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# Application of Graphene Oxide for the Removal of Textile Dye FD-R H/C from Aqueous Solution

**Dewan M. Mahmudunnabi[1], Md. Zahangir Alam[1,*], Md. Nurnabi[1,*]**

[1]*Department of Applied Chemistry and Chemical Engineering*
*University of Dhaka, Dhaka 1000, Bangladesh.*

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nnabi@du.ac.bd,
zahangir@du.ac.bd
*Phone: +8801711577225;*
*Fax: +880-2-9667222*

## Abstract

In this study, graphene oxide (GO) was prepared by modified Hummer's method and Characterized by FTIR, XRD and elemental analysis. Prepared GO was used as an adsorbent for the removal of a synthetic anionic dye, FD-R H/C used in textile industries. Effects of solution pH, adsorbent dose, dye concentration, contact time on adsorption of dye were studied in this study. The Langmuir and Freundlich isotherm models have been applied to explain the distribution of adsorbate on adsorbent surface and the results showed that the adsorption of FD-R H/C on GO followed the Langmuir model. The theoretical maximum sorption capacities found from the Langmuir isotherm was 151.29 mg/g at pH of 2. The experimental data were analyzed using pseudo-first-order and pseudo-second-order models and the result showed that adsorption of FD-R H/C on GO matched well with pseudo-second-order kinetic model. The thermodynamic analyses showed that the adsorption process is more spontaneous at lower temperature and it is a physisorption process.

## 1. Introduction

In Bangladesh textile sector provides a substantial amount of jobs and earns vast foreign currency. It also produces large amount of effluent containing about two percent of the used dye [1]. Dyes are colored, toxic and non-biodegradable. So, they enter into the food chain and affect human and other living beings [2]. To treat this effluent several physical, chemical and biological decolorization methods are used. But adsorption gives the best result to remove coloring materials [3]. Activated carbon is mainly used as adsorbent because of its excellent adsorption capacity. But owing to high cost of activated carbon, this technique is not well accepted by the industrialists [4]. Some low cost and abundant non-conventional adsorbents such as peat, bagasse, rice husk, sawdust, fly ash, clay materials are also used as adsorbents for the removal of dyes [5-8]. But these materials have comparatively low adsorption capacity, retention time is high and regeneration is difficult.

Now-a-days, scientists give attention to graphene and its derivatives for the removal of dyes due to its high surface area. Graphene oxide is a derivative of graphene which can be prepared by simple oxidation of graphite powder using strong oxidizing agent. This oxidation helps layer separation as well as introduces oxygenated functional group to graphite structure which makes it hydrophilic. Many research groups have investigated the removal of dyes using graphene or its derivatives [9, 10]. But the preparation of GO is very costly and they are applied for the removal of model dyes, mainly for cationic dyes. So, it is very significant to develop attractive and cheap technique to prepare graphene and its derivatives and their applications for the removal of commercially used dye. In this study, GO was produced from graphite powder using modified Hummers' method and applied in the removal of commercially used synthetic anionic dye FD-R H/C from aqueous solution.

## 2. Material and Methods

### *2.1. Materials*

The used dye FD-R H/C was collected from local textile industry. Graphite powder and hydrogen peroxide (30%) were bought from Merck (India), sulfuric acid (98%), nitric acid (65%) were obtained from Active Fine Chemicals (Bangladesh), potassium permanganate was purchased from Merck (Germany), sodium nitrate was purchased from Uni-chem (China) and hydrochloric acid (37%) was purchased from RCI Labscan (Thailand).

### *2.2. Synthesis of graphene oxide (GO)*

Graphene oxide was prepared by modified Hummers' method [11]. Briefly, 5 g of graphite powder was dispersed in 125 ml acid mixture (concentrated $H_2SO_4$ and concentrated $HNO_3$ in 3:1 ratio) with vigorous stirring in a water bath. Then 15 g of $KMnO_4$ and 2.5 g of $NaNO_3$ were added slowly to the flask and stirred for 2 hr. After that water bath was removed and the mixture was stirred overnight to afford thick paste. Then 150 ml of deionized (DI) water was added and stirred with heating at 35 °C to produce deep brown reaction mixture. Then 420 ml of DI water was added to the mixture followed by the addition of 20 ml of 30% $H_2O_2$ and the color changed to bright yellow. Finally, 5% HCl (500 ml) was added to remove the manganese ions from graphene oxide. The synthesized GO was washed with DI water several times until the pH of the reached to 7.

## 3. Results and discussion

### *3.1. Physicochemical characteristics of graphene* oxide

Elemental analysis provided information about the chemical composition of prepared graphene oxide. From the elemental analysis (Vario micro CHNS) it was found that GO contained 51.54 %, 40.99%, 3.085%, 4.08% and 0.395% of oxygen, carbon, hydrogen, nitrogen and sulfur, respectively. These values are very much consistent with documented value [12]. The chemical structure of GO was studied by Fourier transformed infrared (FT-IR) spectroscopy (IR Prestige-21, Fourier Transform Infrared Spectrophotometer, SHIMADZU, Japan). In FTIR spectra (Figure 1) peaks are observed at 1620 $cm^{-1}$, 1708 $cm^{-1}$ and 3408 $cm^{-1}$ attributable to C=C, C=O and –OH groups, respectively. These indicate the presence of -COOH group in GO, which is absent in graphite powder.

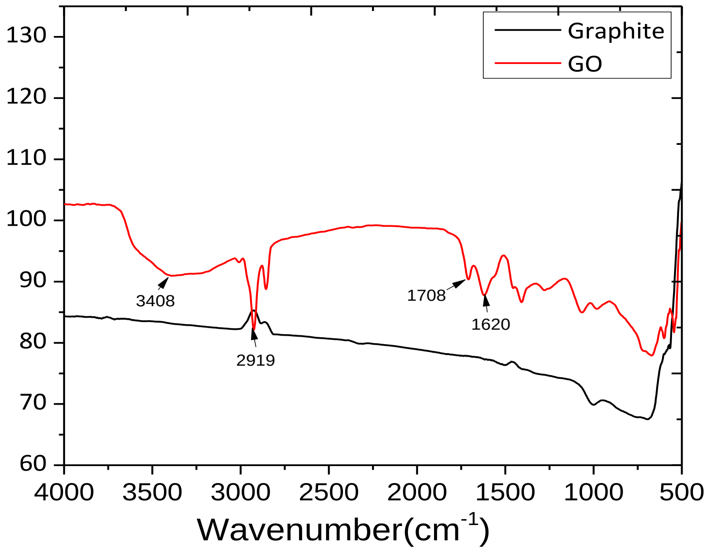

**Figure 1:** FT-IR spectrum of graphite powder and Graphene oxide

X-ray diffraction of graphite and GO was performed on Multipurpose X-ray diffraction system (Ultima IV) with Cu Kα radiation ($\lambda$=0.154 nm, 40 kV, 1.64 mA). Figure 2 showed the XRD patterns of graphite and GO. A sharp and strong peak was observed at $2\theta$ = 26.73°for  damage of regular crystalline pattern of graphite and formation of oxygenated functional groups in GO structure.

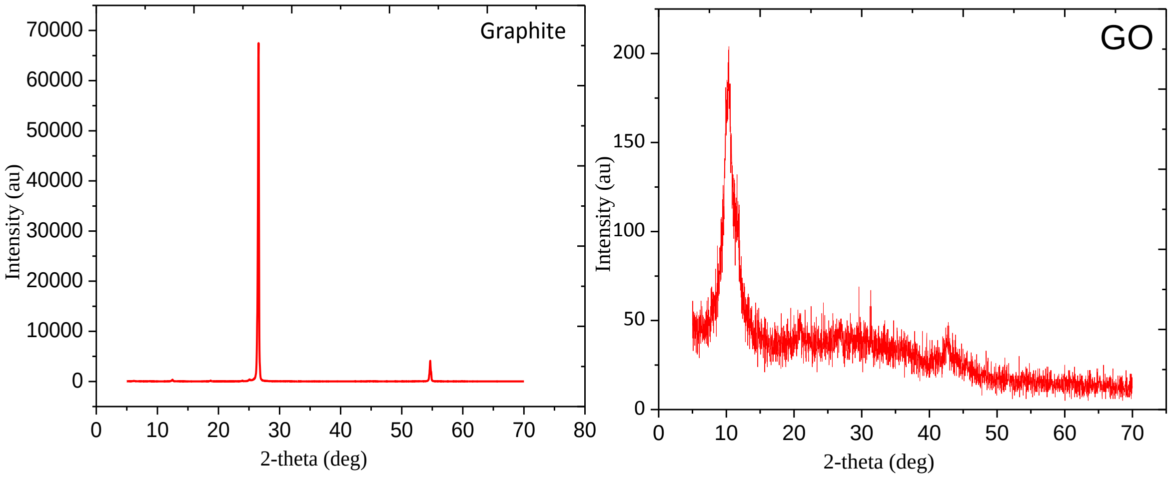

**Figure 2:** XRD patterns of graphite and GO

### *3.2. Characterization of dye FD-R H/C*

As dye FD-R H/C was unknown, the functional groups present in the dye was determined by FT-IR spectroscopy. FTIR spectra (Figure 3) confirmed the presence of $-SO_3$, -OH groups in the dye. FD-R H/C. The presence of sulphur in the dye was also confirmed by Lassaigne's test.

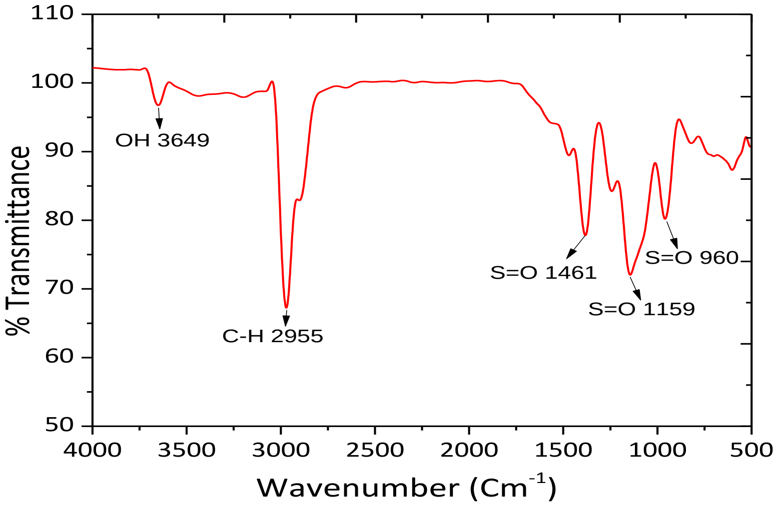

**Figure3:** FT-IR spectrum of dye FD-R H/C

### *3.3. Adsorption studies*

In this study, a standard curve was prepared using 05-200 ppm dye solution by spectrophotometric method  (UV-1700 Pharma Spec UV-VIS Spectrophotometer, SHIMADZU, Japan) at 660 nm. The adsorption capacity q (mg/g) was calculated by the following equation-

$$q = \frac{(C_0 - C_t) \times V}{W} \qquad (1)$$

where, $C_0$ = initial concentration of dye (ppm), $C_t$ = concentration of dye (ppm) at time t, V = volume (L) of the

dye solution and W= mass (g) of the adsorbent.

The equilibrium adsorption capacity qe (mg/g) was calculated by the following equation-

$$q_e = \frac{(C_0 - C_e) \times V}{W} \tag{2}$$

where, $C_e$= concentration of dye (ppm) at equilibrium condition.
And % of removal was calculated by the formula-

$$\% \text{ removal} = \frac{(C_0 - C_t) \times 100}{Co} \tag{3}$$

### 3.3.1. *Effect of pH*

pH of the solution is a very important parameter in adsorption study because pH can change the surface charge of adsorbent and dye. To study the effect of pH on adsorption, the experiments were carried out using 10 ml of 200 ppm dye solution at the range of pH of 2-10. Then 10 mg of disperse GO were added in each solution and the mixtures were shaken at 200 rpm for 60 minutes. After that the mixtures were filtered and concentration changes were determined by UV-Vis spectroscopy. The result showed that maximum adsorption capacity was 133.99 mg/g (Figure 4a) at pH of 2 and the adsorption capacity decreased with an increase in pH of the solution.

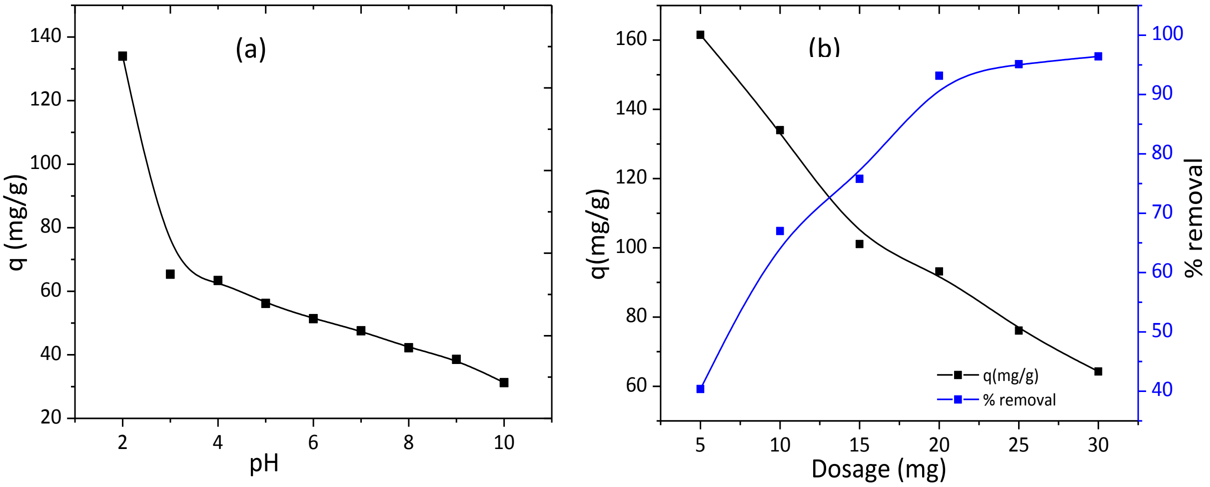

**Figure 4:** Effect of pH (a) and dosage (b) on adsorption capacity

It is assumed that at higher pH carboxylate group of GO gets dissociated and surface negative charge of GO increased with an increase in pH. Simultaneously at higher pH the dye exists as sulfonic acid salt rather than sulfonic acid, and sulfonic acid salt is more water soluble compared to sulfonic acid. So, both the phenomena associated with the adsorbent surface and dye molecule favored higher adsorption at lower pH.

### 3.3.2. *Effects of dosage*

Dose of adsorbent is also a very important parameter for adsorption process. Optimization of the dose of adsorbent was carried out by using 200 ppm solution at pH of 2. The process was carried out for 10 minutes in 05-20 mg dose. It is apparent from Figure 4b that with the increase of adsorbent dose adsorption capacity decreased but % of removal increased. It is readily understood that with the increase of adsorbent dose, the amount of adsorbate per unit mass of adsorbent decreased. As a result with the increase of adsorbent for same concentration and time, adsorption capacity decreased and % of removal increased.

### 3.3.3. *Effects of contact time and dye concentration*

To study the effect of contact time and concentration, solutions of different concentrations at pH of 2 were prepared and 10 mg of disperse GO were added to each solution. Then adsorption test was carried out at various intervals of time ranging from 2-60 minutes with 200 rpm constant agitation. The results showed that adsorption capacity increased with the increase of time and after 30 minutes it became almost constant (Figure 5). The equilibrium adsorption capacity increased with the increase of dye concentration because of increase in concentration gradient between the dye molecule the bulk solution.

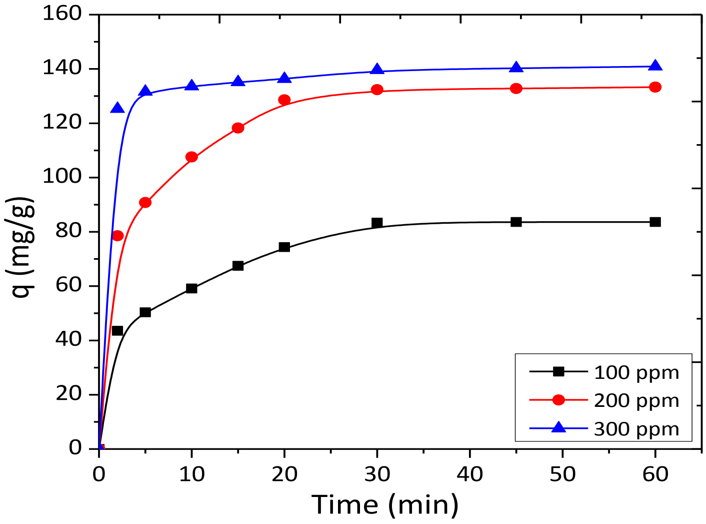

**Figure 5:** Effect of time and concentration on adsorption capacity

### *3.4. Adsorption isotherms*

To determine the distribution of adsorbate molecules on the adsorbent surface Langmuir and Freundlich isotherm models were studied. Langmuir isotherm assumes monolayer adsorption of adsorbate and Freundlich isotherm assumes multilayer adsorption [13, 14]. The linear form of the Langmuir isotherm is-

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{1}{q_m} C_e \tag{4}$$

where, $C_e$ is equilibrium concentration, $q_e$is the equilibrium adsorption capacity, $q_m$is the maximum theoretical adsorption capacity and b is the Langmuir constant.

Langmuir model can be tested by plotting $C_e/q_e$ versus $C_e$ (Figure 6a). The theoretical maximum sorption capacity $q_m$ calculated from the slope was 151.29 mg/g. The separation factor $R_L$ is related to Langmuir constant b through the equation-

$$R_L = \frac{1}{1+C_m b} \tag{5}$$

where, $C_m$ is the maximum initial dye concentration used in the adsorption experiments. $R_L$ gives a qualitative measure of the favourability of the adsorption process; $R_L$ between 0 and 1 indicates a favorable monolayer adsorption process. In our study, $R_L$ value is 0.038. This indicates a very favorable monolayer adsorption process.

The Freundlich isotherm can be described linearly as-

$$\ln q_e = \ln K_F + \frac{1}{n} lnCe \tag{6}$$

The model parameters n can be estimated by plotting $\ln C_e$ versus $\ln q_e$ (Figure 6b). Good adsorption is obtained when n = 2-10 while difficult adsorption at n=1-2 and poor adsorption at n < 1). In this study value of n was found to be 4.184 (Table 1).

### *3.5. Adsorption kinetics*

Adsorption kinetics are of great significance to evaluate the performance of an adsorbent. In this study two kinetic models were employed to describe the adsorption process. In 1998 Lagergren presented a first-order rate equation to describe the kinetic process (Figure 7). The linear form of pseudo-first order rate equation can be represented as follows:

$$\log(q_e - q_t) = \ log q_e - \frac{k_1}{2.303} t \qquad (7)$$

where $q_e$ and $q_t$ are the adsorption capacities at equilibrium and at time t, respectively (mg/g); $k_1$ is the rate constant of pseudo-first order adsorption (L/min).

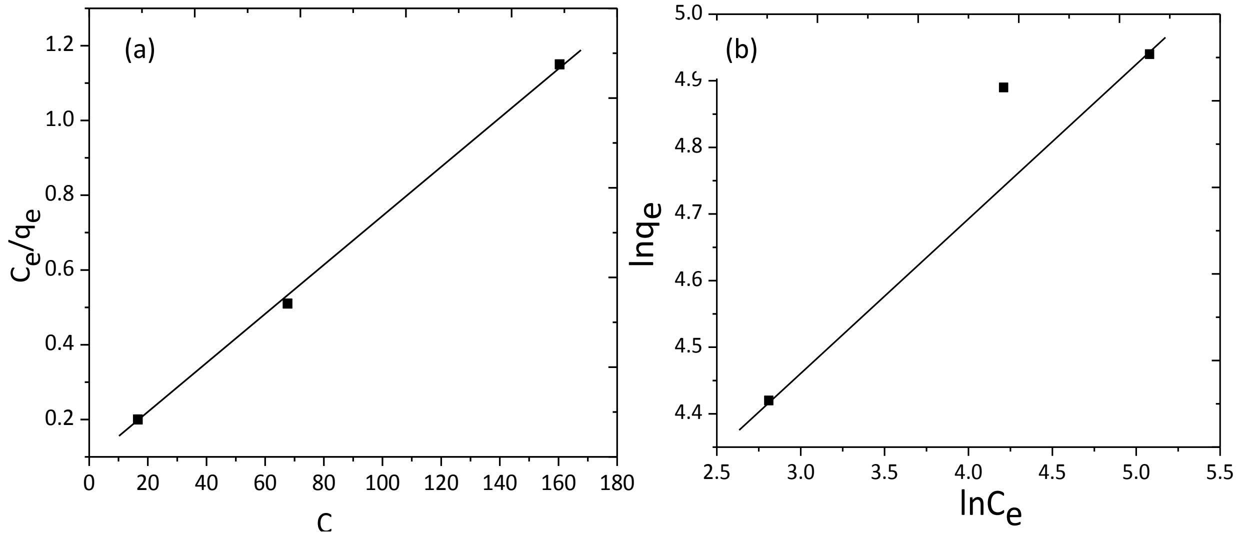

**Figure 6:** Langmuir adsorption isotherm (a) and Freundlich adsorption isotherm (b)

**Table 1:** Theoritical values of qm, b, $R_L$, n, $K_F$ and $R^2$

| Name of isotherm | $q_m$(mg/g) | $R^2$ | b, $Lmg^{-1}$ | $R_L$ | , n | $K_F$ |
|---|---|---|---|---|---|---|
| Langmuir Isotherm | 151.29 | 0.999 | 0.0847 | 0.038 | - | - |
| Freundlich isotherm | - | 0.911 | - | - | 4.184 | 44.03 |

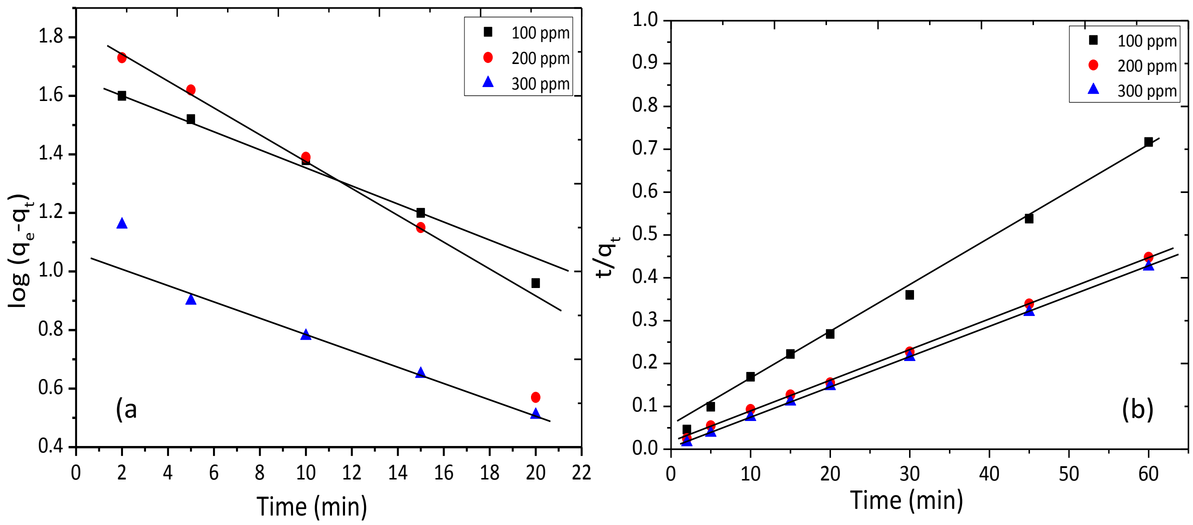

**Figure 7:** Peudo-first order adsorption kinetics (a) andpseudo-second order adsorption kinetics (b)

In 1995 Ho and Mckay presented a pseudo-second order rate equation. The linear form of this equation is:

$$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{1}{q_e} t \qquad (8)$$

where, $k_2$ is the rate constant of pseudo-second order adsorption (g/mg min).

**Table 2:** Kinetic parameters of pseudo-first-order and pseudo-second-order kinetics

| Types of kinetics model | Parameters | Units | Initial concentration of dye | | |
|---|---|---|---|---|---|
| | | | 100 ppm | 200 ppm | 300 ppm |
| Pseudo-first order | $q_{e,exp}$ | mg/g | 83.39 | 132.38 | 139.57 |
| | $q_{e,cal}$ | mg/g | 49.66 | 84.92 | 13.87 |
| | $R^2$ | | 0.985 | 0.942 | 0.940 |
| Pseudo-second order | $q_{e,cal}$ | mg/g | 89.61 | 139.35 | 142.00 |
| | $R^2$ | | 0.997 | 0.999 | 0.999 |

From the parameters it is clear that the pseudo-second order kinetic model showed a better correlation for the adsorption of dye onto graphene oxide compared to the pseudo-first-order model.

### *3.6. Thermodynamic analysis*

The change in Gibb's free energy for dye adsorption on graphene oxide at different temperature was calculated using 200 ppm dye solution at pH of 2 and 10 mg GO was used for 10 ml solution. The mixture was shaken at 30 °C, 40 °C and 50 °C for 05-60 minutes interval at 200 rpm. The free energy $\Delta G^o$ was calculated by the following equation:

$$\Delta G^o = -RT\, ln\, k_d \tag{9}$$

where, $k_d$ is the distribution constant for the equilibrium sorption, R is the universal gas constant (8.314 J $mol^{-1}$ $K^{-1}$) and T is the absolute temperature (K). $K_d$ is calculated by the equation-

$$k_d = \frac{q_e}{c_e} \tag{10}$$

The equilibrium adsorption capacities are 132.38, 122.14 and 115.85 mg/g at 303K, 313K and 323K temperature, respectively. The calculated Gibb's free energy were -1.69, -1.17, -0.86 $KJmol^{-1}$at 303K, 313K and 323K. Using the Van't Hoff equation, the average standard enthalpy change $\Delta H^0$ and entropy change $\Delta S^0$ for the adsorption can be calculated by the following equation:

$$\ln k_d = \frac{-\Delta H^o}{RT} + \frac{\Delta S^o}{R} \tag{11}$$

The standard enthalpy change $\Delta H^o$ obtained from the slope (Figure 8b) was -14.55 KJ $mol^{-1}$ and entropy change $\Delta S^o$ obtained from the intercept is -0.042 KJ $K^{-1}$ $mol^{-1}$.

The value of $\Delta G^o$ increased from -1.69 to -0.86 as temperature increased from 303K to 323 K, which revealed that the adsorption process is more spontaneous at lower temperature. The value of Gibb's free energy also gives information about the nature of adsorption process. $\Delta G^o$ value ranged from 0 to -20 KJ $mol^{-1}$ indicating physisorption process; whereas for chemisorption process this value ranges from 80 to 400 KJ $mol^{-1}$. So, the adsorption of the dye on GO is physical adsorption process. As a result the used GO was regenerated by simple washing with water.

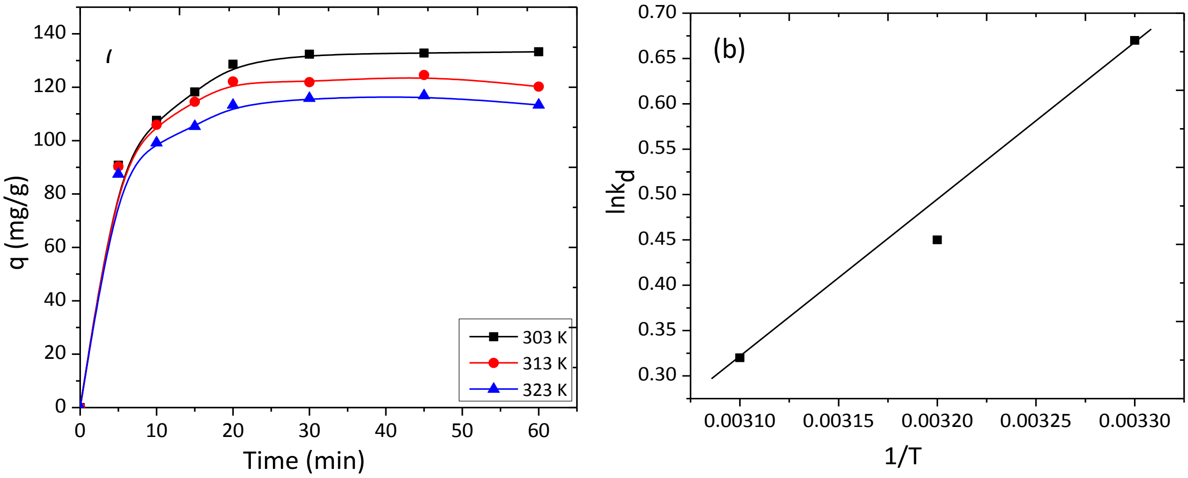

**Figure 8:** Time vs Adsorption capacity (a) and 1/T vs $\ln k_d$ plot at different temperature

## Conclusion

Graphene oxide can be used as an efficient and cost-effective adsorbent for the removal of dyes. The adsorption capacity of the prepared graphene oxide was 151.29 mg/g. The adsorption isotherm fitted well with the Langmuir isotherm and the pseudo-second order kinetic model showed a better correlation for the adsorption of both dyes onto graphene oxide compared to the pseudo-first-order model. The value of Gibb's free energy $(\Delta G^0)$ of adsorption of dye on GO was negative which revealed that dye adsorption on GO was a physical adsorption process.

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