then decreased with a further increase in pH. These changes may be due to two effects: i) the surface hydroxyl functional groups of Fe₃O₄/rGO can attract protons under the acidic condition and provide protons under the neutral and basic condition, following equations (2) and (3); (ii) the electrostatic repulsion between the arsenate species and the negative charges of the sorbent surface would also lead to a decrease in the arsenate removal at pH greater than the PZC [12].

Protonation process:  \[(\text{Fe}_3\text{O}_4/\text{rGO}) - \text{OH} + \text{H}^+ \overset{\text{eq}(2)}{\longrightarrow} (\text{Fe}_3\text{O}_4/\text{rGO}) - \text{OH}_2^+\]

Ionization process:  \[(\text{Fe}_3\text{O}_4/\text{rGO}) - \text{OH} \overset{\text{eq}(3)}{\longrightarrow} (\text{Fe}_3\text{O}_4/\text{rGO}) - \text{O} + \text{H}^+\]

Figure 5. Effect of pH on As(V) adsorption

Figure 6 shows the dependence of adsorption capacity on adsorption time at different As(V) concentrations. It can be seen that the adsorption capacity of Fe₃O₄/rGO for As(V) increases as the initial As(V) concentration increases from 13.1 to 75.8 mg/L. The reason for this is that the increase in the initial As(V) concentration enhanced the interaction between the arsenate and Fe₃O₄/rGO [14]. Moreover, the mass transfer driving force became larger, and thus attributing to higher As(V) uptake from the aqueous solutions [19]. The results showed a very large adsorption rate, which can be verified with the fact that the amount of adsorbed As(V) on Fe₃O₄/rGO composite in the arsenate solution is around 60 % within the first 25 minutes. The time required to reach the adsorption equilibrium between the Fe₃O₄/rGO and As(V) in the solution was less than 170 min.
The pseudo-first-order and pseudo-second-order kinetic models were used to investigate the kinetics of As(V) adsorption on the Fe₃O₄/rGO composite. The pseudo-first-order model in the linear form could be expressed as

$$\ln(q_e - q_t) = \ln q_e - k_1t$$

where $q_e$ and $q_t$ are the amounts of ions adsorbed on adsorbent (mg. g⁻¹) at equilibrium and at time $t$, respectively, and $k_1$ is the rate constant of first-order adsorption (min⁻¹). Straight line plots of $\ln(q_e-q_t)$ against $t$ were used to determine the rate constant, $k_1$ [6].

The pseudo-second-order model in the linear form may be expressed as

$$\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{t}{q_e}$$

where $k_2$ is the rate constant of second-order adsorption (g.mg⁻¹ min⁻¹). Straight-line plots of $t/q_t$ against $t$ were tested to obtain rate parameters [6].

**Table 1.** Adsorption kinetic parameters for As(V) adsorption on the Fe₃O₄/rGO composite

| $C_0$ (mgL⁻¹) | **Pseudo-first-order kinetics** | | | **Pseudo-second-order kinetics** | | |
|---|---|---|---|---|---|
| | $k_1$ (min⁻¹) | $q_e, \text{cal}$ (mg.g⁻¹) | $R^2$ | $k_2$ (g.mg⁻¹.min⁻¹) | $q_e, \text{cal}$ (mg.g⁻¹) | $q_e, \text{exp}$ (mg.g⁻¹) | $R^2$ |
| 13.10 | 0.0112 | 10.84 | 0.9539 | 0.0017 | 16.77 | 15.97 | 0.9841 |
| 23.50 | 0.0099 | 16.36 | 0.9706 | 0.0011 | 25.28 | 24.40 | 0.9831 |
| 34.60 | 0.0156 | 21.07 | 0.8969 | 0.0011 | 32.65 | 30.90 | 0.9866 |
| 50.70 | 0.0160 | 35.56 | 0.9883 | 0.0008 | 43.29 | 39.61 | 0.9936 |
| 75.80 | 0.0206 | 42.77 | 0.9639 | 0.0005 | 53.30 | 44.23 | 0.9896 |

A comparison of the pseudo-first-order and pseudo-second-order kinetic models of arsenate adsorption onto Fe₃O₄/rGO at various initial As(V) concentrations is illustrated in Table 1. The results show that the coefficient of determination ($R^2$) for the pseudo-second-order
model is higher compared with that of pseudo-first-order model, and the calculated \( q_e \) values \((q_{e,cal})\) from this model agree well with the experimental data \((q_{e,exp})\). These results suggest that the kinetics of As(V) adsorption on the Fe₃O₄/rGO follows the pseudo-second-order model.

The adsorption isotherm models of Langmuir and Freundlich were applied to fit the adsorption equilibrium data of As(V) on Fe₃O₄/rGO composite.

The Langmuir isotherm model suggests that adsorption takes place at specific homogeneous sites on the sorbent. Its linear form can be written as

\[
\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m}
\]

where \( q_e \) is the equilibrium amount of arsenic adsorbed onto the Fe₃O₄/rGO (mg/g), and \( C_e \) is the equilibrium arsenic concentration in the solution (mg L⁻¹), \( q_m \) is the maximum monolayer adsorption capacity of the sorbent (mg g⁻¹), and \( K_L \) is the Langmuir adsorption constant (L mg⁻¹) [6].

Freundlich isotherm model assumes a heterogeneous adsorption surface and active sites with different energy, and the Freundlich isotherm model is given in linear form as

\[
\ln q_e = \ln K_F + \frac{1}{n} \ln C_e
\]

where \( K_F \) (mg g⁻¹) is the Freundlich constant, which is a measure of adsorption capacity, \( 1/n \) is an empirical parameter related to the nature and strength of the adsorption process and the distribution of the active sites [6]. Low values of \( 1/n \) indicate that the surface is heterogeneous. For values in the range \( 0.1 < 1/n < 1 \), adsorption is favorable [14].

The Langmuir and Freundlich isotherm parameters for arsenate adsorption onto the Fe₃O₄/rGO were calculated by plotting \( q_e \) versus \( C_e \) and the results are presented in Table 2. The equilibrium data of arsenate adsorption onto the Fe₃O₄/rGO can be well fitted by the two adsorption isotherm models since their coefficients of determination \((R^2)\) are very close. The high correlation to both Langmuir and Freundlich isotherms implies a monolayer adsorption and the existence of heterogeneous surface in the adsorbents, respectively. This observation is similar to the results reported by Kong et al. [10], in which both Langmuir and Freundlich models were well fitted to describe the adsorption of As(V) on nanoscale Fe-Mn binary oxides loaded on zeolite. The maximum adsorbed amount of As(V) over Fe₃O₄/rGO calculated using the Langmuir model is 58.48 mg/g, rather higher than the amount reported in other works [10, 17, 20]. This result shows that the Fe₃O₄/rGO composite synthesized in this work is a potential adsorbent for water sources contaminated with arsenic.

| Langmuir isotherm | Freundlich isotherm |
|-------------------|---------------------|
| \( K_L \) (Lmg⁻¹) | \( q_m \) (mg/g)    | \( R^2 \) | \( K_F \) | \( n \) | \( R^2 \) |
| 0.054             | 58.48               | 0.9965  | 6.751   | 2.080 | 0.9773 |
4 Conclusion

Fe₃O₄/rGO was synthesized by a facile one-step process. The iron oxide in the magnetic iron oxide is highly dispersed over rGO. The Fe₃O₄/rGO nanocomposite exhibits super-paramagnetic properties at room temperature, and saturation magnetization approaches 59 emu g⁻¹. The experimental data are well fitted with the pseudo-second-order model of adsorption kinetics. The adsorption data obey both Langmuir and Freundlich models, which indicates the heterogeneous surface and the monolayer adsorption of the adsorbents. The Fe₃O₄/rGO material also shows excellent As(V) adsorption. The maximum monolayer adsorption capacity calculated using Langmuir equation is 58.48 mg/g. The synthesized Fe₃O₄-rGO nanocomposite is a potential adsorbent for removing As(V) from aqueous solutions.

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