ADSORPTION STUDIES OF GRAPHENE OXIDE FOR LEAD REMOVAL FROM SYNTHETIC WASTEWATER

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ABSTRACT: Lead contamination present in wastewater is one of the major problems due to its toxicity and persistence. This issue increased dramatically and led to the environmental and health concerns worldwide. Therefore, this study aims to remove lead from synthetic wastewater effluent by adsorption process. In this study, nanomaterial called graphene oxide (GO) is used as an adsorbent due to its mechanical strength and high surface area. The parameters were optimized using Fractional factorial design under response surface method. GO demonstrates high adsorption capacity, q_{max} = 500 mg/g at 100 mg/L of initial lead concentration and at optimum pH 9. Adsorption isotherm of lead was also investigated to evaluate the adsorption capacity. The equilibrium data of graphene oxide adsorption was better represented by the Langmuir isotherm and was achieved within 60 minutes. The results showed that GO has potential to be an important adsorbent for lead removal. In the future, GO might be imbedded as adsorbent in the membrane fabrication for wastewater treatment.

KEYWORDS: *Lead; Graphene Oxide; Adsorption; Wastewater;*

1. INTRODUCTION

The growing world population, depleting water resources and climate change causing prolonged droughts, floods and other consequences have rendered clean water a competitive resource worldwide. The United Nations expects that the world's population will face water shortage by 2025. Heavy metals contamination in water is one of the major problems that increased dramatically which leading to the environmental and health concerns worldwide [1]. Heavy metals including lead, arsenic, copper, cadmium, chromium, silver and other hazardous chemical pollutants need to be removed from wastewater effluent to make water safe and consumable to the living things. International Lead Association (ILA, 2017) has reported that global industrial lead production per annum is approximately 5 million tonnes a year with a 9.5% increase over the five-year period. Wastewater effluent containing lead from mining industries such as petroleum mining, smelting, lead-acid battery manufacturing and waste incinerating are major contributors to the water pollution problem. Lead absorption through drinking water will give harmful

effects to human health such as kidney damage, high blood pressure, brain damage and behavioural disruption of children [2]. Besides that, lead exposure also could decrease the men fertility and change of the testicular functions in human beings as well as in the wildlife [3]. According to Malaysia Environmental Quality Report 2015, lead is one of the highest contaminant levels found in water tests and included in Class II risk. The permissible limit for lead to exist in water from upstream and downstream discharge of water supply sources are 0.1 mg/L and 0.5 mg/L, respectively (Malaysia Environmental Act, 1974).

Common conventional methods that had been utilized for heavy metals removal from wastewater effluents are solvent extraction, chemical precipitation, coagulation, ion exchange and electrochemical removal. However, these methods have limitations such as inconvenient, large space needed, incomplete removal, high energy consumption, low efficiency, generation of toxic sludge, and expensive disposal [4] [5] [6]. Therefore, adsorption approach is selected as the best alternative to remove heavy metals from wastewater. It has been proved that adsorption is the most preferred method for water/wastewater treatment due to effectiveness, convenient stability, utility, low-cost, ease of operation and high performance [7][8][9][10][11]. One of the cost-effective adsorbents called activated carbon is widely used in environmental applications and drinking water industry [12] [13]. However, lack of specificity, poor recyclability, low adsorption efficiencies and capacities hindered its application in concentrated solutions [14][15]. In recent years nanomaterials have arisen as a significant approach for the development of nanoadsorbents in water treatment applications. Nanoadsorbents with an increased adsorption capacity, high reactivity, biocompatibility, high surface to volume ratio and high metal binding capability might be designated to remove specific hazardous contaminants from wastewater especially heavy metals.

In this study, nanomaterial called graphene oxide is used as an adsorbent owing to its unique characteristics. Graphene oxide, a small size material in nanoscale (<100 nm) has high specific surface area, superb adsorption properties of heavy metals, and spectacular mechanical strength and considered as one of good adsorbent materials for heavy metal removal [16]. Graphene oxide (GO) is the oxidized form of graphene with oxygenous functional groups which is prepared by chemical oxidation of graphite. The reaction forming hydroxyl and epoxy functional groups in extended graphene sheets and carboxylic acid groups at the edges of graphene is shown below [17] (Fig. 1). These functional groups give great sorption between graphene and heavy metals. Furthermore, this nanomaterial has incredibly large surface area up to 2620 m^2/g of theoretical value [18].

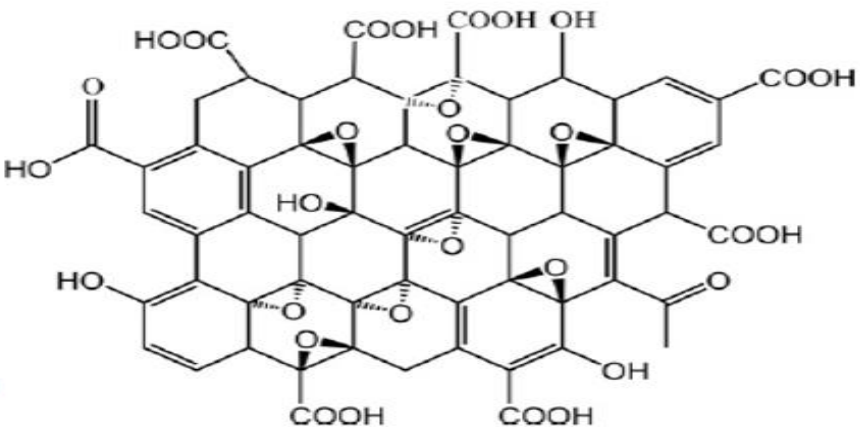


Fig. 1. Structural representation of GO (Source: [17])

2. MATERIALS AND METHODS

2.1 Materials

Graphene oxide (particle size: <35 mesh; Abalonyx AS, Oslo, Norway) was supplied by NanoMalaysia Berhad. Lead nitrate was purchased from R&M chemicals. All other reagents were commercial products of analytical grade. Deionized water was used for samples preparation. The experiments for process optimization and statistical analysis were designed using Design Expert® software version 6.0.8 (STAT-EASE Inc., Minneapolis, USA).

2.2 Characterization of GO

The characteristics of GO were analyzed by Abalonyx [19] company using SEM, TEM, AFM, XRD, Raman and FTIR at the Universities of Zaragoza, Spain, and Oslo, Norway. The details of the characterization are explained below and attached in the Supplementary File as reference [19].

2.2.1 Scanning electron microscopy (SEM)

As shown in Fig. 2, the morphology of two-dimensional GO dried flakes with the size 2-20 µm contain many primary single sheets.

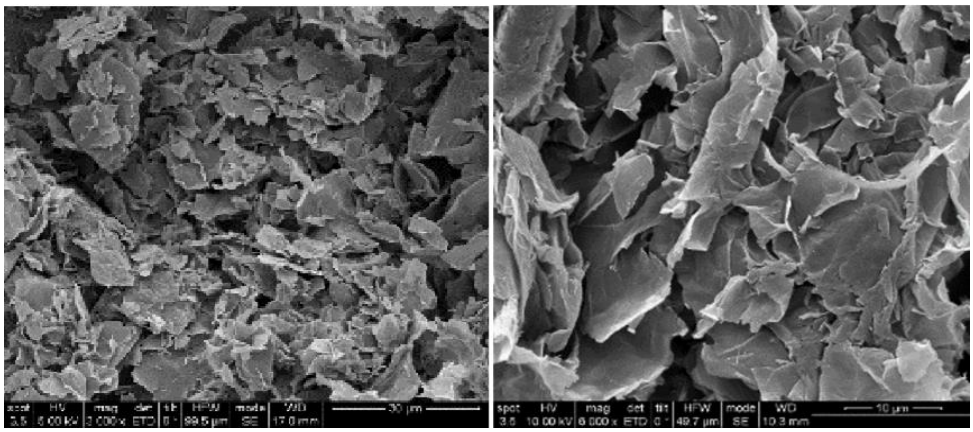


Fig. 2: SEM image of GO flakes (Source: [19])

2.2.2 Transmission Electron Microscopy (TEM) and Electron Diffraction

The image showed the hexagonal shape of electron diffraction pattern (Fig. 3). The TEM imaging displayed the oxidized and non-oxidized region of GO.

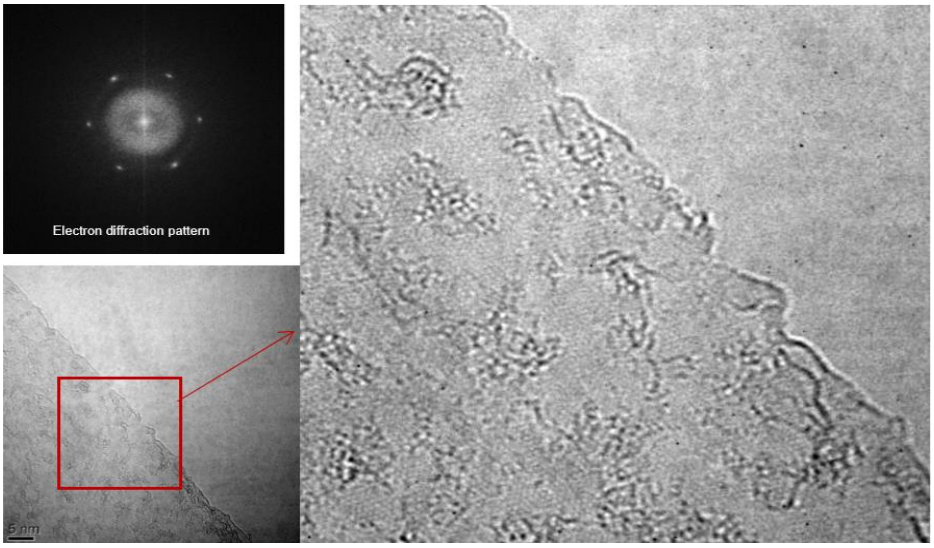


Fig. 3. TEM and Electron Diffraction of GO powder (Source: [19])

2.2.3 Atomic Force Microscopy (AFM)

The topography imaging of GO powder was presented in the Fig. 4 below. Dried dispersion of GO was first prepared on the mica substrate and then the sample was scanned. Brown and yellow sheets are single sheets while the yellow spots are dry salt from dried aqueous solution. The profile of the observed GO powder correlates well to a single sheet about 1 nm thick.

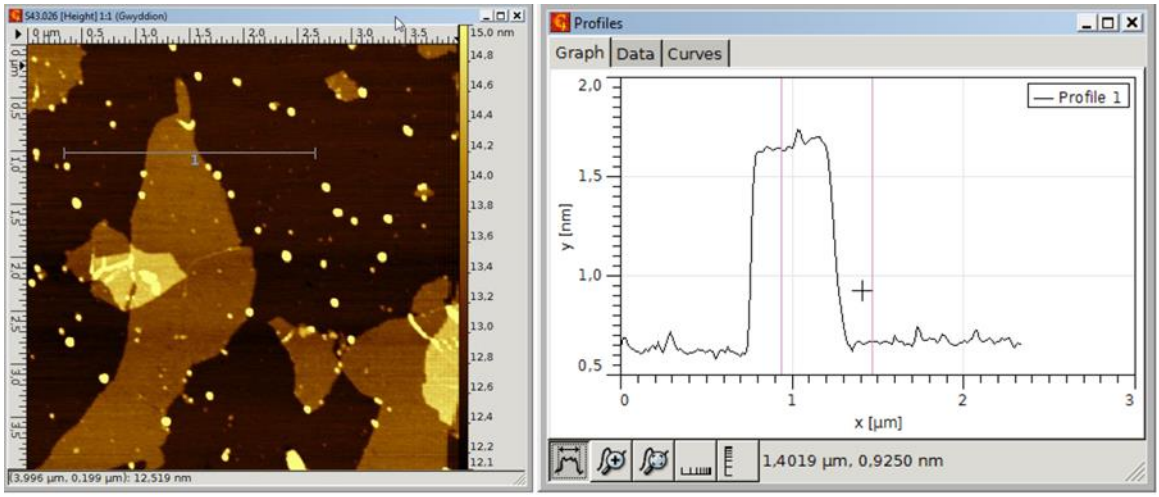


Fig. 4. AFM characterization of GO powder (Source: [19])

2.2.4 Raman Spectroscopy

From the Raman analysis, the high intensity ratio of I_D/I_G= 1.09 (Fig. 5) showed high degree oxidation of GO and the value is close to the ratios on other reported GO.

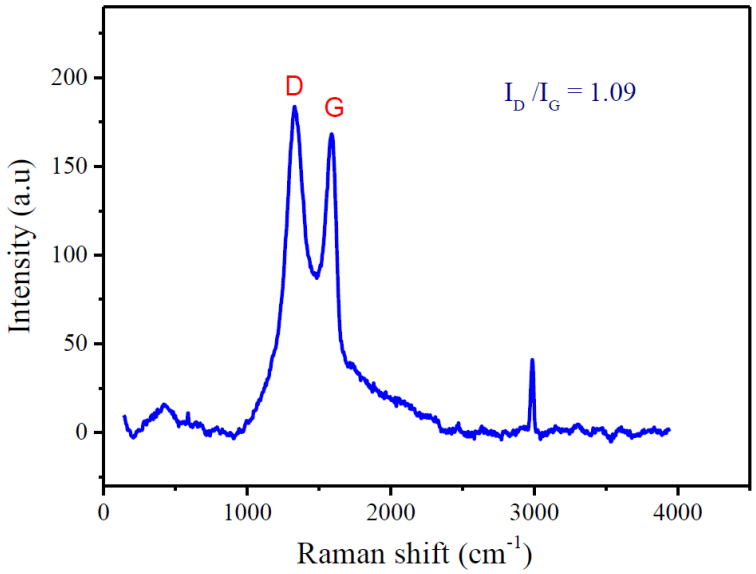


Fig.5. Raman spectroscopy analysis (Source: [19])

2.2.5 X-ray Diffractometry (XRD)

X-ray diffractometry was performed on GO powder using CuKα radiation (angular interval 2–65° 2θ, and count time 4 s per step). The peak at 11.42° is the diffraction peak of GO with a d-spacing of about 0.8 nm (Fig. 6).

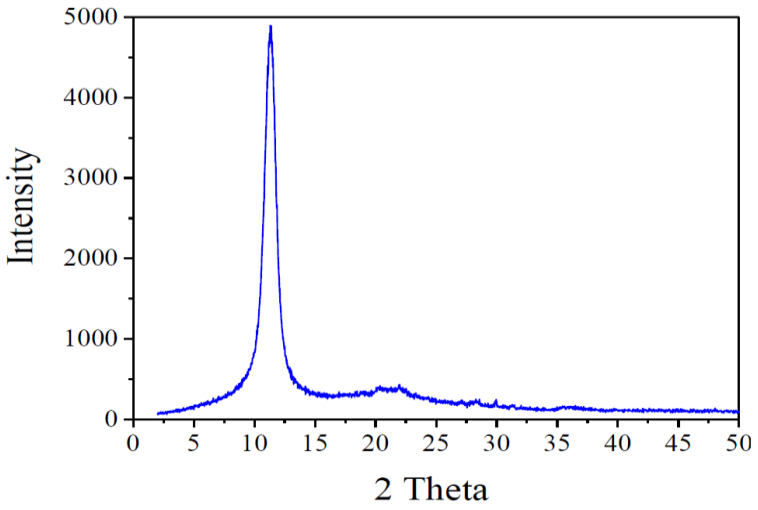


Fig. 6. XRD Peak Analysis of GO powder (Source: [19])

2.2.6 FTIR Analysis

To identify the functional groups existed in GO powder, FTIR analysis was conducted. The result of FTIR spectra displayed at 3434.5 cm^{-1}, 1622.2 cm^{-1}, 1220.1 cm^{-1} and 1049.2 cm^{-1} are corresponding to the hydroxyl (-OH), carbonyl (-C=O), epoxy (-C-O) and alkoxy (-R-O) group respectively (Fig. 7).

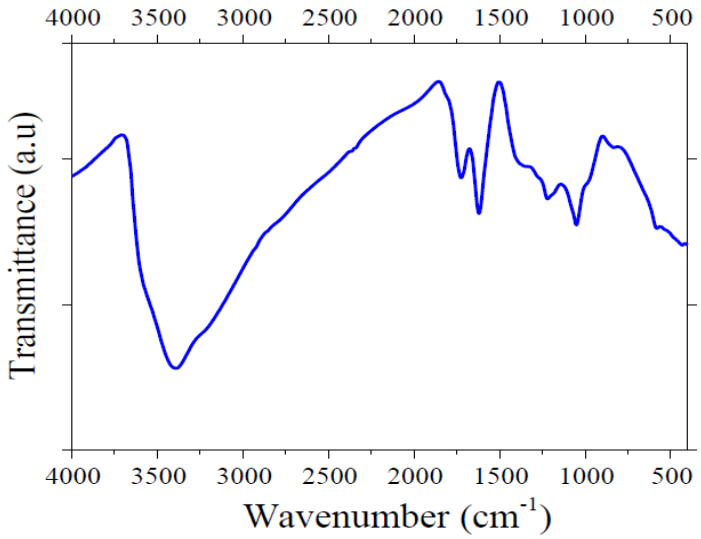


Fig. 7. FTIR Analysis of GO powder (Source: [19])

2.3 Experimental procedure

2.3.1 Design of experiment

Batch adsorption experiments were designed with the aid of Design-Expert software (Stat-Ease, Inc.USA; Version 6.0.8). Fractional factorial design with 2 blocks and

2 center points was selected to reduce the amount of experiment, for every variable, a 2^3 full factorial for the three variables consisting of eight factorial points. The variables' range and levels investigated in this study are shown in Table 1.

Table 1: Range and levels of the variables

Factor	Name	Units	Type	Low Actual	High Actual	Low Coded	High Coded
A	Contact time	Minute	Numeric	10	60	-1	1
B	pH		Numeric	5	9	-1	1
C	Initial concentration of lead	mg/L	Numeric	100	500	-1	1

2.3.2 Batch adsorption

Batch adsorption experiments were conducted to determine the quantitative uptake of lead by GO with 10 runs generated by Design-Expert software (Stat-Ease, Inc.USA; Version 6.0.8). The effect of different parameters (initial concentration, contact time and pH) on adsorption process was investigated. 1000 mg/L stock solution of lead was prepared by dissolving lead nitrate in deionized water. The adsorption experiments were conducted under different initial lead concentrations (100 mg/L, 300 mg/L and 500 mg/L) by diluting lead stock solution in a 150 mL conical flask. Then, pH value was adjusted using either NaOH (1 M) or HCl (1 M) until the required pH values (pH 5, pH 7 and pH 9). 0.01g of GO as a prepared adsorbent was added to each of the synthetic wastewater containing lead and the mixture was agitated using a laboratory shaker continuously with constant speed of 200 rpm. After a pre-determined contact time (10 min, 35 min and 60 min), the treated samples were extracted and sent to Technical Services Unit, Central Laboratory, University Malaysia Pahang to analyse the residual concentration of lead using an Inductively Coupled Plasma Mass Spectroscopy (ICP Optima 7000 DV, Perkin Elmer). The removal efficiency was calculated according to Equation 1:

$$\%\, removal = \frac{C_o - C_t}{C_t} \times 100 \qquad (1)$$

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

2.3.3 Adsorption isotherm

Adsorption isotherm is to identify the equilibrium point of lead adsorption onto GO. Four different initial concentrations of lead (100, 300, 500 and 700 mg/L) were prepared in a 150 mL conical flask. 0.01g of graphene oxide as prepared adsorbent was added to each solution and the mixture was stirred continuously using a laboratory shaker with

constant speed of 200 rpm and fixed pH (pH 9) for 60 minutes at room temperature. Then, the treated samples were extracted and sent to Technical Services Unit, Central Laboratory of University Malaysia Pahang to analyse the residual concentration of lead using an Inductively Coupled Plasma Mass Spectroscopy (ICP Optima 7000 DV, Perkin Elmer).

Adsorption isotherm is investigated using the most commonly used isotherm models which are Langmuir and Freundlich. These two isotherm models may provide useful information on upscaling and designing the adsorption system [20]. The Langmuir isotherm model is given by Equation 2:

$$\frac{1}{q_e} = \left(\frac{1}{bq_m}\right)\frac{1}{C_e} + \frac{1}{q_m} \qquad (2)$$

where, q_e is the quantity of lead adsorbed in mg/g, C_e is the equilibrium concentration (mg/L), b is the constant of adsorption equilibrium (L/mg) which is related to the energy of adsorption, and q_m (mg/g) is the maximum adsorption capacity.

Second model is Freundlich isotherm model, which is expressed in a linear form as shown in Equation (3):

$$\log q_e = \log K_f + \frac{1}{n}\log C_e \qquad (3)$$

Adsorption equilibrium is determined from the uptake-time data. For both isotherm models, linear regression values (R^2) were calculated in search of the best-fitting model in describing the adsorption process. High value of R^2 (~1.0) shows that adsorption process fitted better in that particular isotherm model.

3. RESULTS AND DISCUSSION

3.1 Batch adsorption

The result of batch adsorption was summarized in Table 2. The highest percentage removal of lead, 99.98% was observed when the value of pH was 9 after 60 minutes of contact time. The results followed by pH 9 with 10 minutes of contact time at the same value of initial lead concentration which is 100 mg/L. But, when the initial concentration of lead is increased, the percentage removal is decreased due to equilibrium concentration of a solute on the surface of an adsorbent (GO) was achieved.

The effect of pH on lead removal efficiency was shown in the graph below (Fig. 8). Adsorption is favourable at high pH due to high amount of hydroxyl ions in alkaline solution that will increase the interaction and adsorption capacity between GO and lead. The most important parameter for metal ions adsorption from aqueous solution is pH. pH will give effects on the solubility of the metal ions, counter ions concentration on the

functional groups of the adsorbent and the ionization degree of the adsorbent in the reaction [21].

Table 2: Batch adsorption experiment of GO for lead removal

Run	Contact time (min)	pH	Initial concentration of lead, C_o (mg/L)	Final concentration of lead, C_e (mg/L)	Percentage removal (%)
1	35	7	324.31	13.430	94.30
2	10	9	539.61	22.060	95.90
3	60	9	107.21	0.024	99.98
4	10	5	107.21	47.880	55.30
5	60	5	539.61	54.900	89.80
6	60	9	539.61	20.750	96.10
7	10	5	539.61	52.100	90.30
8	10	9	107.21	0.101	99.90
9	60	5	107.21	71.720	33.10
10	35	7	324.31	18.510	94.30

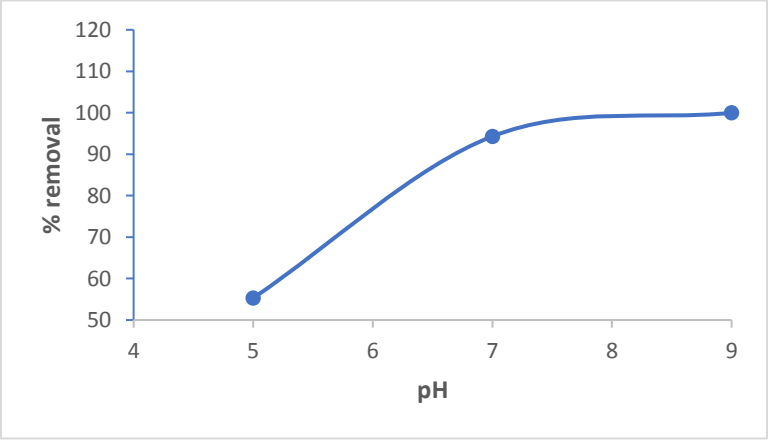


Fig. 8: Effect of pH on lead removal efficiency

3.2 Analysis of Variance (ANOVA) of Batch Adsorption

The regression parameters and graphical interpretation for each response with statistical significance were generated by Design-Expert software (Stat-Ease, Inc.USA; Version 6.0.8). The relationship between the experimental parameters and percentage removal were evaluated by generating diagnostic plots. For process optimization,

maximum product yield as well as adsorption performance were given emphasis to minimize the production cost which is extensively needed for commercialization of prepared GO. Table 3 displayed the analysis of variance values.

Table 3: ANOVA for selected model by Design Expert software

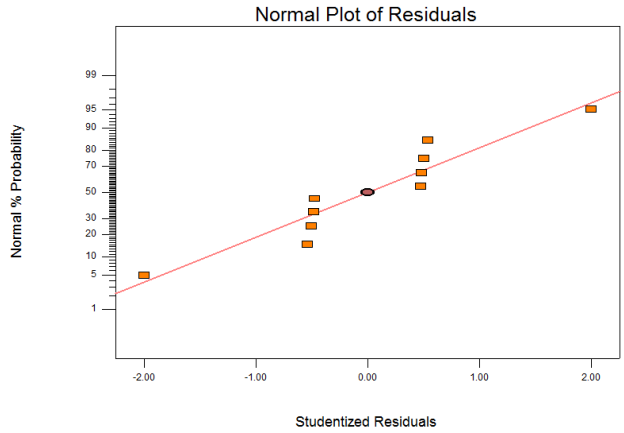
Source	**Sum of Squares**	**DF**	**Mean Square**	**F Value**	**Probability > F**	**-**
Block	46.57	1	46.57	-	-	-
Model	4020.57	3	1340.19	26.8	0.0041	significant
B	1902.83	1	1902.83	38.06	0.0035	-
C	878.22	1	878.22	17.56	0.0138	-
BC	1239.52	1	1239.52	24.79	0.0076	-
Curvature	220.99	1	220.99	4.42	0.1034	not significant
Residual	200.00	4	50.00	-	-	-
Cor total	4488.14	9		-	-	-

The model F-value of 26.80 implies the model is significant. In this case B, C and BC were chosen as significant model terms. Values of "Probability > F" for model A, B and BC less than 0.0539 indicate model terms were significant. Values of "Probability > F" greater than 0.1000 indicate the curvature are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve the model. The "Curvature F-value" of 4.42 implies the curvature (as measured by difference between the average of the center points and the average of the factorial points) in the design space is not significant relative to the noise. There is a 10.34% chance that a "Curvature F-value" this large could occur due to noise.

Table 4: Statistical values of batch adsorption

Standard deviation	7.07	R-Squared	0.9526
Mean	84.90	Adj R-Squared	0.9171
C.V.	8.33	Pred R-Squared	0.7188
PRESS	1249.99	Adeq Precision	10.965

a)



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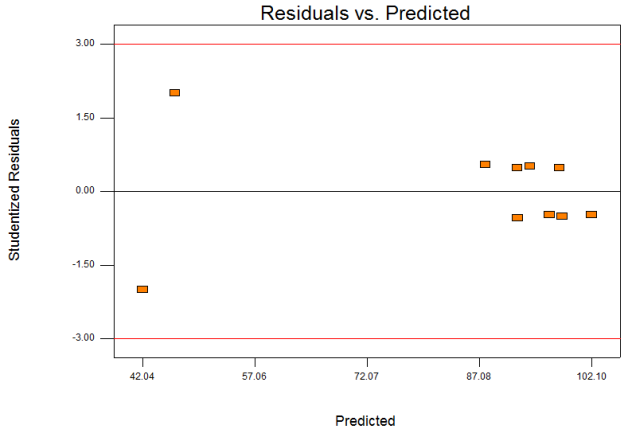

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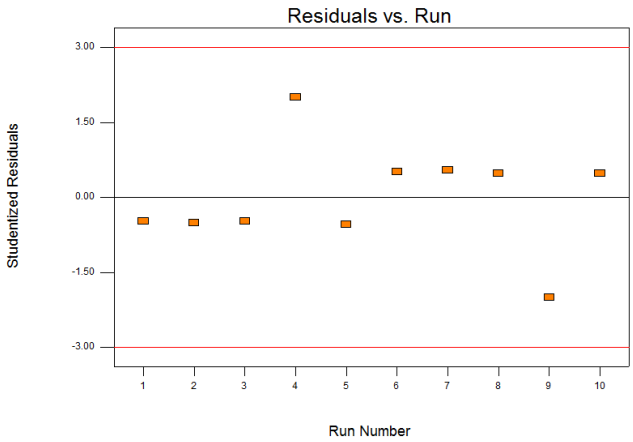

Fig. 9. Diagnostics plot of a) normal residual plot; b) residuals vs predicted and c) residuals vs experimental

All statistical values from the batch adsorption design were displayed in Table 4. The "Pred R-Squared" of 0.7188 is in reasonable agreement with the "Adj R-Squared" of 0.9171 while "Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. The ratio obtained is 10.965 hence it indicates an acceptable signal. This model can be used to navigate the design. The higher the value of CV%, the less reliable is the experiment. The CV value is a measure of residual variation of the data relative to the size of the mean. The value of predicted residual error sum of squares (PRESS) is found to be 1249.99. It is a measurement of how fit of each point in the design. The smaller the PRESS value, the better the model fits the data points.

The normal probability plot given in Fig. 9(a) shows some scattered points along the line indicated that the residuals follow a normal distribution. Residuals versus predicted plot in Fig. 9(b) indicated the residuals versus the ascending predicted response values. The plot showed a random scatter (constant range of residuals across the graph). From Fig. 9(c), the plot represented a high degree of similarity that was observed between the predicted and experimental values. From the three diagnostic plots it can be concluded that the model has satisfied the assumptions of the analysis of variance.

3.2 Adsorption isotherm

Adsorption capacity was evaluated by adsorption isotherm models, Langmuir and Freundlich. The removal efficiency was calculated and the calculation of two isotherm were presented as in Table 5 and the equilibrium graph was plotted as in Fig. 10. The linearized plot of both Langmuir and Freundlich isotherm models were represented by Fig. 11 and Fig. 12, respectively.

Table 5: Equilibrium data for Langmuir and Freundlich isotherms

Equilibrium		**Langmuir**		**Freundlich**	
C_e	q_e	$1/C_e$	$1/q_e$	$\log C_e$	$\log q_e$
2.57	1046.4	0.389105	0.000956	0.409933	3.019697731
15.92	3083.9	0.062814	0.000324	1.201943	3.489107287
42.1	4975.1	0.023753	0.000201	1.624282	3.696801815
276.6	4818.1	0.003615	0.000208	2.441852	3.68287581

From the graph, the calculated values of isotherm parameters for both Freundlich and Langmuir are presented in Table 6.

Table 6: Estimated Isotherm Parameters

Isotherm model	**Estimated isotherm parameter**		
Freundlich	n	K_f (mg/g)	R^2
	3.014	1002.7	0.8684
Langmuir	Q_{max} (mg/g)	K_L (L/mg)	R^2
	500	0.1	0.9964

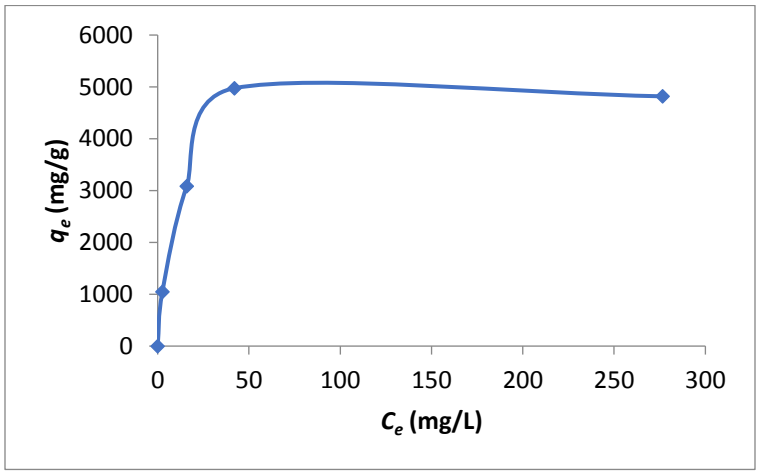

Fig. 10: Graph of equilibrium concentration of lead on the surface of graphene oxide, q_e, versus the concentration of the lead in the solution, C_e

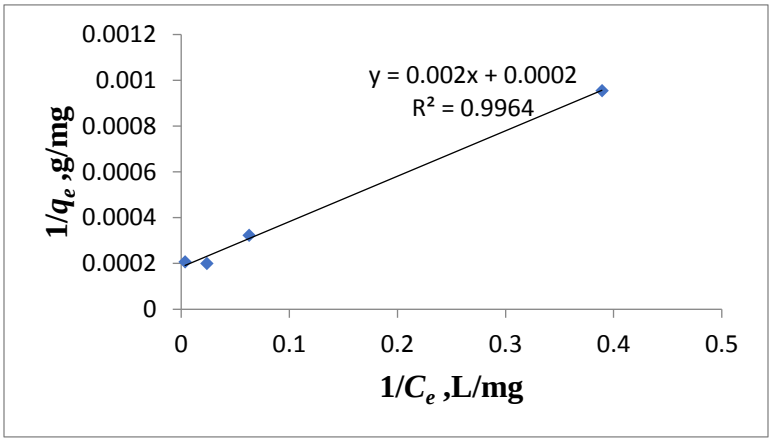

Fig. 11: Graph of Langmuir isotherm;$1/q_e$ versus $1/C_e$

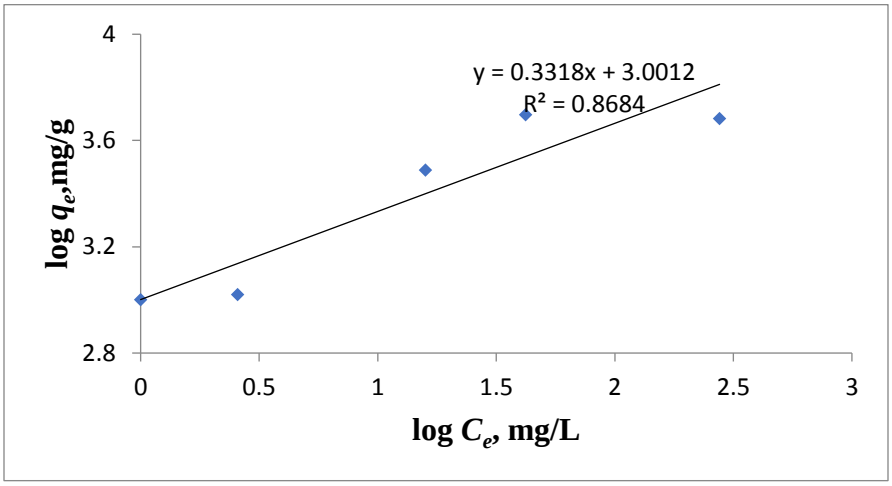

Fig. 12: Graph of Freundlich isotherm; log q_e versus log C_e

K_F is the value of adsorption capacity in which the high value of K_F shows maximum capacity meanwhile *1/n* is a measure of intensity of adsorption. Increased value of *1/n* shows high adsorption intensity occurred. From the equation, the value of K_F and *1/n* are 1002.7 mg/g and 0.3318, respectively. High regression value (R^2) which is ~1.0 represents that adsorption process is well-fitted with the Langmuir isotherm model at value of R^2 is 0.9964 compared to Freundlich isotherm model at R^2 value of 0.8684. The ideal fit of the equilibrium data from Langmuir isotherm expression predicted the monolayer adsorption of lead from synthetic wastewater by GO as an adsorbent. The maximum adsorption capacity of lead onto graphene oxide was found to be 500 mg/g.

4. CONCLUSION

In conclusion, the operating conditions of adsorption by graphene oxide were optimized by fractional factorial design. The highest percentage removal with 99.9 % of lead removal was identified at pH 9, contact time 60 minutes with 100 mg/L of lead initial concentration. The adsorption study fitted well in Langmuir isotherm and the maximum adsorption capacity of lead onto GO was 500 mg/g. The results specified a distinctive potential of GO as an effective adsorbent for lead removal due to high surface area. It is therefore believed that utilization of GO is an excellent alternative to enhance adsorption performance towards efficient wastewater treatment. This work becomes a promising research direction for graphene-based membrane fabrication for heavy metals removal in current and future membrane applications.

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