



## **Removal and Recovery of Phosphorus from Wastewater Using Graphene as an Adsorbent**

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**Abstract :** The aim of this study is to investigate the possibility of graphene adsorbent as an alternative adsorbent for phosphorus removal from wastewater. Adsorption properties of graphene were investigated, including initial concentration, adsorbent dose, pH effect and contact time. The adsorption amount of phosphorus decreased with increasing pH. The experimental data were evaluated by Langmuir, Freundlich and Temkin models to describe the equilibrium isotherms. Equilibrium data fitted well to the Langmuir model. The kinetic parameters achieved at different concentrations were analyzed using a pseudo-first order, pseudo-second order kinetic equation and intra-particle diffusion model. The experimental data fitted very well the kinetic model. Thermodynamic parameters like free energy change, enthalpy change and entropy change showed that the adsorption of phosphorus on graphene was endothermic and spontaneous. The study showed that graphene could be used as an efficient adsorbent material for the adsorption of phosphorus from wastewater.

**Keywords :** Graphene, Wastewater, Adsorption, Phosphorus removal, Equilibrium Isotherm.

### **1. Introduction**

Phosphorus is essential to the growth of algae and other biological organisms. Because of poisonous algal blooms that occur in surface waters, there is presently much interest in controlling the amount of phosphorus compounds that enter surface waters in domestic and industrial waste discharges and natural runoff. Thus, available concentration of P in natural water bodies is usually very low and it is the limiting factor for the algae and other organisms to grow. An excessive amount of phosphorus breaks this limit and rapid microorganism's growth is initiated. In many countries, this limit is 1 mg/L of total phosphorus. This has made it very important to find appropriate technological solution for treatment of wastewater prior to disposal.

There are several methods to remove phosphorus from wastewater like Precipitation, Enhanced biological process, Ion Exchange, Membrane separation and crystallization<sup>1-7</sup>. The main disadvantage of above processes is high maintenance cost, usage of toxic solvents, fouling, swelling, scaling, degradation and disposal issue. One of the promising technologies for phosphorus removal and recovery from wastewater is the adsorption process because of its effective and low-cost treatment method. The various adsorbents used for the removal of phosphorus but Graphene has attracted great interest for its inimitable structure, large surface area, various functionalities, ease of preparation and cheaper<sup>8,9</sup>.

Hence, the proposed method intends to use graphene as an adsorbent for removing and subsequently recovering phosphorus from wastewater. The potential of graphene as an adsorbent is being investigated.

## 2. Experimental

In the present study graphene were used as adsorbent. Municipal wastewater was collected from Adyar canal bank road, Chennai. For each test, 100ml of wastewater was taken in 250mL beaker and 1mL of 11N sulphuric acid, 4ml of ammonium molybdate – antimony potassium tartrate mixes and 2ml of ascorbic acid solution is added. A temperature-regulated platform shaker was used for solution agitation<sup>10</sup>. After 5 minutes, absorbance was measured at 650 nm with a spectrophotometer and the phosphorus concentration is determined from the standard curve. All the experiments were repeated three times for reproducibility and the accuracy of the results are 1%. The amount of phosphorus adsorbed onto graphene was calculated by using the following expression:

$$q_e = (C_0 - C_v) V / m$$

Where :  $q_e$  is the equilibrium adsorption capacity of phosphorus adsorbed on unit mass of the graphene (mg/g);  $C_0$  and  $C_v$  are the initial and final phosphorus concentration (mg/L) at equilibrium respectively;  $V$  is the volume of the phosphorus solution (L); and  $m$  is the weight of graphene (g).

### 2.1. Desorption of Phosphorus on Graphene

Phosphorus recovery was made using base leaching method. 20%-solution of NaOH was used as a base. Graphene and its phosphorous residual was made into 100ml solution and the mixture was stirring at 600 rpm. After 20 min, the mixtures were filtrated using vacuum filter. Samples from the filtrate were taken to find the residual P concentration. Kept on filter graphene was washed three times with distilled water. In one-step base leaching 10 ml of 20%-solution of NaOH was added to washed graphene, stirred for 10 min and then kept settling on magnets. Samples from liquid part were taken to measure the phosphorus amount that was discharged from graphene. One-step process finished at this moment and two-step process run further as follows: graphene was separated from NaOH by decantation and washed three times with distilled water; after that the same phosphorus desorption procedures as described in one-step process was done.

## 3. Results and Discussions

### 3.1. Effect of Adsorbent Dose

To investigate the effect of graphene adsorbent dose on the phosphate adsorption, experiments were carried out with initial phosphate concentration of 20 mg/L and varying adsorbent dose at a constant stirring speed of 200 rpm and 20 min constant contact time (Fig. 1). The results show that the percent removal increased with increasing adsorbent dose due to the increase in the total available surface area of the adsorbent particles. At 0.6gm almost 98 % phosphorous was removed from wastewater.

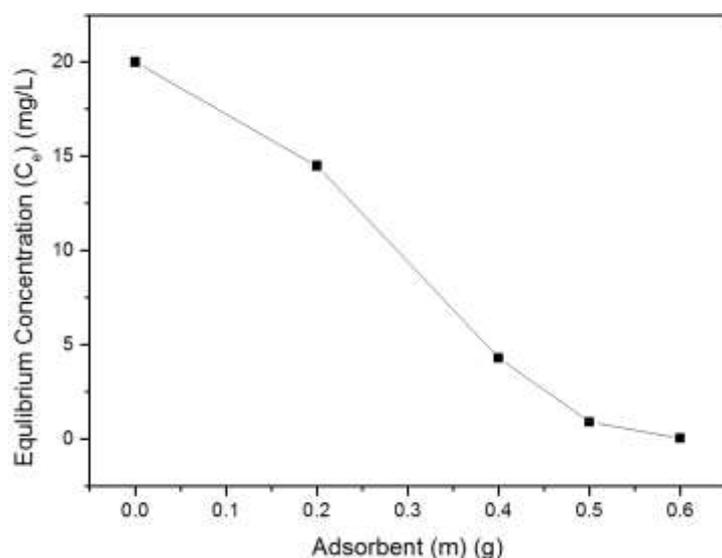


Fig. 1. Effect of adsorbent dose on Phosphorous removal

### 3.2. Effect of pH on Adsorption

The pH of the aqueous solution is an important variable, which influences the sorption of both anions and cations at the solid-liquid interface. The anion exchange capacity is strongly governed by the pH of the solution and by the surface chemistry of the solids. To study the influence of pH on the adsorption capacity of graphene were performed at 20 min constant contact times using various initial solution pH values 3, 5 and 7(Fig. 2). After pH 7 there is no significant removal of phosphorous from waste water.

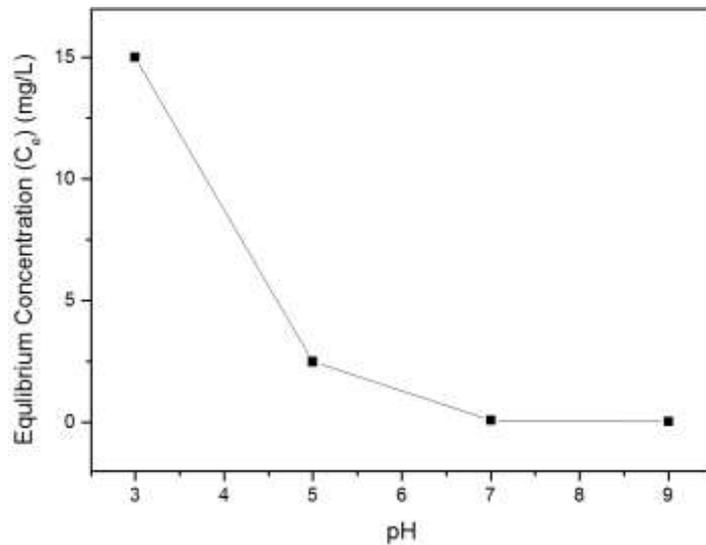


Fig. 2.Effect of pH on Phosphorous removal

### 3.3. Effect of Contact Time on Adsorption

Experiments on the adsorption curve have shown that adsorption time has small impact on the P removal efficiency. The phosphorous removal efficiency increases rapidly before the moment of time 15 min. After, there is no significant effect on removal of phosphorous from wastewater. Those just small variations were observed. After mixing more than 30 min small decreasing in P removal efficiency was observed(Fig. 3). It could be partly explained by desorption of small amounts of phosphorus from graphene.

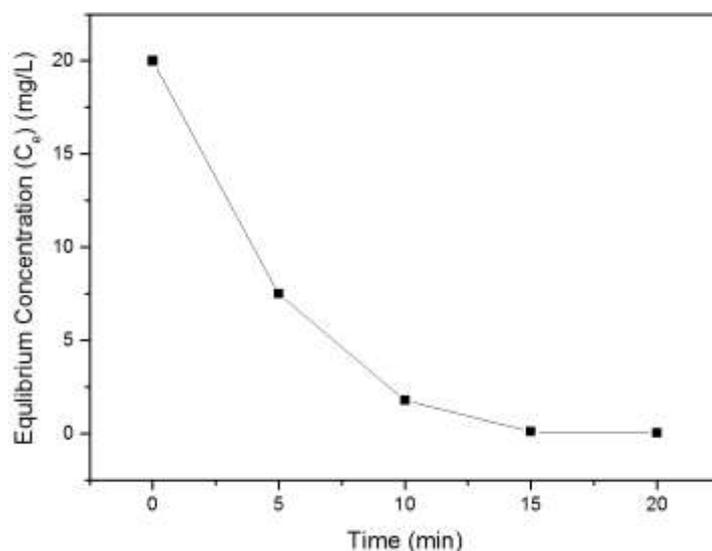


Fig. 3.Effect of contact time on Phosphorous removal

### 3.4. Adsorption Isotherms

The adsorption isotherms indicate the distribution of adsorbed molecules between the solid and liquid phase when the adsorption reaches the equilibrium. The analysis of the isotherm data is important to develop an equation, which accurately represents the results and could be used for design purposes. To investigate the adsorption isotherm, three equilibrium isotherms were analyzed: the Langmuir, Freundlich and Temkin isotherms.

#### 3.4.1. Langmuir Isotherm

The Langmuir isotherm assumes that the adsorbent surface is homogeneous and a site can only be occupied by one pollutant molecule. The theoretical Langmuir isotherm is often used to describe adsorption of a solute from a liquid solution as following equation,

$$C_e/q_e = 1/K_L q_m + C_e/q_m$$

Where:  $q_e$  is the equilibrium adsorption capacity (mg/g);  $C_e$  is the equilibrium liquid phase concentration (mg/L);  $q_m$  is the maximum adsorption capacity (mg/g);  $K_L$  is adsorption equilibrium constant (ml/mg).

#### 3.4.2. Freundlich Isotherm

The Freundlich isotherm is the earliest known relationship describing the adsorption isotherm. This satisfactory empirical isotherm can be used in adsorption from dilute solutions. The ordinary adsorption isotherm is expressed by the following equation:

$$\text{Log}(q_e) = \text{log}(K_F) + 1/n \text{log}(C_e)$$

Where:  $C_e$  is the equilibrium concentration in the solution (mg/l);  $q_e$  is the equilibrium adsorption capacity (mg/g);  $K_F$  and  $1/n$  are empirical constants.  $K_F$  is the adsorption value, the amount adsorbed at unit concentration, that is, at 1 mg/l. It is characteristic for the adsorbent and the adsorbate adsorbed.

The Langmuir and Freundlich parameters and calculated coefficients are listed in table1. From Table 1, the Langmuir isotherm model yielded better fit with higher  $R^2$  values compared to the Freundlich model.

#### 3.4.3. Temkin Isotherm

This isotherm contains a factor that explicitly taking into the account of adsorbent–adsorbate interactions. By ignoring the extremely low and large value of concentrations, the model assumes that heat of adsorption of all molecules in the layer would decrease linearly rather than logarithmic with coverage. As implied in the equation, its derivation is characterized by a uniform distribution of binding energies was carried out by plotting the quantity sorbed  $q_e$  against  $\ln C_e$  and the constants were determined from the slope and intercept.

$$q_e = B_1 \ln K_T + B_1 \ln C_e$$

The Langmuir, Freundlich and Temkin parameters and calculated coefficients are shown in Fig. 4-6. From Table 1, the Langmuir isotherm model yielded better fit with higher  $R^2$  values compared to the Freundlich and Temkin model.

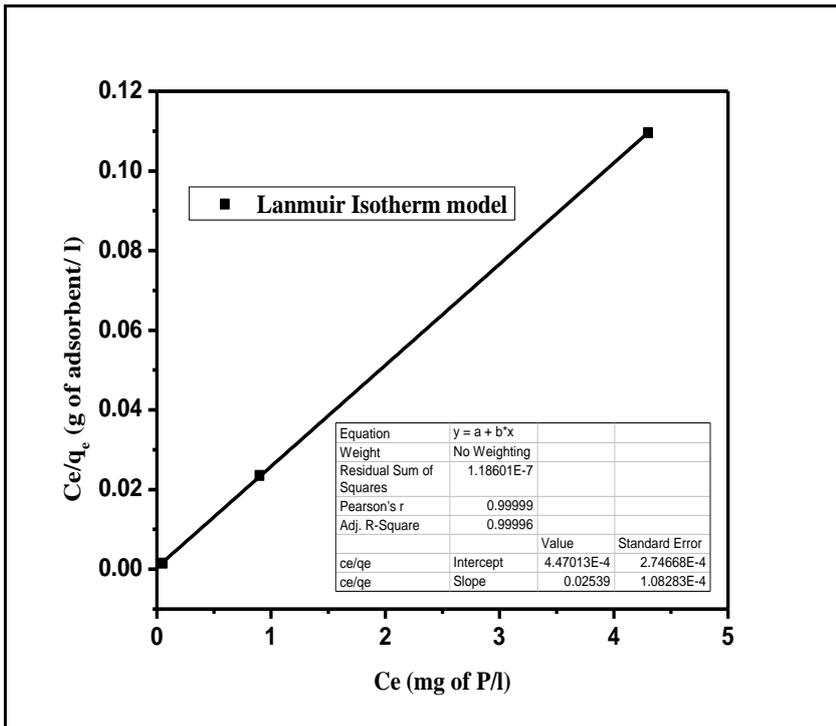


Fig. 4. Linearization of Langmuir isotherm model

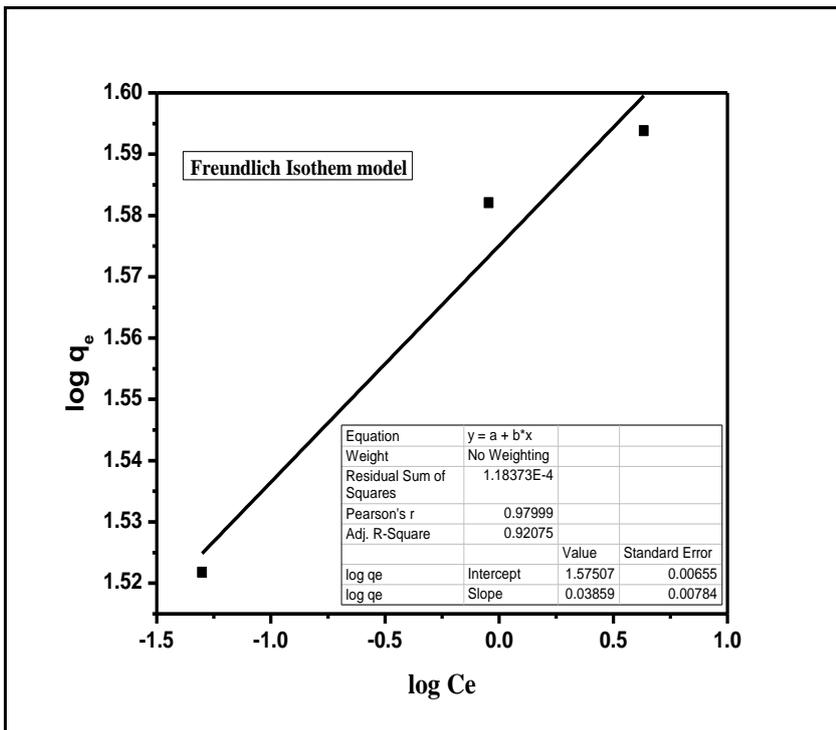


Fig. 5. Linearization of freundlich isotherm model

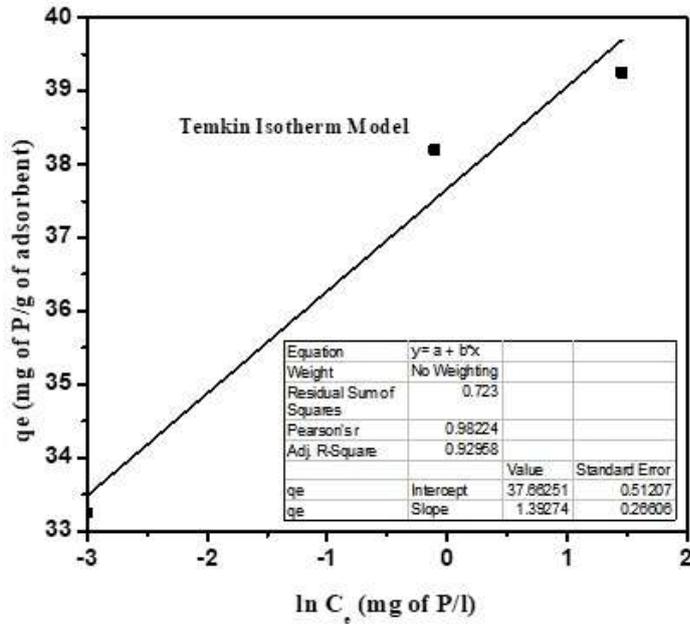


Fig. 6. Linearization of Temkin isotherm model

Table 1. Langmuir, Freundlich, Temkin isotherm parameters for adsorption of phosphorus:

Sl. No.	Isotherm	Parameters	Values
.1	Langmuir	$q_m$ (mg/g)	40
		$K_L$ (l/mg)	56.59
		$R^2$	0.999
2.	Freundlich	$N$	26.31
		$K_F$ (mg/g)	37.58
		$R^2$	0.92
3.	Temkin	$B_1$	1.392
		$K_T$ (L/mg)	1.037
		$R^2$	0.929

### 3.5. Adsorption Kinetics

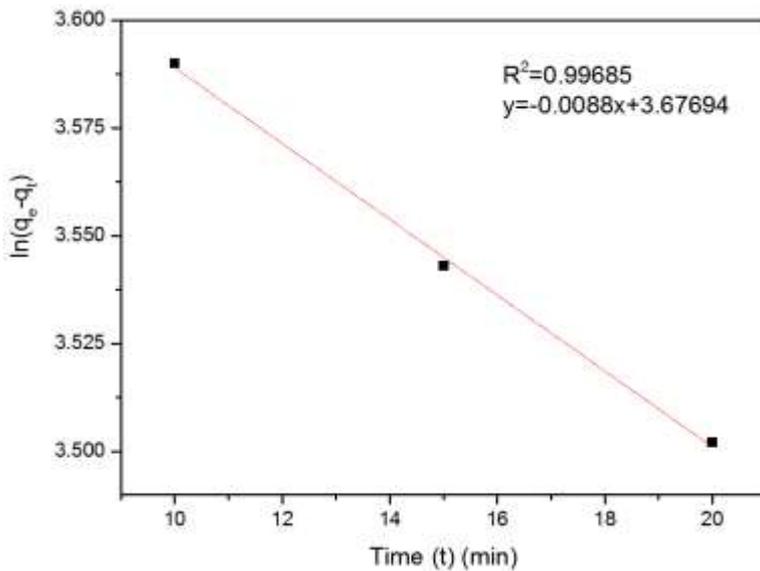
The pseudo-first order, pseudo-second order and intraparticle diffusion models were employed to study the kinetics of adsorption of phosphorus on graphene. To design a fast and effective model, researches are made on adsorption rate.

#### 3.5.1. Pseudo-First Order

The rate constant of phosphorus adsorption is distinctive by the pseudo-first-order kinetic model as:

$$\ln (q_e - q_t) = \ln (q_e) - k_1 t$$

Where :  $q_e$  and  $q_t$  are the amounts of adsorbate adsorbed(mg/g) at equilibrium and at any instant of time  $t$  (min), respectively, and  $k_1$  is the rate constant of pseudo-first-order adsorption.( $\text{min}^{-1}$ ). The values of  $q_e$  and  $k_1$  were determined from the intercepts and the slopes of the plots of  $\ln(q_e - q_t)$  vs.  $t$ , respectively (Fig. 7).



**Fig.7. Pseudo First-Order kinetic modeling of phosphorus adsorption on graphene**

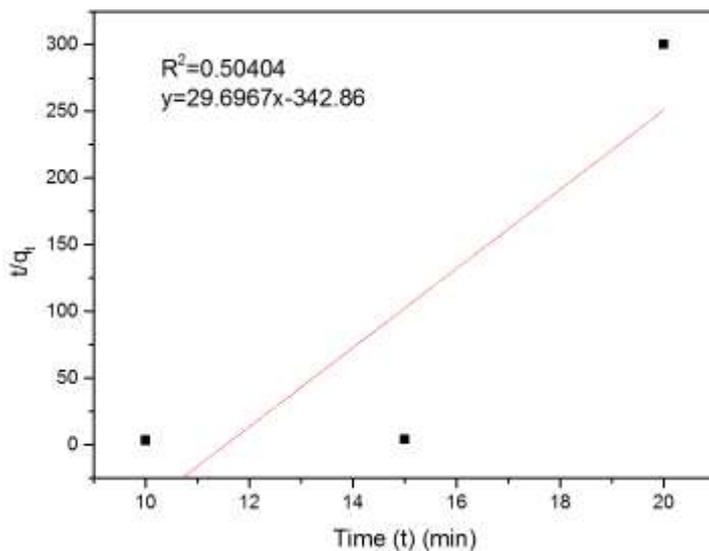
### 3.5.2. Pseudo-Second Order

The pseudo-second-order kinetic model based on equilibrium adsorption, can be demonstrated in the form

$$t/q_t = 1/k_2q_e^2 + t/q_e$$

Where :  $K_2$ :equilibrium rate constant of pseudo-second-order adsorption( $\text{g/mg min}$ ).

A plot of  $t/q_t$  vs.  $t$  gives a linear relationship from which  $q_e$  and  $k_1$  can be determined from the slope and intercept of the plot, respectively(Fig. 8).



**Fig.8. Pseudo Second-Order kinetic modeling of phosphorus adsorption on graphene**

### 3.5.3. Intra Particle Diffusion:

The possibility intra particle diffusion resistance affecting adsorption was proposed by using the intra particle diffusion model as:

$$q = k_i t^{1/2} + C$$

Where:  $q$ ,  $k_i$ , and  $c$  are the amount of phosphorus adsorbed (mg/g) at time  $t$  (min), the intra particle diffusion rate constant (mg/g min<sup>0.5</sup>) and the intercept, respectively (Fig. 9).

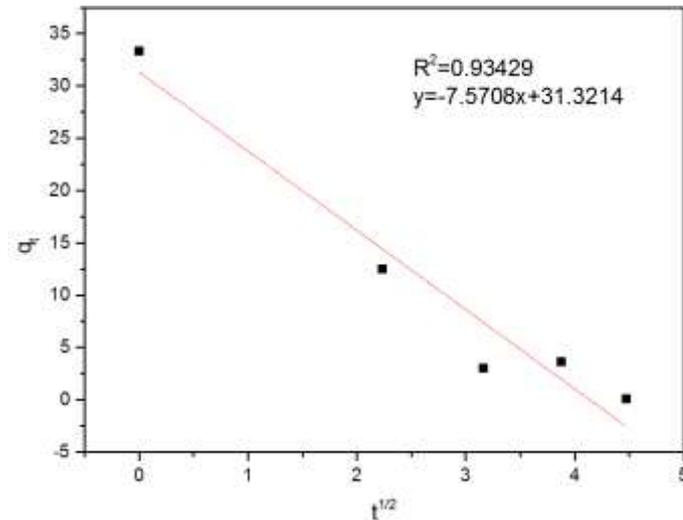


Fig. 9. Intra particle diffusion kinetic modeling of phosphorus adsorption on graphene

Table 2. Constants of pseudo first-order, pseudo second-order and intra particle diffusion adsorption kinetic models

Kinetic model	parameters	Values
Pseudo first order	$q_e$ (mg/g)	39.52
	$K_1$ (1/min)	0.0088
	$R^2$	0.99685
Pseudo second order	$q_e$ (mg/g)	0.033
	$K_2$ (g/mg min)	-2.67
	$R^2$	0.50404
Intra Particle diffusion	$K_i$ (mg/g min <sup>0.5</sup> )	-7.5708
	$C$	31.3214
	$R^2$	0.93429

The values of experimental ( $q_{\text{experimental}} = 36.9$  mg/g) do not agree with the calculated  $q_e$  and the values of correlation coefficient ( $R^2$ ) are relatively low in pseudo-second order and intra-particle diffusion model (Table 2). The correlation coefficient ( $R^2$ ) for the pseudo-first order kinetic model fits are 0.99685, much higher than the correlation coefficients derived from other models. It has also good agreement between the experimental  $q_e$  and the calculated  $q_e$  values. Hence it followed pseudo-first-order kinetics.

### 3.6. Thermodynamic Parameters

The thermodynamic parameters such as Gibbs free energy change ( $\Delta G^0$ ), enthalpy ( $\Delta H^0$ ) and entropy ( $\Delta S^0$ ) were computed using the following equations:

$$\Delta G^0 = -RT \ln K_c$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$

Where  $K_c$  is the distribution constant for adsorption. The Gibbs free energy ( $\Delta G^0$ ) for adsorption of phosphorus by graphene is listed in Table 3.  $\Delta H^0$  and  $\Delta S^0$  were determined from the slope and intercept of the plot of  $\Delta G^0$  versus T and are also tabulated in table. The values of  $\Delta G^0$  were negative at all temperatures and the negative value confirm the feasibility of the process and the spontaneous nature of phosphorus adsorption. The increase of the absolute value of  $\Delta G^0$  as temperature rises indicates that the affinity of phosphorus on graphene was higher at high temperature. The positive value of  $\Delta H^0$  confirms that the adsorption reaction is endothermic. The positive value of  $\Delta S^0$  reflects the affinity of the graphene for phosphorus.

**Table 3. Thermodynamic Parameters for the Adsorption of Phosphorus on Graphene**

$\Delta S^0$ (kJ mol <sup>-1</sup> )	$\Delta H^0$ (kJ mol <sup>-1</sup> )	$\Delta G^0$ (kJ mol <sup>-1</sup> )		
		293 K	298 K	303 K
288	5	-9829.268	-9997.003	-10166.83

#### 4. Conclusion

The phosphorus adsorption performance of graphene was investigated in collectively with adsorbent dosage, pH and contact time. pH and contact time were found to have a great efficacy on the adsorption process. The strongest adsorption turnover was found in the solution at the acidic pH. The following parameter were optimized on removal of phosphorous by use of graphene adsorbent; adsorbent dose: 0.6gm, pH: 7 and contact time:15 min. Furthermore, the experimental data were best explained by the Langmuir isotherm model, and the adsorption kinetics of graphene can be modeled successfully by pseudo-first-order rate equation. Thermodynamic parameters such as Gibbs free energy ( $\Delta G$ ), enthalpy change ( $\Delta H$ ) and entropy change ( $\Delta S$ ) for phosphorus adsorption were found to be negative, positive and positive, respectively. Therefore, the high adsorption turnover and excellent reusability demonstrate that graphene has important potential as an adsorption material to remove phosphorus from aqueous solutions.

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