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Equilibrium, kinetic and thermodynamic studies of phosphoric acid adsorption onto activated carbon

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ABSTRACT

To deduce information that could be used in the treatment of industrial effluents containing phosphoric acid, a thermodynamic, equilibrium, and kinetic study on the adsorption behaviour of phosphoric acid onto grained and powdered activated carbon was carried out. In the experiments, which were run batch-wise, the initial concentration of phosphoric acid and the temperature were varied, and the amount of acid adsorbed at predefined time intervals was measured. The amount of solute adsorbed increased with an increase in acid concentration, and temperature of the milieu. In the thermodynamic study, the variation in entropy, enthalpy and Gibbs free energy were calculated from their dependence on the distribution coefficient, K_D (ratio between the concentration of phosphoric acid adsorbed on the activated carbon (mg/g) and the concentration of phosphoric acid in the aqueous solution (mg/cm^3)) and temperature. The result showed that the adsorption of phosphoric acid onto activated carbon was a spontaneous and endothermic process. The high correlation coefficient values (R^2) showed that the adsorption process on the activated carbon was well represented by the Langmuir and Freundlich isotherms, and the pseudo second order kinetic model.

Keywords: Phosphoric acid, Gibbs free energy variation and enthalpy variation, adsorption isotherms, kinetic models

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INTRODUCTION

Manufacturing processes always generate waste streams, which may be in the solid, liquid or gaseous states. While some of these streams can be used as feed into other industries, some are a major concern to humanity in that they contaminate the environment.

Chemical industries are a major source of environmental contamination. Most wastes from these industries are in the large quantities of liquid streams that are sent out into the environment. Phosphoric acid is one of such contaminants found in waste streams. It a major component in the very useful manufacturing processes such as, the high grade phosphate fertiliser, rust proofing of iron, baking powder, phosphate syrups used in soft drinks, and water softening agents [1].

Despite the usefulness of phosphoric acid, especially in its use in fertilisers, it is still a major danger to the environment. Following the directives of the European Community, the maximum quantity of phosphoric acid destined for aquatic life should be 0.2 mg/L for salmonidae, and 0.4 mg/L for cyprinidae fish families [2]. Unfortunately, phosphate concentration in seas is as high as 4.4 to 16.1 mg/L; an amount that is much higher than the 0.1 mg/L that arises from the influence of the sea water [3]. These high phosphate concentrations, which can only be linked to industrial effluents and decay of organic matter have a tendency of modifying the physicochemical properties of the aquatic environment. The consequence is eutrophication, which deprives aquatic life of oxygen.

To remedy this situation, waste streams from phosphoric acid industries must be pre-treated before being rejected into the environment. Among the many other methods that can be used, adsorption of the acid by various adsorbents is a more practical solution. Some common adsorbents that could be used are activated carbon, smectites and kaolinites.

Adsorption is a surface phenomenon which involves interactions between the three components: the adsorbent, the adsorbate and the solvent. The interactive force that controls it is the affinity of the adsorbate for the adsorbent, as well as the solubility of the adsorbate in the solvent. For example, in aqueous solution, hydrophobic compounds have low solubility and tend to be pushed to the adsorbent surface [4].

The adsorption on activated carbon is the result of van der Waals forces with attractive characteristics. The reversibility of the physical adsorption depends on the magnitude of the attractive forces between the adsorbate and the adsorbent. If they are weak, desorption can occur with relative ease. In the chemical adsorption, energy is necessary to reverse the process because the bonds are much stronger [5].

In the last decades, investigations have confirmed the great potential of activated carbon as an important medium of separation and purification. It is being widely used in many industrial processes to remove harmful and inconvenient substances. For examples, commercial grade activated carbon and activated carbon derived from various biomass materials are used in the removal of organic and inorganic contaminants of product from foods, beverages, pharmaceuticals, and also from chemical and petrochemical industries; in the treatment of drinking water and wastewater, and as an adsorbent of noxious air pollutants [6-15].

The use of activated carbon as an adsorbent is based on a number of parameters: its structure, made up of elementary microcrystals of graphite stacked together in a random fashion [5]; the condensed, aromatic rings in the graphite crystals which give the micro-porous surface its hydrophobic properties [16] cited by [4]; surface area, the pore structure and functional groups in the surface which have high reactivity, and determine the adsorption capacity [17]. Other factors that affect the adsorption in a significant way are the nature of the adsorbate, the pH of the solutions, the granulometric distribution, the ash content, the high mechanical resistance, the activation process to which the activated carbon was subjected during fabrication, the viscosity, the temperature of the liquid phase and the contact time of the adsorbent with the solution [3, 18].

One major advantage of activated carbon over other adsorbents is its high removal efficiency of impurities at low initial concentration, low energy costs [19] and the ease with which it can be regenerated. Although a lot of work has been done on the use of activated carbon, little attention has been given to the thermodynamics of the adsorption process onto it.

The objectives of this work are to study the behaviour of phosphoric acid adsorption onto powdered activated carbon (PAC) and granular activated carbon (GAC). This will involve varying the temperature and the concentration of the solutions used, and then examining the thermodynamic parameters such as the enthalpy change(ΔH), the entropy change (ΔS), and the Gibbs free energy change (ΔG). The kinetics and the equilibrium of the adsorption of phosphoric acid on activated carbon will also be examined.

MATERIALS AND METHODS

The adsorbent used in this study was powdered and granular activated carbon from CHEMVIRON. The powdered activated carbon has 0.18 mmas diameter and 1200m^2/g as it specific surface area, while the granular activated carbon has 0.60 mmas diameter and 900 m^2/g as its specific surface area.

The adsorption experiments were conducted in a batch mode. A water tank with an agitator and a heater (model RM6 LAUDA with three flasks incorporated) was used for shaking the flasks while controlling the temperature. To determine the thermodynamic parameters, adsorption isotherms and kinetic models, 30 mL solutions of phosphoric acid of known concentrations (0.1, 0.2, 0.3, 0.4 and 0.5 M) prepared previously were added into 125 mL conical flasks containing 0.2 g of activated carbon. The flasks were capped and placed in a shaker for times varying between 20 minutes to 2 hours.

The experiments were performed at temperatures of 15^{o}C, 25^{o}C, 30^{o}C and 35^{o}C. After reaching the required contact time between activated carbon and the aqueous solution of phosphoric acid, the contents of each flask were filtered using filterpaper. A sample of each filtrate was removed and titrated with sodium hydroxide (0.2 M) to determine the equilibrium concentration of phosphoric acid. The indicators used were methyl orange and phenolphthalein (0.2 per cent).

The thermodynamic parameters, ΔH (enthalpy variation) and ΔS (entropy variation) were obtained from the equation [20]:

$$\ln K_D = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \qquad (1)$$

where K_D is the distribution coefficient, defined as

$$K_D = \frac{C_c}{C_e} \qquad (2)$$

C_c isthe concentration of the solute adsorbed on the activated carbon in mg/gcalculated by the equation:

$$C_c = \frac{v}{m}\left(C_o - C_e\right) \qquad (3)$$

where$C_o$and $C_e$are respectively the initial and equilibrium concentrations of the solute (mg/cm^3), *v* is the volume of the solution (cm^3) and *m* is the adsorbent mass (g) [20].

The variation in Gibbs free energy, ΔG was calculated from the classical thermodynamic relationship,

$$\Delta G = \Delta H - T\Delta S \qquad (4)$$

The well-established adsorption isotherm models of Langmuir and Freundlich described below by Equations (5) and (6), respectively, were used to correlate the experimental data.

$$\frac{1}{Q_t} = \frac{1}{Q_m K_L C_t} + \frac{1}{Q_m} \qquad (5)$$

$$\ln\left(\frac{Q_t}{m}\right) = \ln K_F + \frac{1}{n}\ln C_t \qquad (6)$$

Q_m is the maximum quantity of solute adsorbed at the saturation of monolayer,
K_L is the constant of Langmuir,
$Q_t$is the quantity of solute adsorbed at equilibrium,
m is the mass of adsorbent,
C_t is the concentration of adsorbate at equilibrium, and
K_F and *n* are the constants of Freundlich.

The equilibrium experimental data for this study was correlated using these isotherms.

In a similar manner, the experimental data for the kinetics were correlated using the first and second order models, described below by Equations (7) and (8) respectively.

$$\ln C_t = -K_1 t + \ln C_o \qquad (7)$$

$$\frac{t}{Q_t} = \frac{1}{K_2 Q_e^2} + \frac{t}{Q_e} \qquad (8)$$

K_1(mol.g/min) is the pseudo first order [21], while K_2(g/mg.min) is the pseudo second order [22] rate constants of adsorption.

RESULTS AND DISCUSSION

3.1 Adsorption Thermodynamics

Figure 1 shows the dependence of the amount of phosphoric acid adsorbed in the batch sorption experiments on the temperature. The amount adsorbed increased with increasing temperature from 15°C to a maximum at about 30°C, from which it underwent a slight drop at 40°C. This trend was exhibited by all the concentrations; to show that beyond 30°C, an increase in temperature no longer favoured but inhibited adsorption of phosphoric acid on activated carbon. This observation was slightly different from that presented in [23] where, it was observed that there was an increase in the amount of phosphorus adsorbed on soils as the temperature increased from 15 to 40°C. This difference may be attributed to the differences in both adsorbent and adsorbate studied, to imply that adsorbent/adsorbate systems differ from each other.

Figure 2 also showed that the distribution coefficient (K_D) of the phosphoric acid increased with increasing temperature, showing that the process of adsorption was favourable. A similar observation had been made by Benkheda et al [19] and Tahir et al [20].

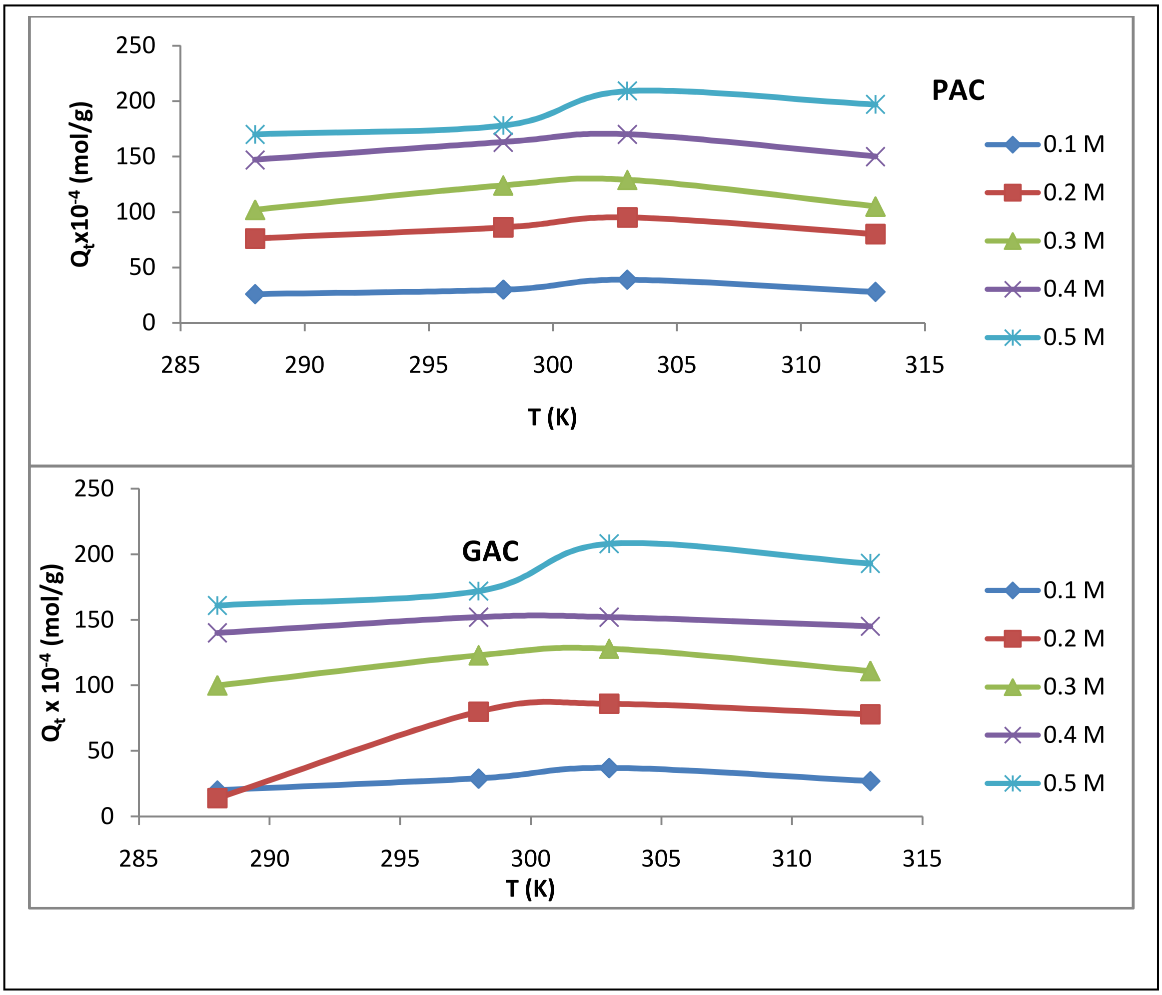

Figure 1: Amount of phosphoric acid adsorbed on 0.2 g of activated carbon as a function of the temperature

All the values of ΔH were positive, indicating that the adsorption process was endothermic. For each presentation of activated carbon, ΔH was highest for the 0.1 mol/L concentration, and the value decreased with concentration, though not in a regular manner. ΔH was also higher for the powdered carbon, to show that the higher the specific area of adsorbent, the greater the heat of adsorption. Overall, the values of ΔH were very low; to suggest that adsorption of phosphoric acid on activated carbon is a physical adsorption process.

ΔS also showed the same trend with respect to concentration as ΔH, and its values were also positive. The positive values of ΔS indicate that during the adsorption process, structural changes may be taking place between the phosphoric acid and activated carbon [24], although the low values of ΔH had suggested physical adsorption. However, according to Aksu and Kabasakal[25], the positive values found for ΔS indicate that the phosphoric acid molecules are in a more random condition in the adsorbed state compared to the same molecules in solution.

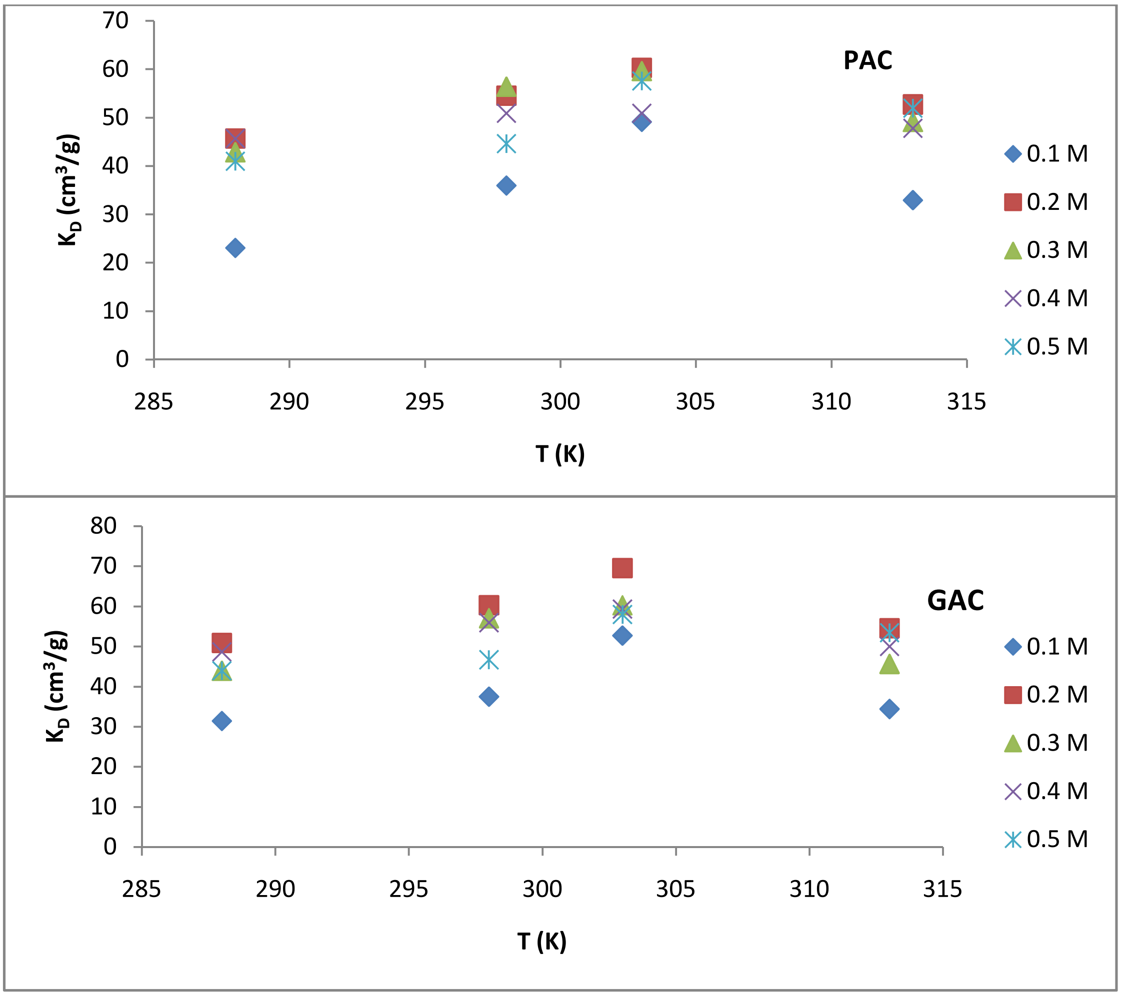

Figure 2: Distribution coefficient, K_D as a function of the temperature of the adsorption of solutions of phosphoric acid on activated carbon (0.2 g of GAC and 0.2 g of PAC

Table 1: Thermodynamic parameters for the adsorption of phosphoric acid onto activated carbon

		Adsorbent : GAC				
			288K (15°C)	**298K (25°C)**	**303K (30°C)**	**313K (40°C)**
C_o(mol/L)	**Δ*S*(J/mol.K)**	**Δ*H*(J/mol)**	**Δ*G*(J/mol)**			
0.1	109.75	23.45	-31585	-32683	-33232	-34329
0.2	84.24	14.88	-24245	-25088	-25508	-26351
0.3	87.55	16.14	-25197	-26072	-26510	-27386
0.4	66.51	9.88	-19146	-19811	-20143	-20808
0.5	74.79	12.56	-21528	-21528	-22650	-23397
		Adsorbent : PAC				
0.1	151.83	36.26	-43691	-45209	-45968	-47486
0.2	79.24	13.68	-22806	-23598	-23995	-24787
0.3	90.67	17.09	-26096	-27003	-27456	-28363
0.4	51.76	5.74	-14900	-15417	-15676	-16194
0.5	84.10	15.42	-4356	-4510	-4587	-4741

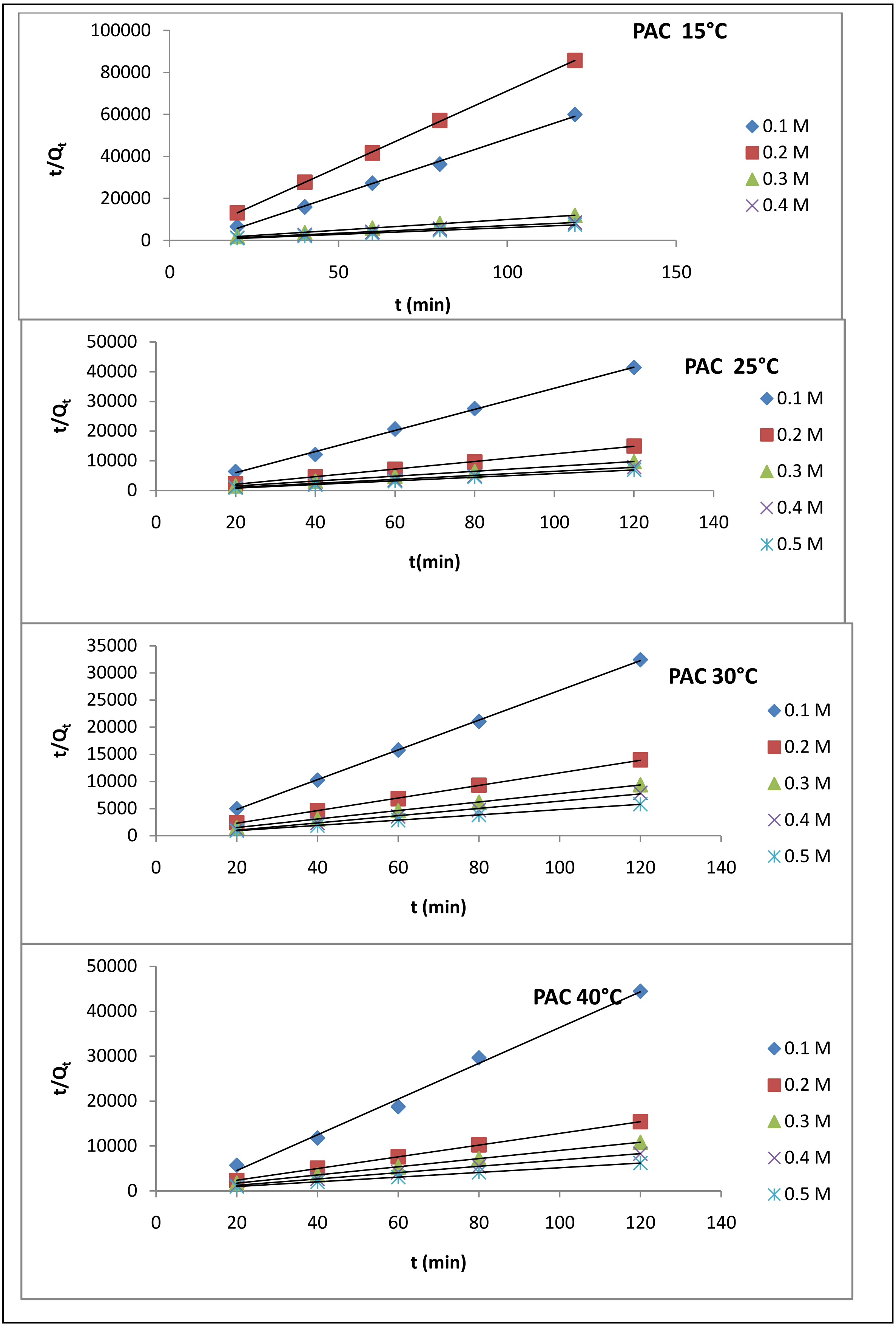

Figure 3: The pseudo second order kinetic model of phosphoric acid adsorption on PAC.

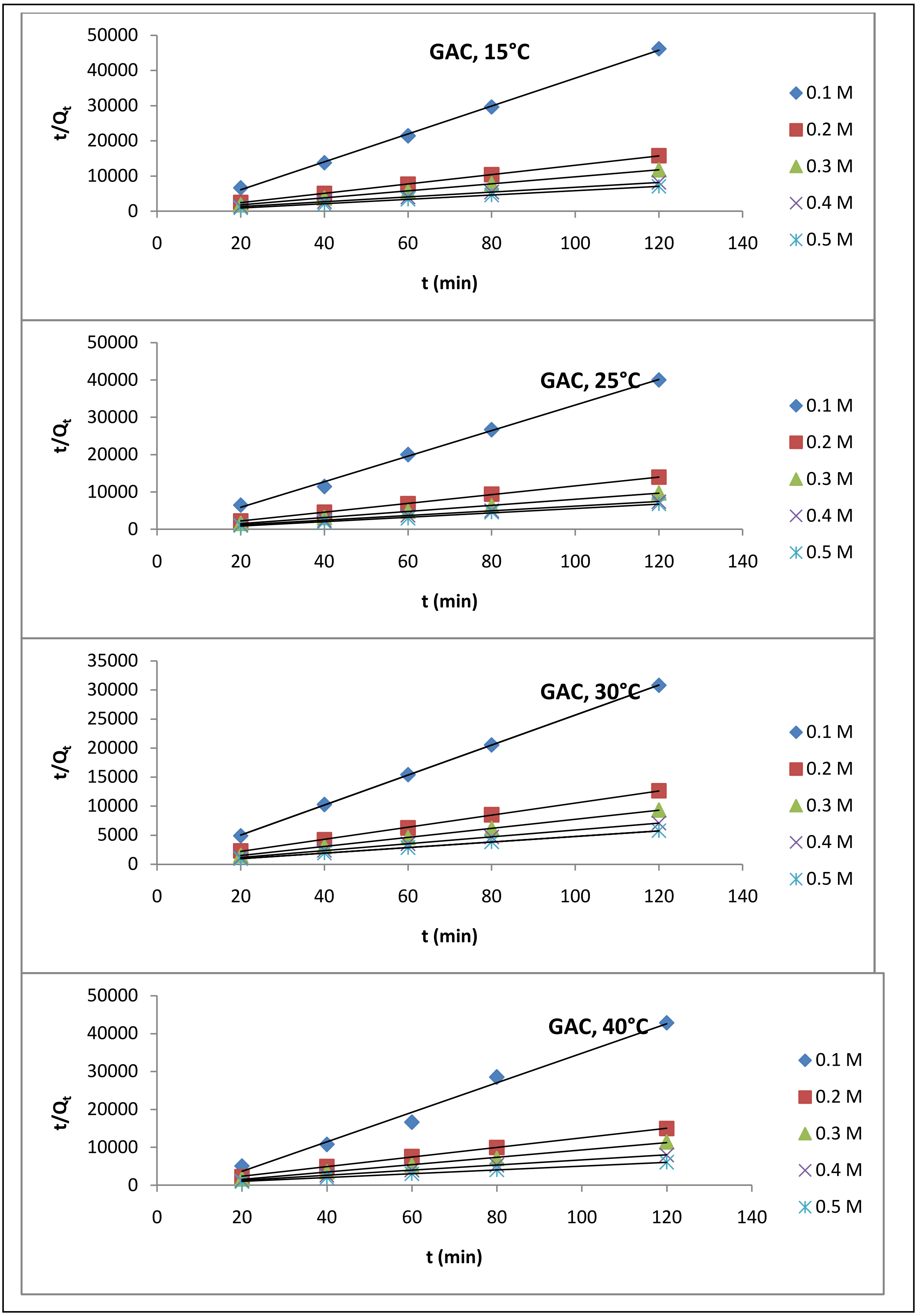

Figure 4: The pseudo second order kinetic model of phosphoric acid adsorption on GAC.

All ΔG values were negative for all the temperatures, and they increased with increasing acid concentration, although in an irregular manner. For any given concentration, ΔG decreased with increasing temperature. These observations suggest that H_3PO_4 adsorption on activated carbon is spontaneous, and it is favourable at higher temperatures. Isah and Yusuf [14] had also found negative values for ΔG and positive values for ΔS when they used activated carbon derived from groundnut shell to adsorb lead from aqueous solution.

Table 2: Values of kinetic constants K_2,Q_e, correlation constants R^2 and initial rate, h_o

Adsorbent	C_0 (M)	Q_ex10^{-3} (mol/g)	K_2 (mol.g/min)	h_0x10^{-4} (mol/g.min)	R^2
GAC 15°C	0.1	2.52	84.790	5.388	0.999
	0.2	7.513	75.837	42.41	0.999
	0.3	10.01	47.990	48.08	0.999
	0.4	14.01	111.707	238.8	1.000
	0.5	16.36	13.318	356.8	0.999
PAC 15°C	0.1	1.876	58.563	2.061	0.997
	0.2	1.376	372.844	7.062	0.999
	0.3	9.823	47.451	45.875	0.999
	0.4	13.782	38.971	74.019	0.999
	0.5	15.363	10.253	24.201	0.997
GAC 25°C	0.1	2.919	111.073	9.804	0.999
	0.2	8.518	121.863	88.42	0.999
	0.3	12.32	53.750	81.57	0.999
	0.4	16.07	57.790	149.3	0.999
	0.5	16.95	10.017	28.78	0.992
PAC 25°C	0.1	2.818	117.93	9.363	0.998
	0.2	7.8688	41.126	25.46	0.999
	0.3	12.17	61.872	91.66	1
	0.4	14.86	15.756	34.81	0.998
	0.5	16.41	10.215	27.53	0.997
GAC 30°C	0.1	3.873	394.481	59.17	0.999
	0.2	9.606	92.464	85.32	0.999
	0.3	12.81	76.743	125.9	1
	0.4	17.01	51.765	149.7	0.999
	0.5	20.81	72.429	313.8	1
PAC 30°C	0.1	3.647	116.063	15.44	0.999
	0.2	8.628	2150.970	1601	0.999
	0.3	12.72	66.264	107.2	0.999
	0.4	14.97	13.538	30.36	0.993
	0.5	20.71	72.873	312.5	1
GAC 40°C	0.1	2.568	368.397	24.30	0.987
	0.2	7.911	141.639	88.65	0.999
	0.3	10.37	27.109	29.17	0.997
	0.4	14.87	84.870	187.5	0.999
	0.5	19.97	311.065	1211.0	1
PAC 40°C	0.1	2.515	46.633	2.950	0.993
	0.2	7.675	79.115	46.60	0.999
	0.3	11.04	140.170	170.8	1
	0.4	14.24	39.426	79.94	0.999
	0.5	19.10	50.166	183.0	1

3.2 Adsorption Kinetics

Figures 3 and 4present the graphs, while Table 2presents the parameters for the second order kinetic model.

For the pseudo first order model, the plots of log (C_t) against t (Equation 7) gave straight lines for all the concentrations, but the values of R^2 were very low; although it is observed that for the 0.2 mol/L concentration for PAC, $R^2 = 0.99$.

This shows that the adsorption of the phosphoric acid on activated carbon does not obey the first order kinetic model.

For the second order kinetic model, the plots of Equation 8 gave straight lines for all the concentrations and temperatures.

By using the results presented in Table 4, the following observations can be made for the pseudo second order model:

- The correlation coefficient isgreater than 0.99 for all the concentrations and at all temperatures. These high values of R^2 show that the adsorption of the phosphoric acid on these adsorbents obeys the second order kinetic model.
- The rate constant K_2 for the second order kinetic model is greater than K_1 for the first.
- For both presentations of the adsorbent PAC and GAC, the initial rate of the adsorption V_o and the rate constant K_2increase with an increase in the concentration of the acid, and also on the mass of the adsorbent.
- PAC, the grain form of activated carbon obeys more the second order kinetic model, and the values of V_o (mol/g.min), and K_2 (mol.g/min) are highest for 0.4 mol/L and 0.5 mol/L at 30°C and 40°C respectively.
- Whatever the mass and the presentation of the adsorbent, the rate constant K_2 and the initial rate V_o are highest at 30°C and 40°C.
- The results obtained show the adsorption of phosphoric acid on activated carbon follows the second order kinetic model.
- We can conclude that the adsorption of the phosphoric acid is governed by the superficial complexation.

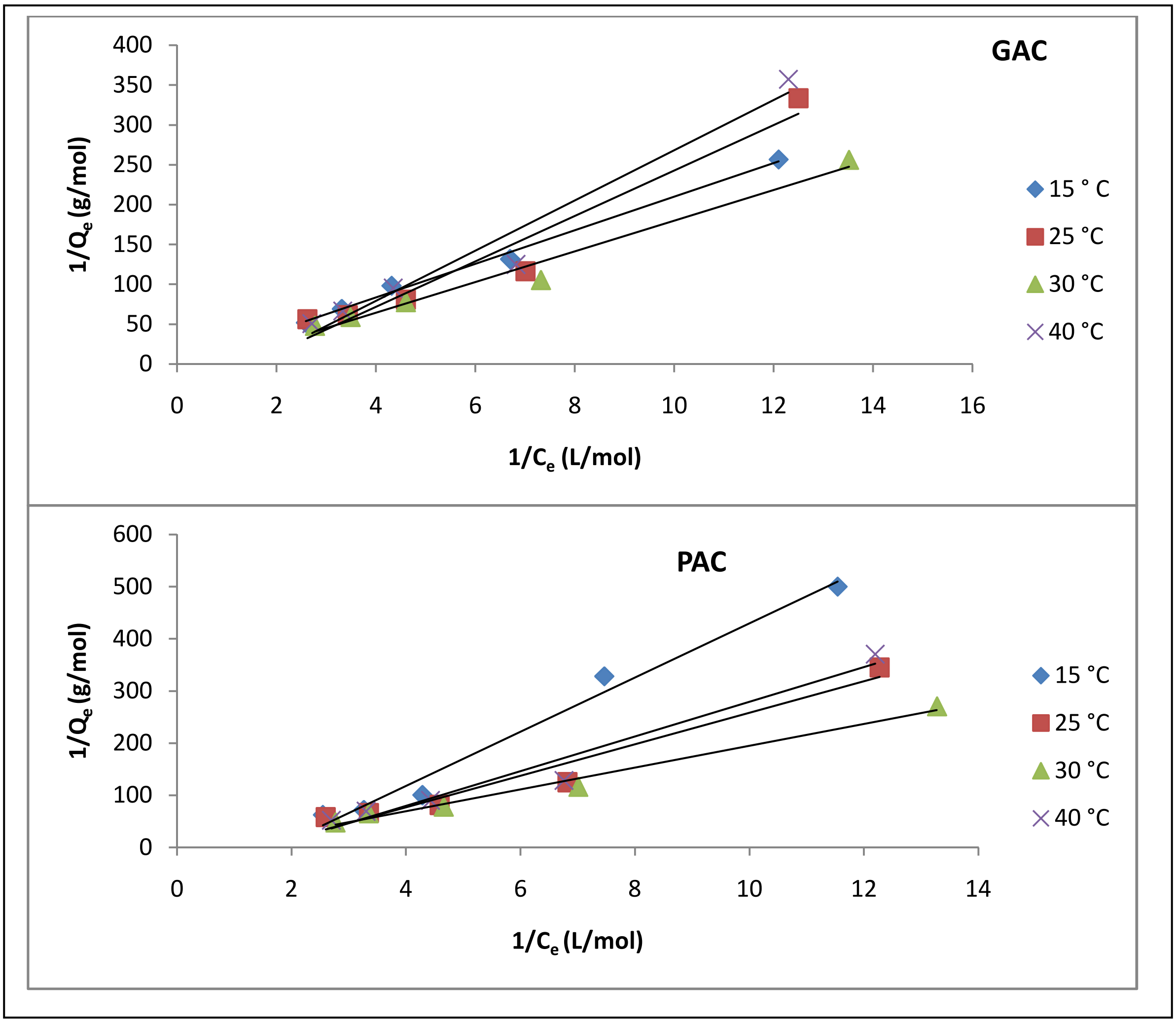

Figure 5:Langmuir isotherm for the adsorption of phosphoric acid on activated carbon, mass, m=0.2 g, Q_m is the maximum quantity of solute adsorbed at the saturation of monolayer, K_L is the constant of Langmuir, $Q_e$is the quantity of solute adsorbed at equilibrium, $C_e$is the concentration of adsorbate at equilibrium

3.3 Adsorption Equilibrium

The adsorption studies were done using the Langmuir and Freundlich isotherms. The plots of the adsorption results obtained under the controlled experimental conditions (temperatures of 15, 25, 30 and 40°C, and concentrations of 0.1, 0.2, 0.3, 0.4 and 0.5 mol/L), are presented in Figures 5 and 6. Table 3 shows the values of the constants of the isotherms of Langmuir, (Q_m, K_L) and Freundlich (n, K_F), that were obtained from the plots $1/Q_t$as a function of $1/C_t$ (Figure 5) and ln (Q_e) as a function of lnC_e(Figure 6) respectively.

The correlation coefficients (R^2) for all temperatures except 40°C were above 90 percent, and the plots were straight lines to show that H_3PO_4 adsorption on activated carbon followed both the Langmuir and Freundlich isotherms.

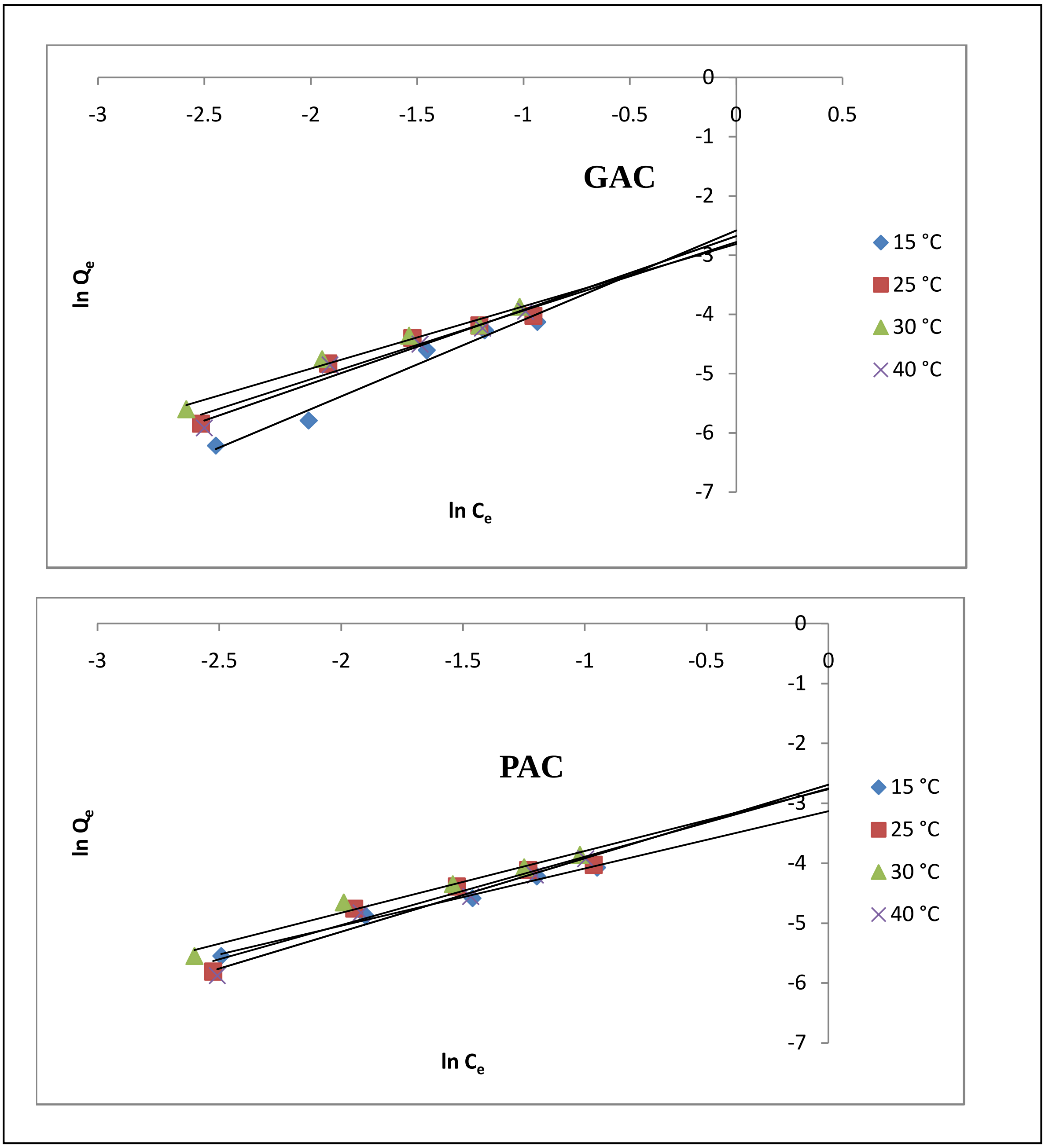

Figure 6: Freundlich isotherm for the adsorption of phosphoric acid on activated carbon of mass, m=0.2 g; $Q_t$is the quantity of solute adsorbed at equilibrium, C_t is the concentration of adsorbate at equilibrium, K_F and *n* are the constants of Freundlich

For the Langmuir isotherm, the values of Q_m, which indicate the retention capacity of the adsorbate were quite high. This shows that activated carbon has a high capacity to adsorb phosphoric acid. Also, the values of K_L, which represent the energy of the adsorption, can also be described as high to indicate that the adsorbent and adsorbate form relatively stable attachments to each other. However, the lack of a trend in the variation in K_L with increasing temperature suggests that the activated carbon-phosphoric acid interaction is not chemical in nature, to confirm the low values of ΔH mentioned earlier. These figures are in the same order of magnitude as those obtained by Freitas*et al*[5] for the adsorption of acetic acid by activated carbon.

The values of K_L and Q_m were both higher for the granulated adsorbent than the grain, to justify the importance of a higher specific area of adsorbent in the adsorption process. This trend had been obtained by Huang et al [26] when they used activated carbon to adsorb cadmium ions.

Table 3:Parameters of Langmuir and Freundlich isotherms of phosphoric acid adsorption on activated carbon at various temperatures

Adsorbent : GAC						
	Langmuir			Freundlich		
T (°C)	K_L (L/mol)	Q_o (mol/g)	R^2	N	K_F (L/g)	R^2
15	1.487	0.021	0.962	0.814	0.068	0.972
25	0.108	0.444	0.994	0.971	0.063	0.978
30	1.489	0.024	0.949	0.877	0.064	0.942
40	0.695	0.075	0.977	0.999	0.04	0.990
Adsorbent : PAC						
	Langmuir			Freundlich		
15	1.606	0.019	0.962	0.803	0.069	0.973
25	0.676	0.071	0.986	0.950	0.060	0.982
30	1.423	0.024	0.959	0.877	0.060	0.949
40	0.707	0.024	0.506	0.590	0.084	0.778

CONCLUSION

The adsorption behaviour of phosphoric acid on activated carbon was studied as a function of the temperature and concentration of the adsorbate. Analysis of the results showed that the phosphoric acid adsorption process on activated carbon was a spontaneous and endothermic process; and that, the amount of adsorbed solute increased with increasing concentration at constant temperature; and it also increased with increasing temperature at constant concentration.

From this study, it can be concluded that the process of phosphoric acid adsorption on activated carbon is well represented by the Langmuir and Freundlich models and by pseudo second order kinetic model.

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