

# Adsorption equilibrium and kinetics of polyvinyl alcohol from aqueous solution on powdered activated carbon

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## Abstract

In this study, powdered activated carbon (PAC) was used to remove polyvinyl alcohol (PVA) from the aqueous PVA solution. The adsorption kinetics has been studied pertaining to various initial PVA concentration and PAC dosage. The rates of adsorption were found to conform to the second-order kinetics with good correlation. Boyd plot confirmed that external mass transfer was the rate-limiting step in the sorption process. The adsorption isotherm obtained resembled with H-type of isotherm, which indicated a high affinity of the solute for the sorption sites. The Freundlich model appeared to fit the isotherm data better than the Langmuir model. The thermodynamic parameters such as  $\Delta H^\circ$ ,  $\Delta S^\circ$  and  $\Delta G^\circ$  were evaluated from the slope and intercept of linear plot of  $\log K_c$  against  $(1/T) \times 1000$ . The change in entropy ( $\Delta S^\circ$ ) and heat of adsorption ( $\Delta H^\circ$ ) of PAC was estimated as  $1.45 \text{ kJ mol}^{-1} \text{ K}^{-1}$  and  $365 \text{ kJ mol}^{-1}$ , respectively. The free energy of the adsorption at all temperatures was negative indicating a spontaneous process. The maximum PVA removal of 92% was obtained at a pH of 6.3 and contact time of 30 min for an adsorbent dose of 5 g/L. © 2007 Elsevier B.V. All rights reserved.

**Keywords:** Adsorption kinetics; PAC; PVA removal; Isotherm; Mechanism

## 1. Introduction

The rapid development and proliferation of process industries have made wastewater treatment a major concern in industrial areas. Industrial wastewaters are more likely to contain recalcitrant contaminants that are toxic and hardly degradable by biological treatment processes. Polyvinyl alcohol (PVA), a well-known recalcitrant pollutant, is commonly used in textile industries as a sizing agent [1]. PVA, prepared by the hydrolysis of polyvinyl acetate is used in adhesive, paper-coating, emulsion paints and detergent based industries. In the pharmaceutical sector, PVA is used as an ophthalmic lubricant and viscosity enhancing agent. The global production of PVA is estimated at about 650,000 tonnes/year, and the enormous amount of PVA discharged from industrial effluents has posed a significant threat to both human health and the natural environment [2]. When released to the environment due to improper handling practices and treatment, PVA containing wastewaters are hardly converted to innocuous end products like carbon dioxide and water. This

causes detrimental effects on the ecosystem and can also get accumulated in the human body through the food chain system. [3]. Aside from the bioaccumulation, PVA can also cause additional environmental problems due to its potential to mobilize heavy metals from sediments in water streams and lakes [4].

The conventional biological systems are not efficient for the degradation of PVA as the PVA degrading capacity of most microbial species is very specific and limited [5]. After 48 days of incubation, mixed cultures acclimatized to PVA solution showed only 40% mineralization of PVA [6]. Moreover, the continual generation of foam in biological reactors during PVA wastewater treatment has made the operation difficult and the treatment inefficient [7]. Therefore, more effective and efficient methods for the removal or pretreatment of PVA from wastewater need to be pursued.

Adsorption is a versatile treatment technique practiced widely in fine chemical and process industries for wastewater and waste gas treatment. The usefulness of the adsorption process lies in the operational simplicity and reuse potential of adsorbents during long-term applications. Carbon adsorption has proved to be the least expensive treatment option, particularly in treating low concentrations of wastewater streams and in meeting stringent treatment levels. Activated carbon based sys-

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### Nomenclature

$C_e$	equilibrium liquid phase concentration (mg/L)
$C_o$	initial liquid phase concentration (mg/L)
$D_i$	effective diffusion coefficient ( $m^2/s$ )
$E_a$	activation energy ( $kJ\ mol^{-1}$ )
$F$	fraction of solute (PVA) adsorbed at any time $t$
$\Delta G^\circ$	change in Gibb's free energy of adsorption ( $kJ\ mol^{-1}$ )
$\Delta H^\circ$	change in enthalpy of adsorption ( $kJ\ mol^{-1}$ )
$k_1$	rate constant of pseudo-first-order adsorption ( $min^{-1}$ )
$k_2$	rate constant of pseudo-second-order adsorption ( $g/mg/min$ )
$K_F$	Freundlich isotherm constant related to adsorption capacity ( $(mg/g)(L/mg)^{1/n}$ )
$K_L$	intensity of adsorption ( $L/mg$ )
$M$	mass of adsorbent (g)
$n$	Freundlich isotherm constant related to adsorption intensity
$q$	amount of adsorption at time $t$ (mg/g)
$q_e$	equilibrium solid phase adsorbate concentration (mg/g)
$Q_o$	maximum adsorption capacity (mg/g)
$R^2$	correlation coefficient
$\Delta S^\circ$	change in entropy of adsorption ( $kJ\ mol^{-1}\ K^{-1}$ )
$V$	volume of solution (L)

tems can remove a wide variety of toxic pollutants with very high removal efficiencies. Adsorption using powdered activated carbon (PAC) has been receiving a considerable attention recently for the removal of refractory contaminants from wastewater [8]. Adsorption onto a porous surface is influenced by the nature of adsorbate and its substituent groups. The presence and concentration of the surface functional groups plays an important role in the adsorption capacity and the removal mechanism of the adsorbates. The use of PAC for removal of recalcitrant organics has increased in recent years, because of the superior performance and operational flexibility that the PAC provides [9]. In addition to this, PAC can be recirculated and reused several times before it is disposed, thereby reducing the overall treatment cost [10].

PVA adsorption onto several materials such as silica, polystyrene particles, kaolin, hectorite, silicon oxide, fuller's earth and montmorillonite has been studied by various workers [11–17]. Adsorption of PVA studied by Bussetti and Fereiro [17] shows that the PVA molecules are strongly adsorbed onto the montmorillonite surface forming stable complexes for different purposes. The adsorption of petroleum contaminated ground water onto PAC has been studied by Ayotamuno et al. [18]. They found that 99.9% of the contaminants were removed by PAC. To our knowledge, so far little information is available on the adsorption of PVA onto PAC. Therefore, the objectives of this research were to study the usage of PAC as an adsorbent for the removal of PVA from aqueous solutions by batch experi-

ments. The adsorption isotherm, kinetics, thermodynamics, and mechanism involved in the sorption process were also carried out.

## 2. Experimental

### 2.1. Adsorbent

The commercially available PAC supplied by Mulim Chemical Co. Ltd., Korea was used as the adsorbent throughout this study. PAC was washed with double distilled water and dried at  $110^\circ C$  for 24 h, cooled and stored in a desiccator prior to use. The manufacture's specification for the PAC is shown in Table 1.

### 2.2. Chemicals

PVA with a degree of polymerization of 1500 and degree of hydrolysis value 86–90% was obtained from Yakuri Pure Chemicals Co. Ltd., Japan. Boric acid and potassium iodide were supplied by DC Chemical Co. Ltd., Japan and iodine (99.5% pure) was obtained from Acros Organics, USA. The chemicals used for experiments were of reagent grade and were used without further purification. All the samples were prepared in double distilled water.

### 2.3. Adsorption studies

Batch adsorption experiments were carried out in a series of 300 mL Erlenmeyer flasks, containing 100 mL of PVA solution. The PAC was added into these flasks and was shaken at 150 rpm in a thermostat controlled shaker (iNtRON Biotechnology Co. Ltd., Korea) at a pre-set temperature for 60 min. The experiments for isotherm studies were carried out at  $20^\circ C$  and at a pH of 6.3. Samples were separated by fast filtration, and the concentrations of PVA at equilibrium ( $C_e$ ) were determined. PVA measurements were done at a  $\lambda_{max}$  of 690 nm using a UV–VIS spectrophotometer (Shimadzu, model UVmini-1240, Japan). The method is based on the blue color produced by reaction of PVA with iodine in the presence of boric acid [19].

The amount of PVA adsorbed by the PAC was calculated from the differences between the PVA quantity added to the PAC and the PVA content of the supernatant using the following equation:

$$q_e = \frac{V(C_o - C_e)}{M}, \quad (1)$$

where  $q_e$  is the PVA uptake (mg/g),  $C_o$  and  $C_e$  are the initial and final or equilibrium concentrations in the solution (mg/L),

Table 1  
Manufacture's specification for the PAC

Parameters	Value
Bulk density ( $g/cm^3$ )	0.24
Specific surface area ( $m^2/g$ )	1050
Total pore volume ( $cm^3/g$ )	0.9
Micropore volume ( $cm^3/g$ )	0.55
Mean particle size (cm)	$45 \times 10^{-8}$

respectively,  $V$  is the volume of the solution (L) and  $M$  is the mass of PAC (g).

For estimating the optimum amount of adsorbent per unit mass of adsorbate, PVA solution was contacted with different amounts of adsorbents till equilibrium was attained. The effect of adsorbent dose was studied with different adsorbent doses and 100 mL of 50 mg/L PVA solution was agitated for equilibrium time. The kinetics of adsorption was determined by analyzing adsorption of PVA from the aqueous solution at different time intervals. For adsorption isotherms, the PAC dosage of 0.5 g was introduced to 100 mL of 25–500 mg/L PVA solution at 293 K. For thermodynamic studies, adsorption of 50 mg/L of PVA by 0.5 g of PAC was carried out at 293, 303 and 313 K in the thermostated rotary shaker, respectively.

### 3. Results and discussion

#### 3.1. Adsorption kinetics

The kinetics of sorption that describes the solute uptake rate governing the residence time of the sorption reaction is one of the important characteristics defining the efficiency of sorption [20]. Hence, in the present study, the kinetics of PVA removal was determined to understand the adsorption behavior of PAC.

##### 3.1.1. Adsorption kinetics at different initial PVA concentration

The relationship between contact time and PVA sorption onto PAC at different initial PVA concentrations is shown in Fig. 1. The adsorption was very fast from the beginning to 10 min and the sorption capacities increased from 4.18 to 11.98 mg/g with the PVA concentration range of 25 to 100 mg/L at a contact time of 10 min. With further increase of time, the sorption kinetics decreased progressively, and finally the adsorption approached to equilibrium within 30 min in all the cases. The sorption capacities corresponding to equilibrium adsorption increased from 4.03 to 14.67 mg/g with the increase in PVA concentration from 25 to 100 mg/L. The fast adsorption at the initial stage is probably due to the increased concentration gradient between the

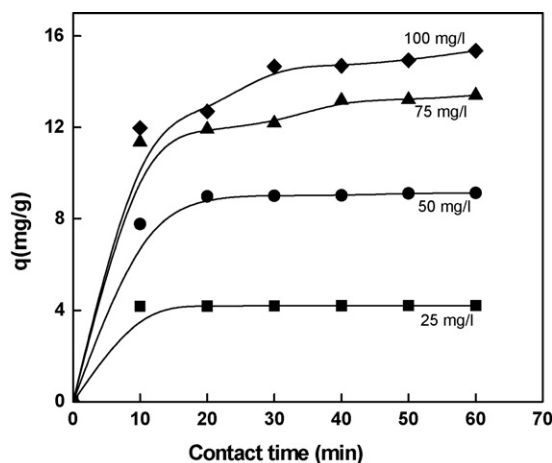


Fig. 1. Effect of various initial PVA concentrations on the adsorption of PVA onto PAC ( $T$ , 20 °C; pH, 6.3;  $V$ , 100 mL; PAC, 0.5 g; agitation rate, 150 rpm).

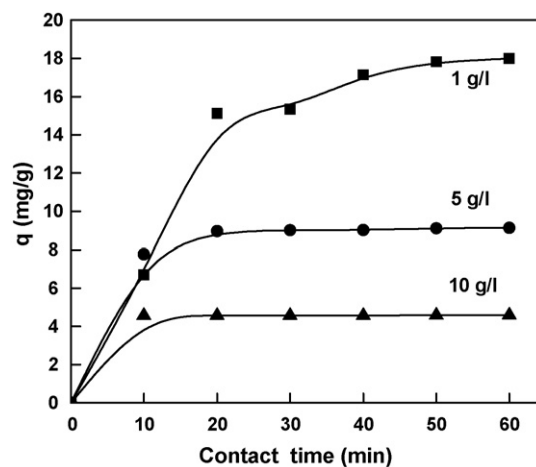


Fig. 2. Effect of PAC dosage on the adsorption of PVA onto PAC ( $T$ , 20 °C; pH, 6.3;  $C_0$ , 50 mg/L;  $V$ , 100 mL; agitation rate, 150 rpm).

adsorbate in solution and adsorbate in adsorbent as there must be increased number of vacant sites available in the beginning. The progressive increase in adsorption and consequently the attainment of equilibrium adsorption may be due to limited mass transfer of the adsorbate molecules from the bulk liquid to the external surface of PAC, initially and subsequently by slower internal mass transfer within the PAC particles. Similar trends were also observed for PVA adsorption onto fuller's earth [16] and montmorillonite [17]. In terms of adsorption removal efficiency, it was 84%, 92%, 81.2% and 73.4% for the PVA concentrations 25, 50, 75 and 100 mg/L, respectively.

##### 3.1.2. Adsorption kinetics at different adsorbent dosage

To study the effect of adsorbent dosage on the kinetics of adsorption, the adsorbent concentration was varied from 1 to 10 g/L, while initial PVA concentration was held constant at 50 mg/L at the temperature of 293 K (Fig. 2). As expected, an increase in the PAC quantity causes a decrease in the residual PVA concentration at equilibrium time and consequently an increase in the sorption removal efficiency. Indeed, the adsorption removal efficiency values increased from 36% to 92%, as the PAC dose was increased from 1 to 10 g/L. Such a trend can be attributed to an increase in the sorptive surface area and the availability of more adsorption sites. However, the decrease in adsorption capacity from 18 to 4.6 mg/g with the increase in PAC dose from 1 to 10 g/L can be explained with the reduction in the available substrate for the adsorbent and consequently effective surface area.

Conversely a solid to liquid ratio varied in the range of 0.001–0.01 g/mL in the present study reveal that the amount of PVA adsorbed decreases with increasing solid to liquid ratio. In fact the solid to liquid ratio in an adsorption system exerts a great effect on the amount of adsorbed solute. A change in solid to liquid ratio not only changes the number of active sites available on the solid but also brings about a change in the number of molecules of the solute invading the solid surface for adsorption. Similar types of results have also been reported by Bajpai and Vishwakarma [16].

### 3.2. Adsorption kinetic modeling

In order to investigate the controlling mechanism of adsorption processes such as mass transfer and chemical reaction, the pseudo-first-order and pseudo-second-order equations are applied to model the kinetics of PVA adsorption onto PAC.

#### 3.2.1. Pseudo-first-order model

The pseudo-first-order equation is

$$\frac{dq}{dt} = k_1(q_e - q), \quad (2)$$

where  $k_1$  is the rate constant of pseudo-first-order model ( $\text{min}^{-1}$ ),  $q$  is the amount of PVA adsorbed at various times ( $\text{mg/g}$ ), and  $q_e$  is the amount of PVA adsorbed on adsorbent at equilibrium ( $\text{mg/g}$ ). After integrating with the initial conditions, the equation becomes [21]:

$$\log(q_e - q) = \log q_e - \left( \frac{k_1 t}{2.303} \right), \quad (3)$$

#### 3.2.2. Pseudo-second-order model

The pseudo-second-order model can be represented in the following form [22]:

$$\frac{dq}{dt} = k_2(q_e - q)^2, \quad (4)$$

where  $k_2$  is the rate constant of pseudo-second-order model ( $\text{g/mg/min}$ ). After integrating with the initial conditions, the form can be obtained as:

$$\frac{t}{q} = \frac{1}{(k_2 q_e)^2} + \frac{t}{q_e}, \quad (5)$$

The slopes and intercepts of plots of  $\log(q_e - q)$  versus  $t$  were obtained to determine the first-order rate constant  $k_1$  and equilibrium adsorption amount  $q_e$  (plot not shown). The correlation coefficients for the first-order kinetic model at different PAC dosage were relatively low and the calculated  $q_e$  values obtained from the first-order kinetic model failed to match the experimental  $q_e$  values, both indicating that the adsorption of PVA onto PAC was not a first-order reaction. The fitting results of first-order kinetic model are shown in Table 2.

The slopes and intercepts of plots of  $t/q$  versus  $t$  were obtained to determine the pseudo-second-order rate constant  $k_2$  and equilibrium adsorption amount  $q_e$ . The correlation coefficients for the pseudo-second-order kinetic model at different PAC dosage were above 0.997 and the calculated  $q_e$  values

were consistent with the experimental values. The high correlation coefficients ( $R^2 > 0.997$  in all cases) and the agreement of calculated and experimental  $q_e$  both demonstrated that the adsorption kinetics of PVA onto PAC followed the pseudo-second-order kinetic model. Similar confirmation has been obtained in the adsorption of various dyes from spent textile dyeing wastewater containing PVA [10,23,24]. Further concerning the rate constant of pseudo-second-order ( $k_2$ ), it was found that the pseudo-second-order rate constant significantly decreased with the increase in initial PVA concentration. As shown in Table 2, the value of  $k_2$  remarkably reduced from 0.66 to 0.014  $\text{g/mg/min}$  as the initial PVA concentration increased from 25 to 100  $\text{mg/L}$ . This varying trend of pseudo-second-order rate constant resulting from the model fitting was in good agreement with the experimental PVA adsorption kinetics, in which the time required for the equilibrium adsorption monotonically increased with the increase in the initial PVA concentration (Fig. 1).

### 3.3. Adsorption mechanisms

It is always important to predict the rate-limiting step in an adsorption process to understand the mechanism associated with the phenomena. For a solid liquid sorption process, the solute transfer is usually characterized by either external mass transfer or intraparticle diffusion or both. Generally three types of mechanisms are involved in the adsorption process, mentioned as follows [25]:

1. Film diffusion, which involves the movement of adsorbate molecules from the bulk of the solution towards the external surface of the adsorbent.
2. Particle diffusion, where the adsorbate molecules move in the interior of the adsorbent particles.
3. Sorption of the adsorbate molecules on the interior of the porous adsorbent.

Of the three steps, the third step is assumed to be very rapid and can be considered negligible. For design purposes, it is required to distinguish between film diffusion and particle diffusion. In order to identify the slowest step in the adsorption process, Boyd kinetic equation [26] was applied, which is represented as:

$$F = 1 - \frac{6}{\pi^2} \exp(-Bt), \quad (6)$$

Table 2  
Comparison of the first- and second-order adsorption rate constants and calculated and experimental  $q_e$  values for different initial concentrations

Initial concentration (mg/L)	$q_{e,\text{exp}}$ (mg/g)	First-order kinetics			Second-order kinetics		
		$k_1$ ( $\text{min}^{-1}$ )	$q_{e,\text{cal}}$ (mg/g)	$R^2$ (I order)	$k_2$ (g/mg/min)	$q_{e,\text{cal}}$ (mg/g)	$R^2$ (II order)
25	4.216	0.113	1.59	0.739	0.66	4.224	1.00
50	9.132	0.111	4.56	0.905	0.071	9.23	0.999
75	13.40	0.08	8.40	0.912	0.022	14.0	0.998
100	15.36	0.069	9.69	0.915	0.014	16.39	0.997

and

$$F = \frac{q}{q_e}, \quad (7)$$

where  $q_e$  is the amount of PVA adsorbed at equilibrium (mg/g) and  $q$  represents the amount of PVA adsorbed at any time  $t$  (min),  $F$  represents the fraction of solute adsorbed at any time  $t$ , and  $Bt$  is a mathematical function of  $F$ .

Eq. (6) can be rearranged by taking the natural logarithm to obtain the equation

$$Bt = -0.4977 - \ln(1 - F), \quad (8)$$

The plot of  $[-0.4977 - \ln(1 - F)]$  against time  $t$  can be employed to test the linearity of the experimental values [27].

If the plots are linear and pass through origin, then the slowest (rate controlling) step in the adsorption process is the internal diffusion, and vice versa. From Fig. 3, it was observed that the plots are linear but do not pass through the origin suggesting that the adsorption process is controlled by film diffusion. The calculated  $B$  values were used to calculate the effective diffusion coefficient,  $D_i$  ( $\text{m}^2/\text{s}$ ) using the relationship:

$$B = \frac{\pi^2 D_i}{r^2}, \quad (9)$$

where  $D_i$  is the effective diffusion coefficient of solute in the adsorbent phase and  $r$  is the radius of the adsorbent particles. The  $D_i$  values were found to be  $9.66 \times 10^{-22}$ ,  $9.51 \times 10^{-22}$ ,  $6.83 \times 10^{-22}$  and  $6.0 \times 10^{-22}$   $\text{m}^2/\text{s}$ , respectively for an initial PVA concentration of 25, 50, 75 and 100 mg/L.

### 3.4. Adsorption isotherms

The functional relationship between the amount of solute adsorbed per unit weight of the adsorbent and the concentration of adsorbate in bulk solution at a given temperature under equilibrium conditions is generally correlated by adsorption isotherm. It is important to establish the most appropriate correlations for the batch equilibrium data using empirical or theoretical equations as it plays a functional role in predictive modeling procedures for analysis and design of adsorption

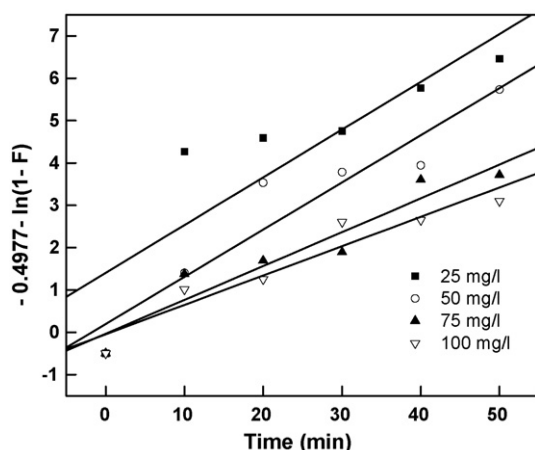


Fig. 3. Boyd plot for the adsorption of PVA onto PAC.

systems. Several equilibrium models have been developed and employed for such analysis. However, no general model has been found to fit the experimental data accurately under any given condition. A particular one that fits the data under one set of conditions may completely misfit under another [28]. The two most commonly employed equilibrium models for such analysis are the Langmuir and Freundlich equations. In the present investigation, the experimental data were tested with respect to both these isotherms.

The Langmuir model was originally developed to represent chemisorption on a set of well-defined localized adsorption sites having the same adsorption energy, independent of surface coverage and with no interaction between adsorbed molecules. This model, also called as the ideal localized monolayer model, is valid for monolayer sorption on to a surface with a finite number of identical sites, and is given by [29]:

$$q_e = \frac{Q_o K_L C_e}{1 + K_L C_e}, \quad (10)$$

where  $Q_o$  is a constant related to the area occupied by a monolayer of adsorbate, reflecting the maximum adsorption capacity (mg/g),  $C_e$  is the equilibrium liquid-phase concentration (mg/L),  $K_L$  is a direct measure of the intensity of adsorption (L/mg) and  $q_e$  is the amount adsorbed at equilibrium (mg/g). This equation can be linearized as follows:

$$\frac{1}{q_e} = \left( \frac{1}{K_L Q_o} \right) \left( \frac{1}{C_e} \right) + \frac{1}{Q_o}, \quad (11)$$

From the data of  $1/q_e$  versus  $1/C_e$ ,  $K_L$  and  $Q_o$  can be determined from the slope and intercept.

The Freundlich adsorption isotherm usually fits the experimental data over a wide range of concentrations. This empirical expression encompasses the surface heterogeneity and exponential distribution of the active sites and their energies. The widely used empirical Freundlich equation based on sorption on a heterogeneous surface is given by [29]:

$$q_e = K_F C_e^{1/n}, \quad (12)$$

where  $K_F$  ( $(\text{mg/g})(\text{L/mg})^{1/n}$ ) and  $n$  (dimensionless) are constants incorporating all factors affecting the adsorption process such as adsorption capacity and intensity, respectively. This equation can be linearized as follows:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e, \quad (13)$$

The values of  $n$  and  $K_F$  were calculated from the slope and intercept of the plot of  $\log q_e$  versus  $\log C_e$ .

The applicability of the isotherm equations was compared on the basis of correlation coefficient,  $R^2$ . From Table 3, it was clear that the Freundlich model yields a better fit than the Langmuir model for the adsorption of PVA onto PAC. The H-type isotherm, subgroup 3 [30] was observed for PVA adsorption onto the PAC (Fig. 4). An H-type (high affinity) isotherm results when the solute molecules are large or ionic and have a very high affinity for the sorption sites. Solute molecules are completely adsorbed by the adsorbent at lower concentrations and there are decreasing sites available for adsorption on the adsorbent surface with the

Table 3  
Isotherm constants for the Langmuir and Freundlich isotherm

Adsorbent	Langmuir isotherm			Freundlich isotherm		
	$Q_0$ (mg/g)	$K_L$ (L/mg)	$R^2$	$K_F$ ((mg/g)(L/mg) <sup>1/n</sup> )	$n$	$R^2$
PAC	26.6	0.066	0.76	3.37	2.45	0.90

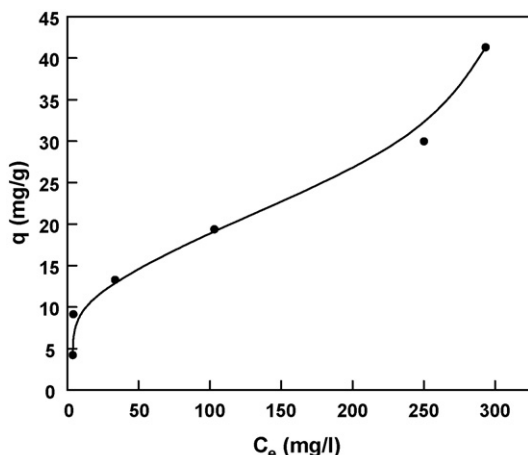


Fig. 4. Adsorption isotherm of PVA onto PAC ( $C_0$ , 25–500 mg/L; pH, 6.3;  $T$ , 20 °C).

increasing system concentration. Bussetti and Fereiro [17] found the H-type of isotherm, subgroups 1 and 2, respectively, when studying the PVA adsorption on Ca-Mt and/or Na-Mt. Bajpai and Vishwakarma [16] found an adsorption isotherm of L III-type suggesting a multilayer formation of PVA chains over the clay surfaces while studying the PVA adsorption onto Fuller's earth.

The Freundlich constant  $K_F$  indicates the adsorption capacity of the adsorbent and  $n$  is a measure of the deviation from linearity of the adsorption. If the value of  $n$  is equal to unity, the adsorption is linear. If the value of  $n$  is below unity, this implies that the adsorption process is chemical, but the value of  $n$  above unity indicates that the adsorption is a favorable physical process [31]. The value of  $n$  at equilibrium was 2.45 at 293 K, which represents favorable adsorption and that the adsorption bond becomes weak with van der Waals' forces.

### 3.5. Thermodynamic parameters

The activation energy ( $E_a$ ) of the PVA adsorption on the PAC particles was calculated using the Two-Point form of Arrhenius equation:

$$\log \left( \frac{K_1}{K_2} \right) = \left[ \frac{E_a}{(2.303R)} \right] \left[ \left( \frac{1}{T_2} \right) - \left( \frac{1}{T_1} \right) \right], \quad (14)$$

where  $E_a$  is the activation energy of adsorption ( $\text{kJ mol}^{-1}$ ),  $R$  is universal gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ),  $K_1$  and  $K_2$  are the rate constants corresponding to temperatures  $T_1$  and  $T_2$ , respectively. From Eq. (14), the activation energy ( $E_a$ ) of adsorption was found to be  $47.9 \text{ kJ mol}^{-1}$ . The thermodynamic parameters for the adsorption process,  $\Delta H^\circ$  and  $\Delta S^\circ$ , were evaluated using

the Van't Hoff equation:

$$\log K_c = \frac{\Delta S^\circ}{2.303R} - \frac{\Delta H^\circ}{2.303RT}, \quad (15)$$

where  $\Delta S^\circ$  and  $\Delta H^\circ$  are the entropy ( $\text{kJ mol}^{-1} \text{ K}^{-1}$ ) and enthalpy ( $\text{kJ mol}^{-1}$ ) change of adsorption, respectively,  $R$  is universal gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ), and  $T$  is the absolute temperature (K).

The values of  $\log K_c$  were defined as follow [32]:

$$\log K_c = \frac{F_e}{1 - F_e}, \quad (16)$$

where  $F_e$  is the fraction of PVA adsorbed at equilibrium.

At different temperatures (293–313 K), the corresponding  $C_e$  values for different fixed  $q_e$  were calculated. The values of  $\Delta H^\circ$  and  $\Delta S^\circ$  were calculated from the slope and intercept of linear regression of  $\log K_c$  versus  $(1/T) \times 1000$ . The values of  $\Delta G^\circ$  were estimated by:

$$\Delta G^\circ = -RT \ln K_c, \quad (17)$$

The plot shown in Fig. 5 is linear at the range of temperature investigated. The calculated thermodynamic parameters such as  $E_a$ ,  $\Delta H^\circ$ ,  $\Delta S^\circ$  and  $\Delta G^\circ$  are given in Table 4.

The negative value of  $\Delta G^\circ$  at all temperatures indicates that PVA adsorption onto PAC is spontaneous. The decrease in the value of  $\Delta G^\circ$  with increase in temperature suggests that process is favored at higher temperatures. The positive value of  $\Delta H^\circ$  for the adsorption reaction of PVA on the PAC particles indicates that the adsorption process is endothermic. The PVA molecules are hydrated in aqueous solution. When the PVA molecules get adsorbed on the adsorbent surface, water molecules previously bonded to the PVA molecules get released and dispersed in

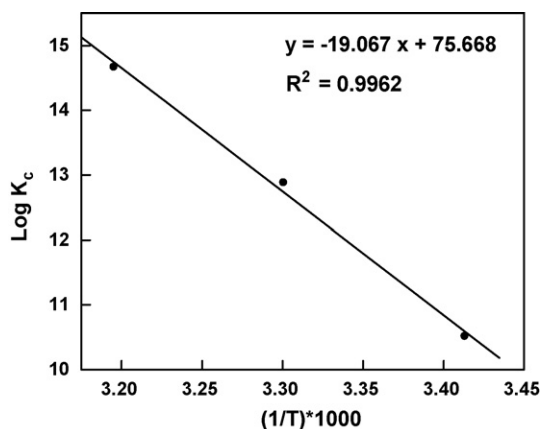


Fig. 5. Plot of  $\log K_c$  vs.  $(1/T) \times 1000$  for the estimation of thermodynamic parameters for the adsorption of PVA onto PAC.

Table 4  
Thermodynamic parameters for the adsorption of PVA on PAC

	$C_o$ (mol L <sup>-1</sup> )	$E_a$ (kJ mol <sup>-1</sup> )	$\Delta H^\circ$ (kJ mol <sup>-1</sup> )	$\Delta S^\circ$ (kJ mol <sup>-1</sup> K <sup>-1</sup> )	$\Delta G^\circ$ (kJ mol <sup>-1</sup> )		
					293 K	303 K	313 K
PAC	0.416	47.9	365	1.45	-59.00	-74.8	-88.00

the solution, resulting in the increase in entropy. During the adsorption of PVA on PAC, the increased randomness at the solid/solution interface is manifested from the positive value of  $\Delta S^\circ$ .

#### 4. Conclusion

The present study shows that the PAC can be used as an effective and favorable adsorbent for the removal of PVA from aqueous solution. The adsorption reached equilibrium within 30 min at the experimental conditions in all the cases. Pseudo-first-order and pseudo-second-order models were employed to fit the adsorption kinetics. The fitting result indicated that the adsorption of PVA on PAC follow pseudo-second-order kinetics. External mass transfer was confirmed as the rate-controlling step in the sorption process. The H-shaped adsorption isotherm indicates that there is a high affinity of the solute for the sorption sites. The equilibrium data were best fitted to the Freundlich isotherm model. Thermodynamic parameters ( $\Delta G^\circ$ ,  $\Delta H^\circ$ , and  $\Delta S^\circ$ ) were determined and their values indicated that the adsorption process was thermodynamically favorable, spontaneous, and endothermic in nature. The positive value of the entropy change suggests the increased randomness. Under the prevailing conditions, the maximum PVA removal efficiency was found to be 92%.

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