

A comparative study on As(v) removal by graphene oxide (GO) and functionalized reduced graphene oxide (fRGO)

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Industrial wastewater contains heavy metals like arsenic which may enter into the food chain and may affect human beings. In this study As(v) removal was done by GO and fRGO and a comparative study was made. At equilibrium pH (pH 6) fRGO gives more As(v) removal than GO. For both the materials, Langmuir adsorption isotherm fit better than Freundlich isotherm. The adsorption capacities of GO and fRGO are determined (12.04 mg/g) and (28.57 mg/g) respectively. Both materials follow pseudo-second order removal kinetics and fRGO (0.09 g/mg/min) shows a faster removal rate than GO (0.07 g/mg/min). It was found that fRGO can remove 2.4 times more arsenic than graphene oxide (GO).

Keywords: Arsenic, adsorption, comparative study, GO, fRGO.

Introduction

Because of rapidly growing industrialization and urbanization, it resulted in a huge amount of discharge of heavy and toxic metals which is a challenging issue. Among all the toxic metals, the World Health Organization (WHO) recorded arsenic contamination in natural water source as a first priority issue¹. Arsenic (metalloid, atomic number 33) is a toxic, ubiquitous and carcinogenic chemical element² and has no taste and colour. South East Asia specially Bangladesh and West Bengal in India reported to be highly contaminated and concentrations as high as 0.3 mg/L of As is reported. It is reported that around 60 million people are drinking groundwater containing arsenic more than 0.01 ppm and more and more places are reported to be newly contaminated. Arsenic is found with valence state -3, 0, +3 and +5. Arsenite [As(III)] is mainly obtained in reduced groundwater and arsenate [As(V)] in an oxidized condition¹. Oxyanions of [As(v)] are found in four different states; H_3AsO_4 at pH < 2, H_2AsO_4^- at pH 3–6, HAsO_4^{2-} at pH 8–10 and AsO_4^{3-} at pH >12⁴.

As(III) is more toxic than arsenic(v). Long-time intake of highly concentrated water leads to serious health damage like skin cancer, melanosis, cardio-vascular disease, keratosis, anemia, lung cancer etc.^{13–15}. Thus, WHO had lowered

As concentration in drinking water from 0.05 ppm to 0.01 ppm in 1993³.

Toxicity of As(III) is 60–80 times more than that of As(V) and toxicity of organic arsenic is about 100 times less than that of inorganic arsenic. Many industries specially pharmaceuticals, pesticides, paint, animal feed, wood preservative discharges arsenic contaminated water. Thus arsenic can contaminate surface water by industrial discharges and subsequently can enter into the food chain through if remain untreated^{4,5}.

Numerous methods have been improvised to remove the As(v) such as reverse osmosis⁶, oxidation, adsorption⁷, ion exchange⁸, membrane separation and co-precipitation⁹. Among all these treatment technologies, adsorption is the most efficient method due to its environmentally friendly, economical and efficient removal of arsenic.

Since the innovation of buckyballs, a rapidly increasing new field, nanotechnology, is developing rapidly in the last two decades¹⁷. Initially, nanotechnology was used for medicine, electronics, and biotechnology. But, recently it is found to be beneficial in water treatment. Nanoparticles can show an array of novel properties, because of its small size, which is responsible for the development of new technology and

the improvement of existing ones¹⁶. Graphene is a two-dimensional structure that consists of sp²-hybrid carbons, containing only one atomic thickness and used for electronic, magnetic, power storage, water and wastewater treatment². Synthesis of this material reported elaborately elsewhere¹¹. In this study functionalized reduced graphene oxide (fRGO) was prepared by impregnation of iron into reduced graphene oxide (RGO)¹⁰. A comparative study between graphene oxide (GO) and fRGO is carried out for arsenic removal from contaminated water.

Materials and methods:

Synthesis of GO and fRGO:

GO was synthesized via Hummer's method¹¹. 5 g graphite powder and 2.5 g NaNO₃ was mixed and 120 mL H₂SO₄ was mixed dropwise in 1 L beaker. After that, the mixture was mixed for half an hour in magnetic stirrer in the presence of an ice bath. When vigorous stirring was maintaining, 15 g KMnO₄ was added in very control manner so that the temperature of this solution is maintained below 20°C. After that, the solution was removed from the ice bath and stirred at 35°C for half an hour. At the time of reaction, the solution becomes pasty, the colour transformed into light brown. The temperature of this compound was changed rapidly. It is raised to 98°C and it was retained for 15 min by heating externally. After stopped the heating, the pasty compound was cooled in a water bath for 20 min. To stop the oxidation process 450 ml DI water is used. 15 mL aliquot H₂O₂ was mixed to the mixture, and the colour changed to yellowish. The solution is then washed and centrifuged several time with 10% HCl and DI water at pH 7.

The powdered GO was dispersed in DI water. Hydrazine hydrate was mixed in the solution and heated for 2 h at 100°C with stirring. The mixture was then brought in a water cooling condenser. After 24 h, black solid precipitation was formed as reduced graphene oxide (RGO). N,N-Dimethylformamide (DMF) was mixed with the solution at DMF/H₂O ratio 9:1. From this, a mixture of 3 mL was dispersed in DI water and 15 mg FeSO₄·7H₂O was added in this dispersion. The solution was mixed for 24 h at 27°C. After 24 h, 5 mL of 0.1 N NH₄OH was mixed until the pH was achieved 8 and the colour changes to deep brownish red which signifies formation of ferric hydroxide. The precipitate was filtered and dried in an oven at 85°C for 12 h to get fRGO¹⁰.

Effect of pH: Batch studies were performed to calculate percentage removal of arsenic at varying pH values. For studying effect of adsorption on arsenic removal at different pH, six trial solutions of pH varying from 2–12 is prepared for each adsorbents. After that, 10 mg of adsorbents are mixed with 100 mL of 0.2 mg/L of prepared arsenic solution. The solutions were kept in the shaker and shaken at 150 rpm for 4 h. The samples were filtered and resulting arsenic concentration of filtrate was determined. The removal was plotted against final equilibrium pH.

Effect of dose of adsorbent: Batch adsorption experiment were performed with various doses of GO and fRGO. To analyze the effect of doses on arsenic removal, five different solution of doses ranging from 10 mg to 100 mg is added in 100 mL of 0.2 mg/L of arsenic synthetic solution for both the adsorbents. Adjust the pH to equilibrium pH which is approximately 6 of all the solutions. The samples were then shaken at 150 rpm for 4 h. Then the solutions were passed through 0.45 µm filter paper.

Effect of time: Batch kinetics were performed with equilibrium dose of about 100 mg of GO and fRGO in 100 mL of 0.2 mg/L of arsenic sample. Set the pH to the equilibrium pH of about 6 of all samples. The samples were then shaken at varying time period from 10 min to 4 h. 8 different trial solutions were analyzed for each case at varying time interval and filtered using 0.45 µm filter^{18–20}. Arsenic content in all the samples were measured with atomic absorption spectrometer (WFX-130, China).

Results and discussion

Effect of pH: pH is an essential aspect that influence the amount of surface charge ionization and adsorbate speciation. The adsorption statistics of GO and fRGO for the removal of arsenic is shown in the Fig. 1. Optimum adsorption takes place at pH 6 for both the adsorbents. The variation in initial and final pH is in between ±0.2. Results shows that at equilibrium pH 6 arsenic removal efficiency of GO and fRGO is 62% and 76% respectively. As the pH value increases the % removal of As(v) is decreased. It is seen that at pH 8 the % removal of As(v) is 54% and 68% respectively and further increases the value of pH, the % removal of As(v) decreases rapidly.

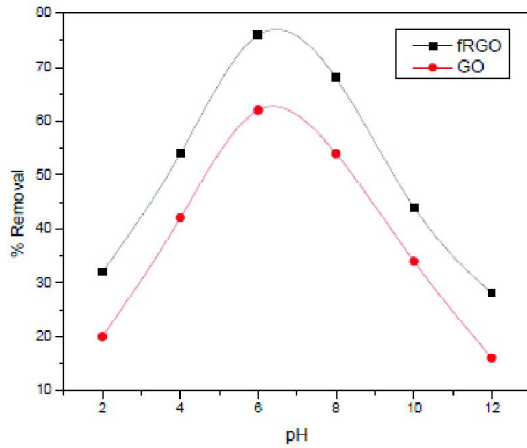


Fig. 1. % Removal with variation of pH.

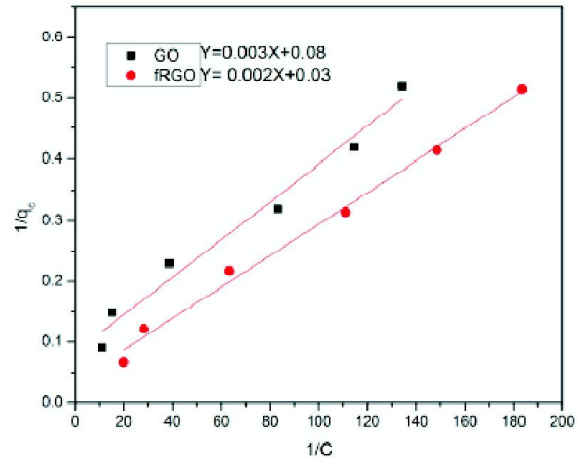


Fig. 2. Langmuir adsorption isotherm model.

Adsorption Isotherm: Two basic adsorption isotherm namely Freundlich and Langmuir isotherm were investigated for arsenic removal by GO and fRGO. For characterizing the single layer adsorption morphology, the Langmuir adsorption isotherm is used where the Freundlich adsorption isotherm characterize a heterogeneous surface with intermediary and low concentrations²⁰. Following linier equation is represented the Langmuir adsorption isotherm

$$\frac{1}{q_c} = \frac{1}{q_{\max} C_e K_L} + \frac{1}{q_{\max}} \quad (1)$$

where C_e (mg/L) = the equilibrium solute concentration, q_e (mg/g) = the equilibrium adsorption capacity, q_{\max} (mg/g) = the maximum adsorption capacity, and K_L (L/mg) = the Langmuir constant which is related to the intensity of adsorption Langmuir isotherm model of arsenic removal by GO and fRGO is shown in Fig. 2.

The is represented by the following equation represents Freundlich adsorption isotherm

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (2)$$

where q_e (mg/g) = equilibrium adsorption capacity, K_F (mg/g) = adsorption capacity, n (L/g) = adsorption intensity and C_e (mg/L) = equilibrium concentration. Freundlich adsorption isotherm model of arsenic removal by GO and fRGO is shown in Fig. 3.

From Table 1 it is observed that Langmuir isotherm fits better ($R^2 = 0.989$) than Freundlich isotherm for both GO

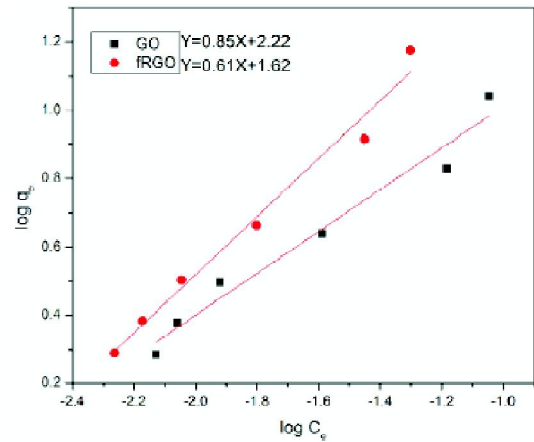


Fig. 3. Freundlich adsorption isotherm model.

Adsorbent	Langmuir isotherm			Freundlich isotherm		
	q_{\max}	K_L	R^2	K_F	n	R^2
GO	12.02	26.92	0.971	41.68	1.64	0.962
fRGO	28.21	13.68	0.991	165.96	1.17	0.977

and fRGO which implies that monolayer adsorption takes place for both the adsorbent. Adsorption capacity (q_{\max}) of fRGO (28.57 mg/g) is found to be 2.35 times more than GO (12.04 mg/g).

To ascertain the spontaneity of adsorption process, free energy of adsorption for the two materials were calculated using the following equation.

$$\Delta G = -RT \ln K \quad (3)$$

where ΔG is the Gibbs free energy, T is the absolute temperature (K), R is the gas constant (8.314 J/mol K), K is the Langmuir isotherm constant.

Free energy for fRGO and GO at experimental condition (25°C) are found to be -8158.32 J/mol and -6481.17 J/mol respectively. The negative values of ΔG signifies that the adsorption processes were spontaneous for both GO and fRGO.

Kinetic study: The study on kinetics of arsenic adsorption on both the materials were conducted by varying the time ranging from 10 min to 240 min. Removal of arsenic seemed to take place in two different phase. At first phase of (upto 1 h) rapid arsenic adsorption takes place followed by slower adsorption of arsenic. From Fig. 4 it is cleared that adsorption kinetics are rapid within initial first 1 h and about 55.5% and 63.95% arsenic is removed by GO and fRGO respectively. After that adsorption rate reduces and tends towards equilibrium. Within 4 h 88.9% and 96.4% As^V is adsorbed by GO and fRGO respectively.

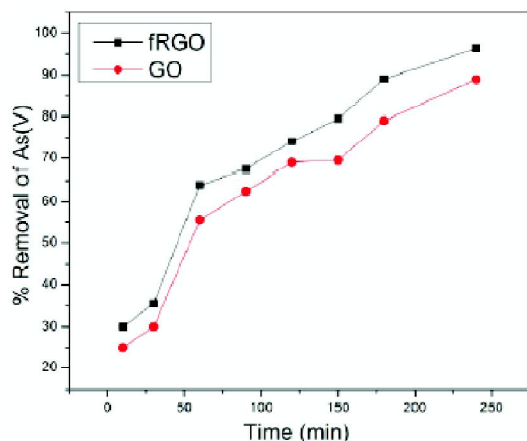


Fig. 4. % Removal of As(v) vs time (min).

The time dependent removal of arsenic on GO and fRGO were tested by three different kinetic models, namely, (1) pseudo-second order kinetic model, (2) Elovich model, and (3) intra-particle diffusion model. Pseudo-second order equation is represented by eq. (4)

$$\frac{t}{q_t} = \frac{1}{q_e^2 K} + \frac{t}{q_e} \quad (4)$$

whereas q_e and q_t (mg/g) are the adsorbed amount of ar-

senic on the fRGO and GO at equilibrium and at time t (min). K is the pseudo-second order rate constant.

Elovich model is represented by eq. (5):

$$q_t = \ln(\alpha\beta) + \frac{1}{\beta} \ln t \quad (5)$$

whereas α (mmol/g/h) is the initial adsorption rate and β (g/mmol) is the desorption rate constant.

The intra-particle diffusion model is represented by the eq. (6):

$$q_t = k_{diff} t^{0.5} + C \quad (6)$$

whereas k_{diff} (mg/g h^{-0.5}) is the intra-particle diffusion rate constant and C (mg/g) is a constant.

Pseudo-second order model, Elovich model and intra-particle diffusion model are shown in Fig. 5, Fig. 6, and Fig. 7 respectively. The model constants of different models are obtained and presented in Table 2.

It is cleared from the Table 2 that pseudo-second order kinetic model ($R^2 = 0.967$) and intra-particle diffusion model ($R^2 = 0.96$) fit good. This is due to the fact that in fRGO the surface is functionalized by iron which form oxides or hydroxides of iron which is responsible for chemisorptions and intra-particle diffusion by $As(v)$. For GO through the surface is not functionalized with iron still there remains different functional groups like, oxides, hydroxides, carboxylic, phenolic which may contribute the $As(v)$ adsorption and intra-particle

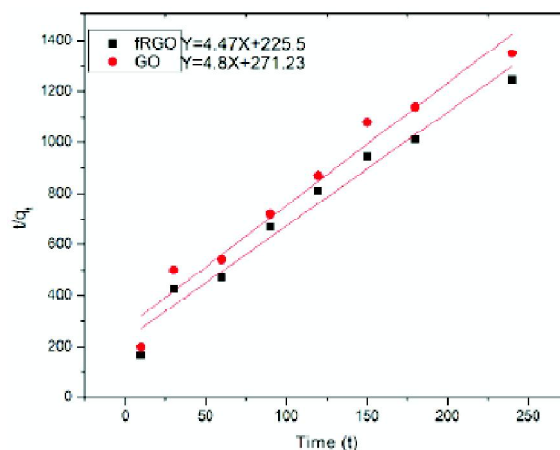


Fig. 5. Pseudo-second order model.

Table 2. Kinetic constants

Adsorbent	Pseudo-second order model			Elovich model			Intra-particle diffusion		
	q_e	k	R^2	α	β	R^2	K	C	R^2
GO	0.21	0.08	0.959	0.04	24.4	0.92	0.01	0.01	0.96
fRGO	0.22	0.09	0.967	0.04	22.98	0.93	0.01	0.02	0.96

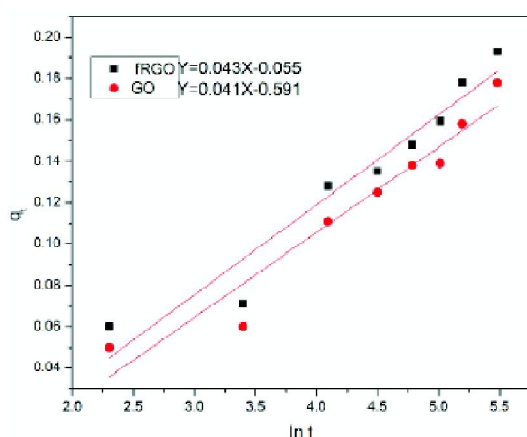


Fig. 6. Elovich model.

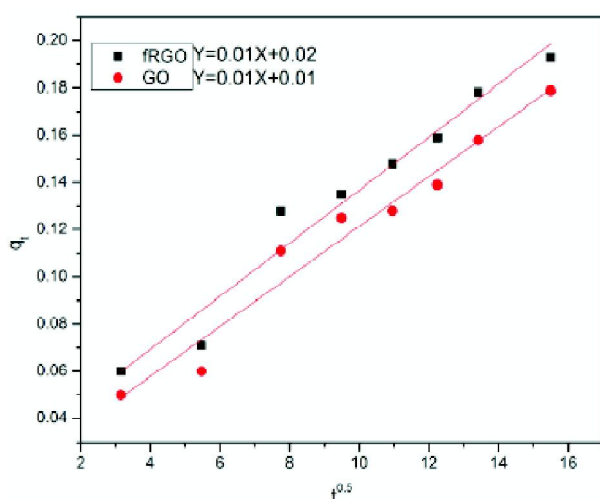


Fig. 7. Intra-particle diffusion model.

diffusion. However as it is not functionalized with iron, arsenic removal is significantly less compared to fRGO²² removal of arsenic by nano iron particles.

Conclusions

It is clear from this study that GO can remove arsenic from contaminated water. The removal is pH dependent and

for efficient removal of this contaminant, GO requires functionalization by iron. The material can be used for arsenic treatment with small footprint and efficient removal. However, more studies still require if any toxicity exists by GO/fRGO treated water.

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