

Adsorption of arsenic from aqueous solution using magnetic graphene oxide

A.I.A. Sherlala^{1,2}, A.A. Raman^{1,*} and M.M. Bello¹

¹Department of Chemical Engineering, Faculty of Engineering, University of Malaya, 50603 Kuala Lumpur, Malaysia

²Department of Chemical Engineering, College of Engineering Technology-Janzour, Libya

E-mail: azizraman@um.edu.my

Abstract. A binary of graphene oxide (GO) and iron oxide (IO) was prepared and used for the removal of arsenic from aqueous solution. The synthesized compound was characterized using XRD analysis. The prepared composite was used for the adsorption of arsenic from aqueous solution. Central Composite Design was used to design the adsorption experiments and to investigate the effects of operational parameters (initial concentration of arsenic, adsorbent dosage, pH and time) on the adsorption capacity and efficiency. The adsorbent shows a high adsorption capacity for the arsenic. The adsorption efficiency ranges between 33.2 % and 99.95 %. The most significant factors affecting the adsorption capacity were found to be the initial concentration of arsenic and the adsorbent dosage. The initial pH of the solution slightly affects the adsorption capacity, with the maximum adsorption capacity occurring around pH 6 – 7. Thus, the developed adsorbent has a potential for effective removal of arsenic from aqueous solution.

1. Introduction

The environmental pollution caused by heavy metals has attracted concern globally due to the detrimental effects of heavy metal to human health and the environment. Heavy metals are ubiquitous and unlike organic pollutants, are stable and possess low levels of biodegradability [1]. Heavy metals have been associated with various health problems such as hematopoietic, renal, gastrointestinal, cardiovascular, and reproductive systems [2]. Discharging effluents containing heavy metals is therefore a source of serious concern. Therefore, the removal of heavy metal ions from wastewater streams elicits attention.

There are many technologies that have been investigated for heavy metal removal such as ion-exchange, coagulation, reverse osmosis, and electrochemical processes. Most of these processes have some limitations such as selectivity and sensitivity to the solution pH. Adsorption is a very effective method for the removal of heavy metals from wastewater [3]. Activated carbon is the widely used adsorbent but its high cost limits its application. Other low-cost materials such as grape bagasse [3], bentonite clay [4], cow bone [5] and palm shell [6] have been investigated as alternative adsorbents. These materials exhibit low adsorption capacities [7]. Thus, there is need to develop effective adsorbent for heavy metals removal from the environment.

Thus, this study was conducted to synthesize and magnetic graphene oxide and apply it in the adsorption of a model heavy metal from aqueous solution. One of the heavy metals of particular concern



is arsenic which is known to have carcinogenic, dermatological, cardiorenal and gastrointestinal effects [8,9]. Thus, arsenic is used as the model pollutant. In order to study the effects of operational parameters, response surface methodology (RSM) was employed. RSM is a multivariate statistical tool that can be used to design experiments, develop empirical model and study the effects of the independent variables [10].

2. Methodology

2.1. Chemicals

All chemicals used were of analytical reagent grade and used without further purification. Graphite powder (particle size $<20\ \mu\text{m}$) was obtained from Sigma Aldrich Malaysia. Other chemicals such as Ferric chloride (99%), ferrous chloride (99%), Potassium permanganate (99%), Ammonia solution (30%), Hydrogen Peroxide (30% w/v) and Sodium Arsenite (98.5%) was procured from R&M marketing Essex UK. Deionized water was used for samples preparation.

2.2. Synthesis of the adsorbent

Graphene oxide (GO) was synthesized according to improved Hummer's method. A graphite powder (3.0 g) was mixed with concentrated H_2SO_4 (70 ml) in an ice bath. Under vigorous agitation, KMnO_4 (9.0 g) was added slowly to keep the temperature of the suspension lower than $20\ ^\circ\text{C}$. Sequentially, the reaction system was transferred to oil bath which was maintained at $40\ ^\circ\text{C}$. The reaction mixture was vigorously stirred for 30 minutes. Subsequently, 150 mL of the water was added and solution was stirred for 15 min at $95\ ^\circ\text{C}$. Later, 500 mL of water was added followed by the slow addition of 15 mL H_2O_2 . As a result, the color of the solution was turned from dark brown to yellow. The resulting mixture was filtered and washed with 1:10 HCl aqueous solution (250 mL). The filtered solids were dried in air and as a result graphene oxide (GO) powder was obtained.

Iron oxides were prepared by chemical precipitation. 2.43 g of FeCl_3 and 0.99 g of FeCl_2 were dissolved in 80 mL of deionized water and mixed properly. Subsequently, 6 mL of ammonia solution was added and sonicated for 1 h. The resulting mixture was decanted, washed two time with deionized water and separated again. The separated solids were dried in oven at $50\ ^\circ\text{C}$.

The iron oxide particles were mixed with 0.2 g of graphene oxide in 50 mL of deionized water. The mixture was stirred for 18-24 h and centrifuged. The separated solid content was washed and centrifuged. The process was repeated two times and dried in oven at $50\ ^\circ\text{C}$ to obtain GO/Iron oxide binary.

2.3. Analysis

The morphologies of the synthesized adsorbents were characterized by Field Emission Scanning Electron Microscope-E. The chemical constituents in the adsorbents were analyzed using Energy-dispersive X-ray (EDX) analysis. The crystalline phase of iron oxide was investigated using X-ray diffraction (XRD) technique. Fourier Transform Infrared spectroscopy was used to study the functional groups of the adsorbents within the frequency range of $4000\text{-}400\text{cm}^{-1}$. The concentration of arsenic in the aqueous solution was determined using Inductively coupled plasma mass spectroscopy (ICP Optima 7000 DV, Perkin Elmer).

2.4. Experimental Design

Response surface methodology (RSM) was used to design the adsorption experiments with the aid of Design-Expert 8. Central composite design (CDD) was used as the design domain because of its effectiveness in the design and optimization of chemical process. Four independent variables (initial arsenic concentration, adsorbent dosage, pH and time)) were selected as the factors while the arsenic removal (%) and adsorption capacity (mg/g) were chosen as the responses. The ranges of the independent variables used are shown in Table 1.

Table 1. Range of operational parameters used in the RSM.

Independent variables	Coded	Low Actual Value	High Actual Value
Initial As Concentration (ppm)	A	10	100
Adsorbent dosage (mg)	B	0.1	0.5
pH	C	2	12
Time (min)	D	30	120

2.5. Experimental Procedure

The adsorption of heavy metals was performed in a batch experiment. 0.1-0.5 gram of synthesized adsorbents added to 100 mL of arsenic solution at desired concentrations. The arsenic solution was prepared using a deionized Millipore water. The mixture was stirred and pH of the solution was adjusted according to the desired value by adding 1.0 M NaOH or 1.0 M HNO₃. The stirring time was also varied accordingly. After a desired time, the solid phase was removed from the supernatant by decantation with magnet and centrifuge at 4000 rpm for 30 min. Arsenic content in the obtained supernatant is determined by ICP.

After separation, the treated solution was sampled and analyzed to determine the arsenic removal efficiency. The removal efficiency was calculated according to equation 1:

$$\% \text{ Removal} = \frac{C_o - C_t}{C_o} \times 100 \quad (1)$$

Where C_o and C_t are the initial and equilibrium concentrations of arsenic in the solution (mg/L).

3. Results and discussion

3.1 Characteristics of the adsorbent

XRD patterns were obtained to investigate the phase and structure of graphite, GO, IO and hybrid of GI-IO. As shown in figure 1(a), the graphite displays a characteristic peak at $2\theta = 27^\circ$. After oxidation, the characteristic graphite peak disappeared and was replaced by a well-defined peak at $2\theta = 11.5^\circ$ (figure.1 (b)) indicating the introduction of oxygen-containing groups to form the GO [11]. The increased d-spacing of GO is ascribed to the presence of copious oxygen-containing functional groups. For the pattern of iron oxide (figure 1 (c)), there appears five main peaks around $2\theta = 30.38, 35.84, 43.62, 57.46, 63.02$ degrees, all of which can be indexed to the (220), (311), (400), (511), and (440) planes of γ -Fe₂O₃ (JPDS no. 39-1346). However, the hybrid of GO and γ -Fe₂O₃ exhibited almost the same pattern as the pristine γ -Fe₂O₃ (figure 1 (d)). This may be due to the presence of small amount of GO, compared to the amount of IO in the hybrid.

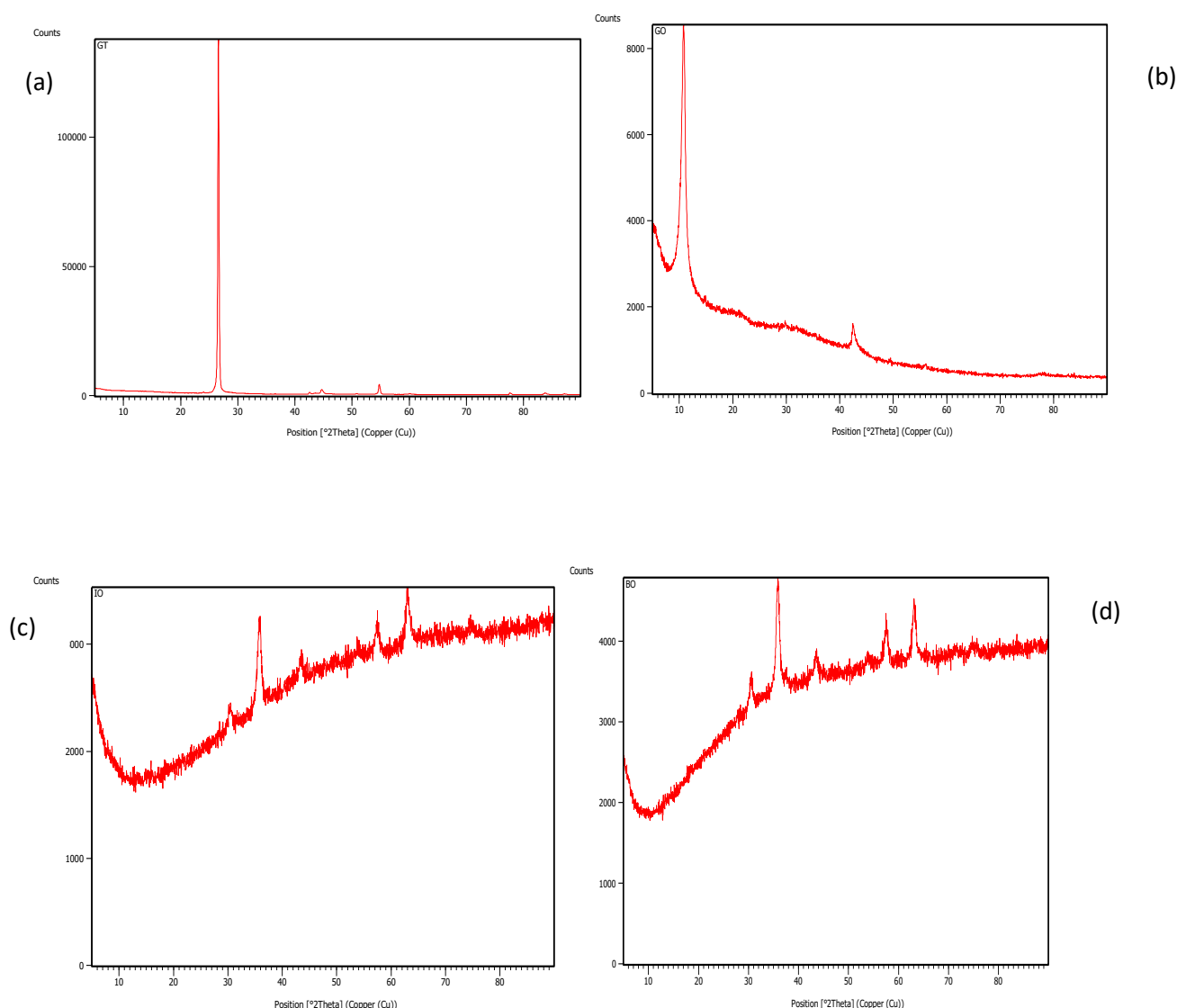


Figure 1. XRD pattern for (a) GT, (b) GO, (c) IO and (d) BO.

3.2. Adsorption studies

3.2.1. RSM-CCD Design. In order to study the performance of the synthesized adsorbent and the effects of the process variables on the adsorptive removal of arsenic using the developed adsorbents, central composite design was used to design the experiment with the aid of Design-Expert 8. The four important process parameters selected include the initial concentration of the arsenic, adsorbent dosage, pH and the adsorption time. The response selected was the adsorption efficiency. The 30 experiments suggested by the CCD were run and the observed responses are shown in table 2. The highest removal efficiency was 99.95 % obtained with run 22 while the lowest observed adsorption efficiency was 33.2 % obtained with run 13. These values were input into the Design-Expert and analysed using the designed CCD model. The responses as predicted by the model are also shown in table 2. It can be observed that, for both responses, the predicted values are in reasonable agreement with the experimental values.

Table 2. Experimental and predicted responses.

Run	Initial As conc. (ppm)	Adsorbent dosage (g)	pH	Time (min)	Adsorption Efficiency (%)	
					Exp.	Pred.
1	10	0.5	12	30	75.35	76.38
2	55	0.1	7	75	51.5272	54.29
3	10	0.3	7	75	94.64	85.26
4	55	0.3	7	75	76.3090	86.62
5	55	0.3	7	30	71.7272	78.16
6	10	0.5	2	120	94.08	87.96
7	10	0.1	2	30	51.55	46.98
8	55	0.3	12	75	47.7090	79.43
9	10	0.5	2	30	90.37	104.30
10	100	0.5	12	120	52.18	60.98
11	100	0.5	12	30	51.68	43.24
12	100	0.5	2	120	55.3	66.27
13	100	0.1	12	30	39.77	33.00
14	55	0.3	7	75	77.8545	86.62
15	55	0.5	7	75	88.7418	68.46
16	100	0.1	2	30	35.98	40.61
17	10	0.1	2	120	54.49	63.08
18	100	0.5	2	30	47.71	48.53
19	10	0.1	12	120	36.21	39.62
20	10	0.5	12	120	60.75	60.05
21	55	0.3	7	75	71.7090	86.62
22	10	0.1	12	30	34.34	23.52
23	100	0.1	2	120	91.359	90.78
24	55	0.3	7	75	99.9109	86.62
25	55	0.3	7	75	99.92	86.62
26	100	0.3	7	75	99.953	85.26
27	55	0.3	2	75	99.9109	93.80
28	100	0.1	12	120	99.949	89.95
29	55	0.3	7	75	99.870	86.62
30	55	0.3	7	120	99.8727	95.08

3.2.2. Model development and ANOVA.

The removal efficiency was found to fit a reduced quadratic model. Equation 2 shows the quadratic model proposed by the RSM in terms of the coded parameters. The positive terms indicate positive effect on the arsenic removal. In this case, adsorbent dosage, adsorption time, interaction between initial arsenic concentration and pH, and the interaction between initial arsenic concentration and time have positive effect on the arsenic removal. On the other hand, negative terms indicate negative effects on the arsenic removal. Thus, initial arsenic concentration, initial pH, interaction between initial arsenic concentration and adsorbent dosage, interaction between adsorbent dosage and pH, interaction between

adsorbent dosage and time, and the quadratic effect of adsorbent dosage have negative effect on the arsenic removal.

The analysis of variance (ANOVA) was used to test the adequacy of the model. Table 3 shows the ANOVA. The first step is to check the p-value of the model. For the model to be valid, the p-value must be less than 0.0500, indicating that the model is significant. In this case the p-value is 0.0002, indicating that there is only 0.02 % chance that the model value is due to error. Thus, the model is significant. The 'lack of fit' measure is required to be non-significant (above 0.0500) for the model to be valid. For this model, the p-value for the lack of fit is 0.5306. This means that there is 53.06 % chance that the value of the lack of fit is due to error. The adequate precision which measures the signal to error ratio is required to be above 4. The adequate precision in this case is 9.674, much higher than the minimum desirable value. On the other hand, the R^2 was found to be 0.7816. Although this value is not very high, the adjusted R^2 is in reasonable agreement with the predicted R^2 . This is required for the model to be valid. Also, figure 2 shows the graph for the predicted versus actual percent removal. The straight line and well distributed data shows a reasonable agreement between the experimental and predicted data.

$$\text{Percent removal} = +86.62 - 1.36A + 7.09B - 7.19C + 8.46D - 12.35AB + 5.66AC + 8.52AD - 1.11BC - 8.11BD - 25.24B^2 \quad (2)$$

Table 3. ANOVA for percent removal

Source	Sum of squares	df	Mean square	F value	P value	Remark
Model	12926.84	10	1296.68	6.80	0.0002	Sig.
A-Arsenic Conc.	33.26	1	33.26	0.17	0.6804	Not Sig.
B-Adsorbent dosage	903.93	1	903.93	4.75	0.0420	Sig
C-pH	929.98	1	929.98	4.89	0.0394	Sig
D-Time	1288.35	1	1288.35	6.78	0.0175	Sig.
AB	2439.82	1	2439.82	12.83	0.0020	Sig.
AC	511.89	1	511.89	2.69	0.1173	Not Sig.
AD	1161.07	1	1161.07	6.11	0.0231	Sig.
BC	19.85	1	19.85	0.10	0.7502	Not Sig.
BD	1052.00	1	1052.00	5.53	0.0296	Sig.
B^2	4586.70	1	4586.70	24.12	< 0.0001	Highly Sig.
Residual	3612.64	19	190.14			
Lack of Fit	2683.75	14	191.70	1.03	0.5306	Not Sig.
Pure Error	928.90	5	185.78			
Cor Total	16539.48	29				
Adeq precision	9.674					
R^2	0.7816					
Adjusted R^2	0.6666					
Predicted R^2	0.4682					

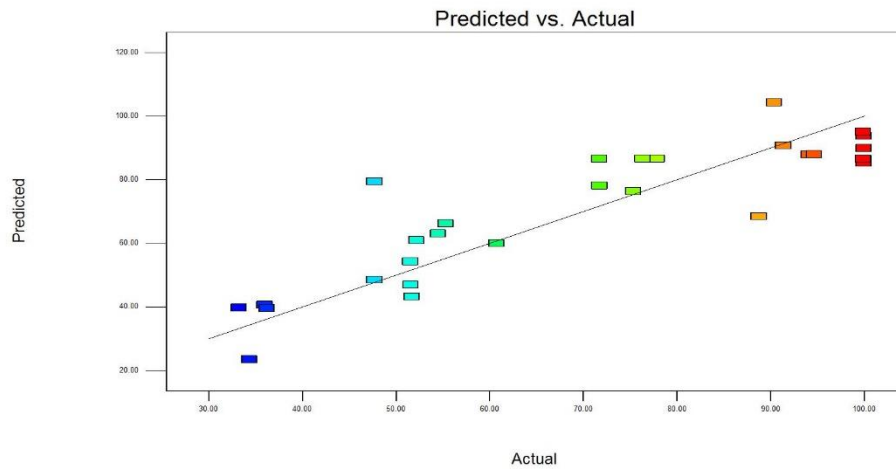


Figure 2. Predicted versus actual percent removal.

From the ANOVA in table 3, it can be seen that the initial arsenic concentration does not have a significant effect on the arsenic removal. On the other hand, the adsorbent dosage, pH and time have significant effect on the arsenic removal efficiency. This can be clearly seen in the perturbation plot shown in figure 3. A perturbation plot compares the effects of independent variables on the response at a particular point in the design space. A steep slope shows that the response is sensitive to that variable. A relatively flat line shows that the response is not sensitive to the variables. In Figure 3, B (adsorbent dosage) has the highest curvature, indicating that the arsenic removal is most sensitive to the adsorbent dosage. This is followed by C and D. However, the curve of A (arsenic concentration) is relatively flat. This shows that the arsenic removal is not sensitive to the initial concentration of the arsenic.

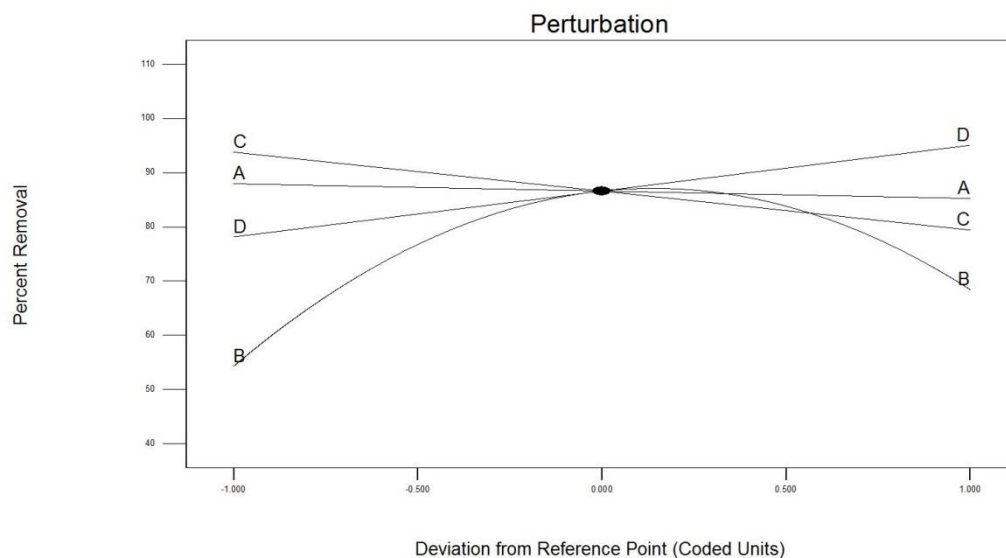


Figure 3. Perturbation plots for arsenic removal efficiency

4. Conclusion

This study was conducted to develop an effective graphene-based adsorbent for the removal of arsenic from aqueous solution. The magnetite-graphene oxide was successfully synthesized as verified by the XRD analysis. The adsorbent shows a high adsorption capacity for the arsenic. The adsorption efficiency ranges between 33.2 % and 99.95 %. The most significant factors affecting the adsorption capacity were

found to be the initial concentration of arsenic and the adsorbent dosage. The arsenic removal can be predicted by a second order model developed through RSM-CCD. Although this binary has shown potential for arsenic removal, functionalization using appropriate material can enhance its adsorptive capacity.

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