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ARTICLE

## Adsorption Studies of Lead Ions by Functionalized Graphene

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### ABSTRACT

Graphene oxide and highly reduced graphene oxide was synthesized by chemical method and characterized by FTIR, SEM and XRD. Synthesized graphene oxide (GO) and reduced graphene oxide (RGO-U) was used as adsorbent to remove lead ions from aqueous solution. Batch experiments were conducted to study the effect of pH, adsorbent dosage, contact time and initial concentration of lead ion. Maximum adsorption was done in first 45 min between pH 5 and 6. It is believed that the adsorption occurs due to binding of metal with functional groups (-C-O-C, -COOH, C=O and -OH) present at the surface of graphene oxide. This adsorption method may also be used for the removal of heavy metal ions from industrial wastewater.

### KEYWORDS

Graphene oxide, Reduced graphene oxide, Adsorption, Lead ions.

### INTRODUCTION

Public awareness has increased towards the toxic effects of water containing dissolved metal ions. Numerous industrial processes produce effluents containing heavy metal contaminants. These pollutants concentration must be reduced to meet ever increasing legislative standards and recovered where feasible. According to WHO, the metals of most immediate concern are aluminum, chromium, manganese, iron, cobalt, nickel, copper, cadmium, mercury and lead. Lead is a toxic element and has been recognized as carcinogen for human [1]. Elevated environmental level of Pb(II) ions arises from a variety of sources such as wastewater from metal plating industries, mining, pigments, vehicular emission, *etc.* Lead is hardly found in source water, but enters through the corrosion of lead pipe line supply and household plumbing material. Other contamination of lead metal is by the industries which are using lead chemicals in batteries, production of petrol, paints, ceramic glaze, food cans and in crystal glass ware [2,3].

Chemical precipitation, ion-exchange, membrane separation, reverse osmosis, solvent extraction, electrodeposition, electrocoagulation, cementation, adsorption and biosorption have been employed to remove toxic metals from water systems [4]. Most of these techniques are of high cost, produce toxic waste and unable to meet the government legislation. The

adsorption of heavy metals by a variety of substances has been the subject of many studies, but high cost of the commercially available sorbents makes their large scale applications difficult. Efforts have been made to develop methods for the removal of heavy metals from effluents using natural and waste materials as sorbents which are abundant and inexpensive, such as zeolite for lead, cadmium, zinc, chromium, nickel, copper and cobalt [5], flyash for lead [6], goethite for chromium, nickel, zinc, copper and cadmium [7], lignite for copper, cadmium and zinc [8], kaolin and ball-clay for cadmium, zinc, chromium, nickel and copper [9].

The objective of this study was to determine the sorption characteristics of Pb(II) ions onto graphene oxide. There are very few studies regarding the use of graphene oxide as sorbent for example, graphene oxide (GO) used as a sorbent for the preconcentration of trace of Co(II), Ni(II), Cu(II), Zn(II) and Pb(II) [10]. Graphene oxide nanosheets have also been exploited as sorbents for heavy metal ions [11]. Graphene oxide has also been utilized to remove divalent metal ions from aqueous solutions [12]. Tremendous affinity of graphene toward metal ions in solutions creates a window of its applications in solid phase extraction technique. In the present work, new adsorbents graphene oxide and reduced graphene oxides (RGO-U) were synthesized and characterized. Graphene oxide is prepared from graphite (allotrope of carbon), which is cheaper and easily available in Pakistan. Graphite composed of many layers of graphene, while graphene may be monolayer or bilayer [13]. GO surface contains a number of functional groups such as  $-C-O-C$ ,  $-COOH$ ,  $C=O$  and  $-OH$  [14]. Presence of these functional groups on the GO surface makes it an important binder for the metals ions. These functional groups increase the hydrophilic properties of synthetic graphene oxide and it is much more soluble in water rather than reduced graphene oxide (RGO) (Fig. 1a).

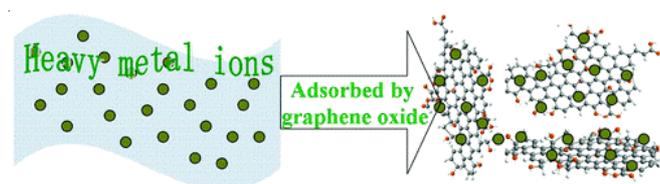


Fig. 1a. Binding of metal ions on the surface of graphene oxide

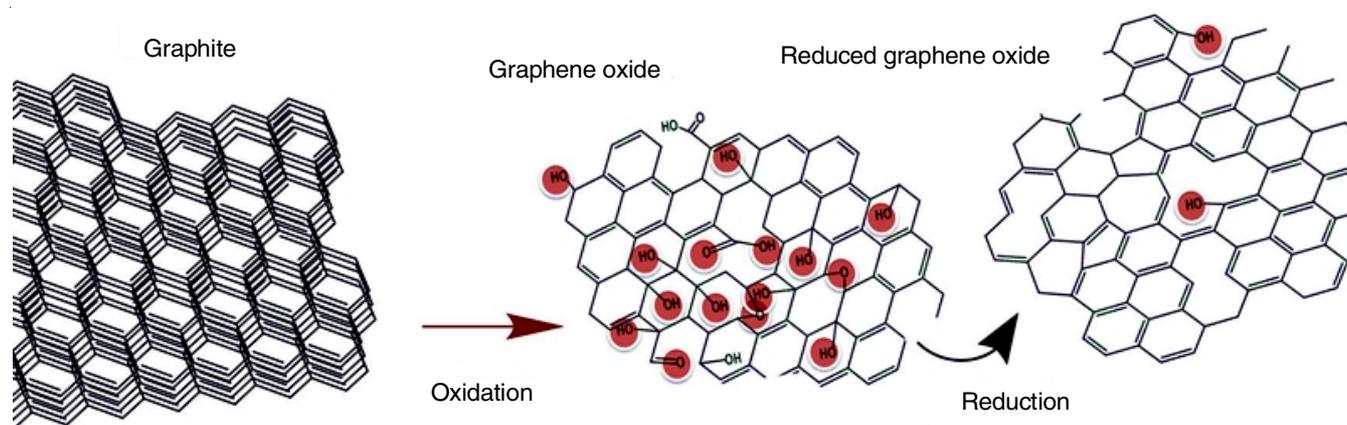


Fig. 1b. A schematic diagram for the conversion of graphite into graphene oxide and reduced graphene oxide

## EXPERIMENTAL

Graphite powder,  $H_2SO_4$  (98 %),  $H_2O_2$  (30 %), HCl, urea,  $KMnO_4$  and all other chemicals were reagent grade and purchased from Merck. A stock solution (1000 ppm) of Pb(II) ions was prepared from  $Pb(NO_3)_2$  in double distilled deionized water. Further concentrations were prepared by the successive dilution of the stock solution. The pH of the solution was adjusted by adding 0.1 M NaOH or 0.1 M HCl. The adsorption of Pb(II) ions onto graphene oxide and reduced graphene oxide was carried out at room temperature.

**Synthesis of graphene oxide:** Graphene oxide was synthesized by Hummers process [15]. 0.50 g of graphite particles was properly mixed with 100 mL of  $H_2SO_4$ . 12 g of  $KMnO_4$  was slowly added into the mixed material, during the addition the temperature was maintained between 0 and 4 °C in an ice bath. After the complete addition of  $KMnO_4$ , the mixture was slowly heated at about 40 °C for 30 min, followed by addition of 20 mL of deionized water and heated at 95 °C for 30 min. The mixture was further diluted by adding 300 mL of distilled deionized. Finally 40 mL of 35 %  $H_2O_2$  was added and left for about 1 h. Filtered off the solution by suction pump and washed the filtrate with hydrochloric acid so that solution becomes free from  $SO_4^{2-}$  ions followed by washing with distilled deionized water and dried.

**Reduction of graphene oxide:** Graphene oxide thus obtained was further treated with 1 M urea solution to obtain reduced graphene oxide. 6 g of urea was dissolved in 100 mL of water then treated with a weighed amount of graphene oxide and put the solution in oven at 95 °C for about 5 h. Clearly noted the colour change of the solution from brown to dark black (Fig. 1b). Filtered off the colloidal solution and dry it.

**Characterization of adsorbent:** Characterizations of GO and RGO-U were performed by Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM) and X-ray diffraction (XRD) technique. FTIR spectra was (KBr pellets) recorded by FTIR-4100 type A, in the polymer laboratory at UET Lahore, Pakistan. X-Ray diffraction (XRD) spectroscopy was recorded on Bruker D8 Advance at National Centre for physics (NCP), Islamabad, Pakistan, Having copper anode using  $k-\alpha_1$  wavelength 1.5406 and  $k-\alpha_2$  wavelength 1.54439. The operating current was 40 kv. The morphology of the adsorbents was investigated by the scanning electron

microscopy (SEM) at Centre for advance studies in physics (CASP) Government College University, Lahore, Pakistan and it was carried on JSM-6480.

**Adsorption experiments:** All the experiments were performed by using batch adsorption technique. Lead(II) ions solution of different concentrations was treated with known amount of functionalized graphene for about 24 h to achieve the equilibrium. The pH was adjusted by using buffer solution of known pH or by adding negligible amount of 0.1 M NaOH or 0.1 M HCl. Functionalized graphene was treated with 200 mL of 100 mg/L of lead ion solution. The concentration of Pb(II) was measured by using atomic absorption spectrophotometer (AAS). The adsorbed amount of the lead ion was calculated from the difference between equilibrium concentration and the initial concentration. The adsorption capacity ( $q_e$ ) and the adsorption percentage were calculated from the following equations and used further for Langumir adsorption isotherm.

$$q_e = \frac{C_o - C_e \times V}{m} \quad (1)$$

$$\text{Adsorption (\%)} = \frac{C_o - C_e}{C_o} \times 100 \quad (2)$$

In these equations  $C_o$  is the initial concentration,  $C_e$  is the equilibrium concentration of Pb(II) ions in (mg/L);  $V$  is the volume of lead ion of known concentration unit and  $m$  is the mass of functionalized graphene in grams. To check the accuracy in results the unabsorbed metal concentration in solution was also calculated by titration method.

## RESULTS AND DISCUSSION

**FTIR:** Oxidation of graphite particles was carried out in the presence of  $\text{KMnO}_4/\text{H}_2\text{SO}_4$ . The product obtained is the brownish colour graphene oxide. Complete reduction of GO was performed in the presence of urea. The colour of the reduced product changes from brownish to black. To study the impact of oxidation and reduction FTIR study of the material was performed. The FTIR spectra of GO and RGO-U completely explain the fruitful oxidation of graphite particles to graphene oxide and explained the reduction of graphene oxide to graphene as shown in Fig. 2.

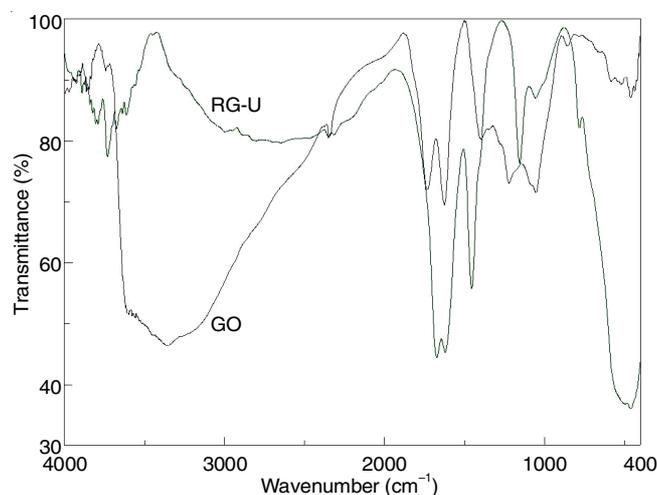


Fig. 2. FT-IR spectra of GO and RGO-u

The existence of different types of oxygen functionalities in graphite oxide at  $3364 \text{ cm}^{-1}$  a very broad peak shows the presence of OH group. A peak at  $1735 \text{ cm}^{-1}$  shows the presence of C=O. Similarly a peak at  $1222 \text{ cm}^{-1}$  of medium intensity shows the presence of C-O stretching. The peak appeared at  $1625$  and  $1395 \text{ cm}^{-1}$  could be recognized to the skeletal vibration of C=C double bond from oxidized graphite ring and due to C-O-C stretching band respectively. When the graphite oxide is reduced to graphene the spectra clearly shows the absence of O-H and C=O stretching band peak and a peak appears at  $1620 \text{ cm}^{-1}$  might be due to C=C skeletal vibration. Stretching vibration peak appeared at  $1054 \text{ cm}^{-1}$  in both spectra show the presence of C-C skeletal vibration of the graphite ring. These results show that after reduction the structure and hybridization is  $sp^2$  [14].

**SEM:** The morphology of the GO and RG-U were investigated by the SEM. The SEM micrographs of the prepared samples were taken at 500 magnifications, which are shown in Fig. 3a and 3b. The surfaces of the adsorbents are homogeneous but spots at some places might be due to presence of functional groups.

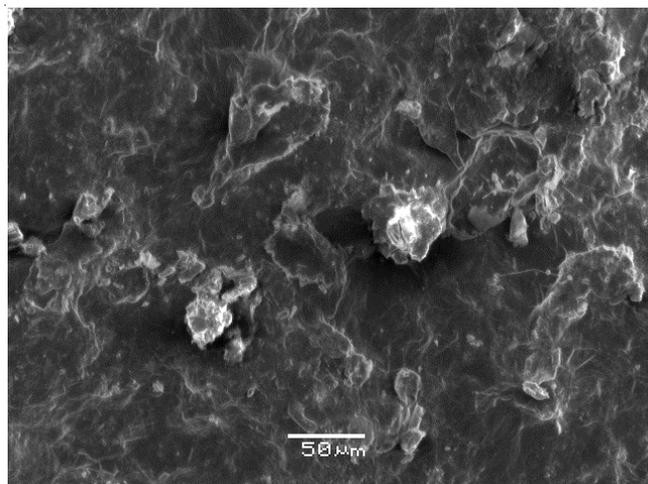


Fig. 3a. SEM image of graphene oxide

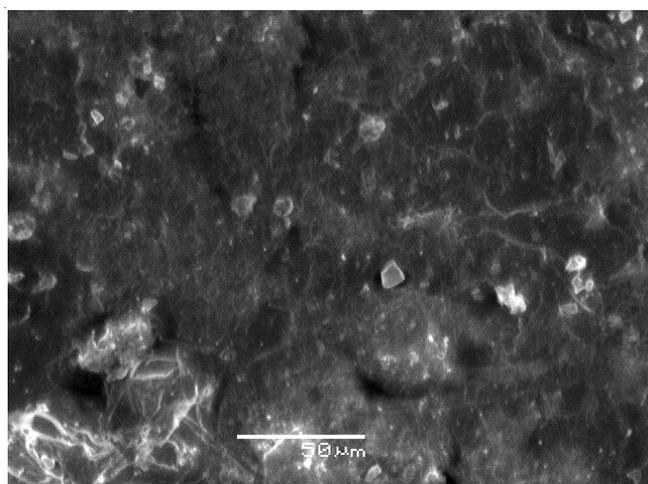


Fig. 3b. SEM image of reduced graphene oxide

**XRD:** In Fig. 4a, the strong peak of  $2\theta$  at  $11.6^\circ$  in compliance to an interlayer spacing of about  $0.76 \text{ nm}$  conforming the

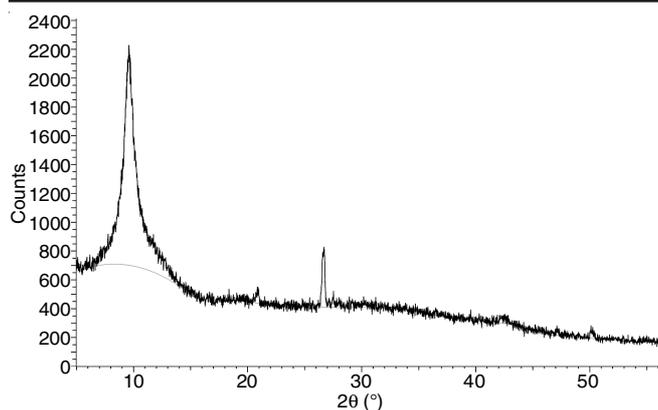


Fig. 4a. XRD of graphene oxide

presence of oxygen functional group. For chemical reduction to synthesize the highly reduced graphene equal mole ratio of graphene oxide and urea were treated. XRD analysis of this reduced graphene oxide show (Fig. 4b) an intense peak at approximately 23 and small peaks at 25 and 30 might be due to amino group. Higher values of  $2\theta$  indicate that interlayer spacing reduced to 0.34 nm [14].

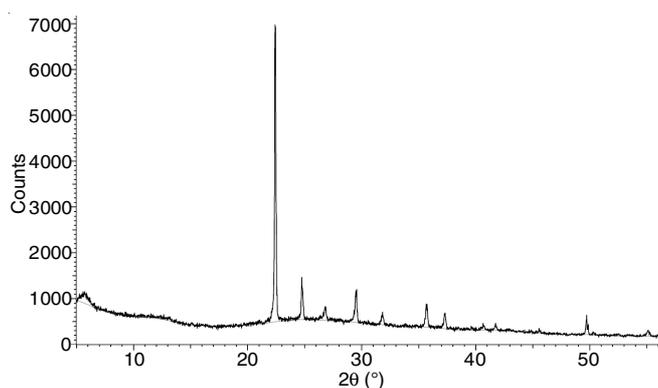


Fig. 4b. XRD of reduced graphene oxide

**Effect of pH:** Different parameter such as a selection of a suitable sorptive medium, amount of sorbent, initial concentration of sorbate, the contact time between the two phases control the sorption of metal ions at trace and subtrace levels [16]. Therefore, the sorption of Pb(II) ions onto graphene oxide and reduced graphene oxide is optimized first keeping all the experimental conditions constant except one, which is under investigation.

The pH of sorptive medium is the major factor that controls the binding of sorbate onto the surface of graphene oxide and reduced graphene oxide. The adsorption properties of Pb(II) ion were studied at pH in the range of 2-8. The maximum absorption of Pb(II) ions was noticed at pH 5.5. There is an increase in removal capacity of graphene oxide upto pH 5.5, beyond this pH value the adsorption process occur but at a slower rate as shown in Fig. 5. The dominant species upto pH 6 would be  $Pb^{2+}$ , at pH 7  $Pb^{2+}$  (82 %),  $Pb(OH)^+$  (18 %), at pH 8  $Pb(OH)^+$  (58 %),  $Pb^{2+}$  (38 %). And polymeric specie of  $Pb_3(OH)_2^{2+}$  (3 %) and  $Pb(OH)_2$  ((1 %)) [17].

**Effect of contact time on adsorption capacity:** Contact time is also an important parameter in the removal efficacy of the sorbent. It provides the information about the reaction

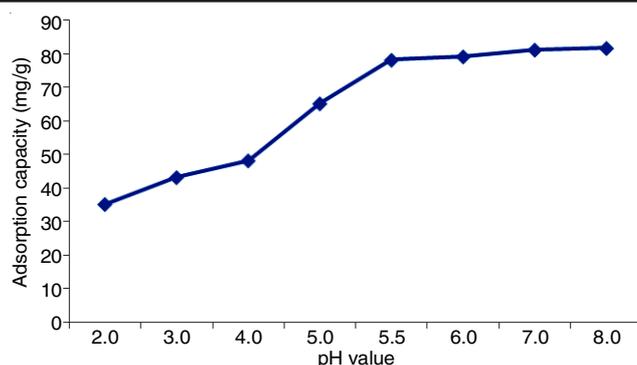


Fig. 5. Effect of pH on the removal of lead ion

kinetics of the sorption phenomenon. In present study a complete surface coverage is achieved after 60 min. There after almost horizontal line is observed. This shows that maximum sorption is within the first 60 min of the reaction time (Fig. 6).

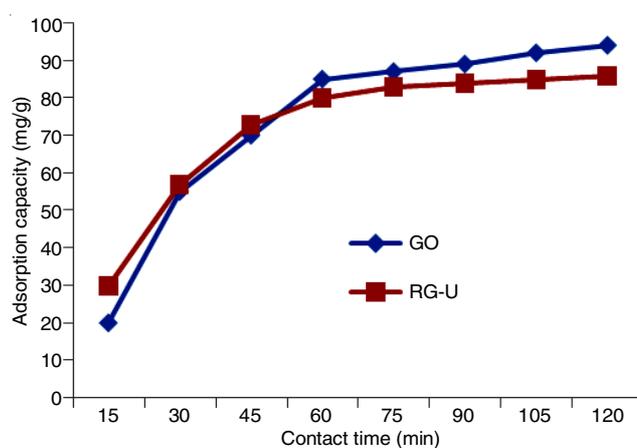


Fig. 6. Effect of contact time on the removal of lead ion

**Effect of adsorbent dosage:** Influence of the amount of sorbent is examined from 0.25 to 3.0 g using 60 min shaking time at 150 rpm speed at pH 5.5. The percent sorption first increases and attains a maximum value (about 90 %) around 1.5 g and remains almost constant up to 3 g. Results are shown in Fig. 7 [11]. Result suggest that increasing amount of sorbent create an atmosphere of over saturation which hinders the accumulation of Pb(II) ion after 1.5g. It is an indication of the effectiveness of sorbent in lower amount.

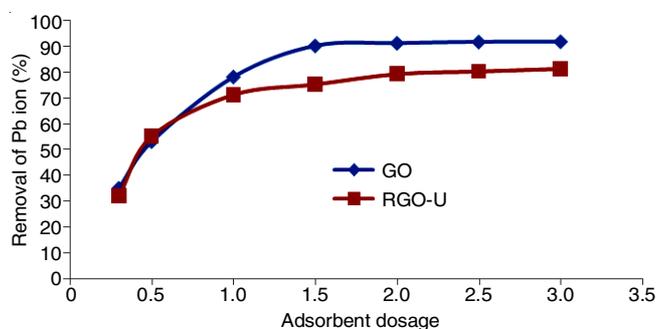


Fig. 7. Effect of adsorbent quantity on the removal of lead ion

### Adsorption isotherm

**Langmuir adsorption isotherm:** The adsorption equilibrium of lead ions was modeled by Langmuir adsorption iso-

TABLE-1  
PARAMETERS ASSOCIATED WITH LANGMUIR AND FREUNDLICH MODELS

Metal ions	Materials	Langmuir adsorption isotherm			Freundlich isotherm		
		Q <sub>o</sub> (mg/g)	B (L/mg)	R <sup>2</sup>	K <sub>f</sub> (mg/g)	N	R <sup>2</sup>
Pb(II)	Graphene oxide	94	0.122	0.9309	66.17	2.23	0.93
	Reduced graphene oxide	86	0.035	0.8840	13.00	1.27	0.80

therm. It explains the monolayer adsorbent and the binding of metal at the outer surface of the adsorbent. Langmuir parameters were calculated from equation [18]:

$$\frac{C_e}{q_e} = \frac{1}{bQ_o} + \frac{C_e}{Q_o}$$

where, C<sub>e</sub> (mg/L) and q<sub>e</sub> (mg/g) are the equilibrium solution phase and solid phase concentration respectively. b (L/g) is the Langmuir constant and Q<sub>o</sub> (mg/g) is the maximum adsorption capacity. The plot of C<sub>e</sub>/q<sub>e</sub> versus C<sub>e</sub> should be a straight line in order for an adsorption process to follow Langmuir isotherm. From Table-1 and graph it can be seen that Langmuir adsorption model shows the good agreement with the experimental data with a correlation coefficient of 0.9309 for graphene oxide and 0.884 for reduced graphene oxide.

A dimensionless constant, commonly known as a separation factor (R<sub>L</sub>) [19] represented as:

$$R_L = \frac{1}{1 + bC_o}$$

where b (L/mg) represents Langmuir constant and C<sub>o</sub> (mg/L) represents adsorbate initial concentration. This dimensionless factor is used to assess whether adsorption process is favourable or not under the applied conditions. If the value of R<sub>L</sub> > 1 then the adsorption process is unfavourable; if R<sub>L</sub> = 1 adsorption process is linear; and if 0 < R<sub>L</sub> < 1 adsorption is favourable and if R<sub>L</sub> = 0 adsorption is irreversible.

**Freundlich model:** The experimental data has been used for analyzing the Freundlich isotherm by following equation:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e$$

where q<sub>e</sub> is the adsorption amount of metal, C<sub>e</sub> is the equilibrium concentration of metal. The constant K<sub>f</sub> represents adsorption capacity and n is the Freundlich intensity constant. The graph is plotted between log q<sub>e</sub> vs. log C<sub>e</sub>. From the intercept and slope the calculated values of K<sub>f</sub> and n for GO was 66.17 mg/g and 2.23, respectively. For RGO its values were 13 mg/g and 1.27.

In essence, graphene oxide has two important characteristics: (a) it can be produced using inexpensive graphite as raw material by cost-effective chemical methods with a high yield and (b) it is highly hydrophilic and can form stable aqueous colloids to facilitate the assembly of macroscopic structures by simple and cheap solution processes, both of which are important to the large-scale uses of graphene. A key topic in the research and applications of graphene oxide is the reduction, which partly restores the structure and properties of graphene.

## Conclusion

From the experimental adsorption data, it is clear that graphene oxide and reduced graphene oxide are good absorber for the treatment of wastewater. The percentage removal of lead ion for graphene oxide is more than the percentage of reduced graphene oxide, because graphene oxide has many different functional group and provide different sites for complexation. Batch experiments were conducted and the results showed that removal of lead ions are pH dependent, time dependent and adsorbent quantity dependent. Both adsorption model Langmuir and Freundlich have significant correlation with experimental data.

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