

Modeling and Thermodynamics of Methylene Blue and Acid Blue 80 Adsorption onto Potato Residue Based Activated Carbon

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Abstract A study was made on the adsorption kinetics and thermodynamics of methylene blue(MB) and acid blue 80(AB80) onto powder of activated carbon(PAC) prepared by chemical method from dry potato residue(DPR). The PAC was characterized by N₂ adsorption-desorption isotherms analysis and scanning electron microscopy. The maximum adsorption capacities of PAC for MB and AB80 at 303 K are 532.19 and 156.22 mg/g, respectively. The results indicate that the adsorption kinetics of the selected dyes on PAC is well-described by the pseudo-second order model. And their thermodynamic data were analyzed *via* the isotherms of Langmuir, Freundlich, Redlich-Peterson, Toth and Sips, and the thermodynamic parameters were calculated. The results show that PAC is a fast and effective adsorbent for removing the cationic dyes from aqueous solutions.

Keywords Adsorption; Activated carbon; Methylene blue; Acid blue 80

1 Introduction

The world-wide production and usage of dyes generate colored wastewaters, which has aroused people's concern about environmental protection. The runoffs from the manufacturing and textile industries are discarded directly into rivers and lakes, altering the biological stability of surrounding ecosystems^[1]. Most of the dyes are stable to photodegradation and biodegradation^[2–4]. Thus, the conventional treatment of colored wastewater is a challenge. Thus far, many methods such as coagulation and flocculation^[5], membrane separation^[6], oxidation or ozonation^[7,8], electro-coagulation^[9], photocatalysis^[10,11] and adsorption^[12–17] have been utilized for removing dyes from wastewater. Among these methods, adsorption technique has been proven to be effective and attractive for the treatment of dye-bearing wastewaters^[18]. Adsorption is also considered as a comparatively cheap and effective method in the removal of dyes. The adsorption characteristics of dyes on various adsorbents, such as activated carbon(AC), agriculture waste, silica, clay, industrial solid wastes, sewage sludge have been extensively investigated^[19].

Among these adsorbents, AC is the most widely used adsorbent for the dye removal based on its high adsorption capacity and fast removal rate because of its huge specific

surface area and specific surface reactivity^[20]. However, it is prohibitively expensive. The waste materials and by-products from the agriculture are assumed to be low-cost adsorbents due to their abundance in nature. The raw agricultural solid wastes, such as rice husk^[21], leaves^[22], seeds^[23], the residue of diosgenin production^[24] and the waste materials from forest industries, such as date pits^[17] and sawdust^[25] etc. have been used as adsorbents for the removal of dyes. However, potato residue has been used only very rarely.

We investigated the removal of two different kinds of dyes, methylene blue(MB) and acid blue 80(AB80), from aqueous solution using AC prepared under optimized conditions from dry potato residue(DPR). And the equilibrium isotherms, kinetics, and thermodynamics for MB and AB80 adsorption on the PAC were evaluated.

2 Experimental

2.1 Materials

The cationic dye(MB), and the anionic dye(AB80), were purchased from Shanghai Zhongqin Chemical Reagent Co., Ltd.(China), and Haining Deer Chemical Reagent Co., Ltd.(China), respectively. The molecular structures of the two dyes are shown in Fig.1.

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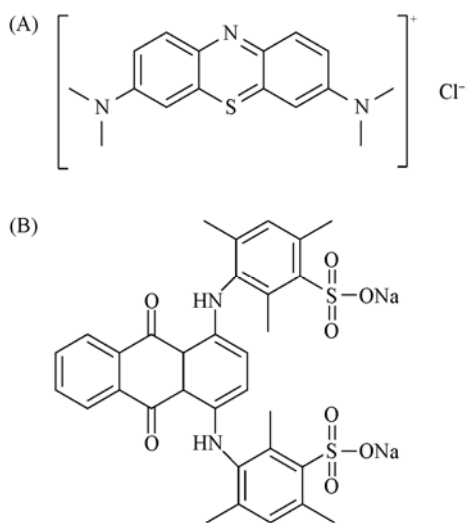


Fig.1 Molecular structures of methylene blue(A) and acid blue 80(B)

2.2 Preparation and Characterization of PAC

Potato residue was collected from Huining County, Gansu Province, China. It was air-dried at room temperature and ground to pass through an 80-mesh sieve. DPR was mixed with a ZnCl₂ solution (50%, mass fraction) at an impregnation ratio (mass ratio of ZnCl₂ solution to DPR) of 1.5 g/g and kneaded. This mixture was then maintained at room temperature for 24 h to prepare the impregnated sample. After that, the impregnated sample was filled in ceramic crucibles, which were respectively covered with a fitting lid^[26], and pyrolyzed in a muffle furnace at a heating rate of 10 °C/min from room temperature to 600 °C, and then activated at 600 °C for 1 h. At the end of activation the carbonized samples were withdrawn from the furnace and allowed to cool. The samples were then soaked with a HCl solution (5%) and repeatedly washed with distilled water until the pH value of filtrate reached 6.5–7.0. After that, the samples were dried at 110 °C for 24 h in a vacuum drying oven. Finally the samples were ground and stored in valve bag.

The samples were characterized in terms of specific surface area, pore volume, and pore diameter *via* the adsorption of nitrogen (Micromeritics, TRISTAR II 3020) at 77 K. The surface area was determined from isotherms with the help of the Brunauer-Emmett-Teller equation (BET)^[27]. The micropore volume was calculated with *t*-plot micropore volume and the mesopore volume was calculated as the difference between total pore volume and micropore volume, and the pore size distribution was calculated by the BJH method.

2.3 Batch Adsorption Studies

Batch adsorption was performed in a set of 50 mL conical flasks containing 15 mL of dye solution (pH=6.5–7.0) and 15 mg of PAC was added to each flask and kept at 303 K on a shaker (130 r/min). For kinetic studies, the aqueous samples were taken at preset time intervals. The amount of dye adsorbed at any time, q_t (mg/g), was calculated *via* Eq.(1):

$$q_t = \frac{(c_0 - c_t)V}{m} \quad (1)$$

where c_t (mg/L) is the liquid-phase concentration of dye solution at time t (min); c_0 is the initial concentrations of MB (200, 400 and 600 mg/L); AB80 (100, 200, 300 mg/L); V (L) is the volume of solution; m (g) is the mass of PAC used. Pseudo-first order model and pseudo-second order model were used to analyze the kinetic data^[17].

Pseudo-first order model:

$$q_t = q_e [1 - \exp(-k_1 t)] \quad (2)$$

where q_e and q_t (mg/g) are the uptake of dyes at equilibrium and at time t (min), respectively; K_1 (min⁻¹) is the adsorption rate constant; K_2 (g·mg⁻¹·min⁻¹) is the rate constant of second-order equation.

Pseudo-second order model:

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (3)$$

For equilibrium studies, the same procedure was followed, but the different initial concentrations (100–600 and 50–400 mg/L) of MB and AB80 were used respectively. And the experiments were carried out for 3 and 12 h respectively to ensure equilibria of MB and AB80. The collected supernatants were analyzed by UV-Vis spectroscopy (PERSEE TU-1901 UV) at 664 and 626 nm for MB and AB80, respectively.

The amount of dye adsorbed onto PAC, q_e (mg/g) was calculated *via* Eq.(4):

$$q_e = \frac{(c_0 - c_e)V}{m} \quad (4)$$

The normalized standard deviation, Δq (%), was calculated with the aid of Eq.(5):

$$\Delta q (\%) = 100 \sqrt{\frac{\sum [(q_{e, \text{exp}} - q_{e, \text{cal}}) / q_{e, \text{exp}}]^2}{N - 1}} \times 100\% \quad (5)$$

where N is the number of data points, $q_{e, \text{exp}}$ and $q_{e, \text{cal}}$ (mg/g) are the experimental and calculated equilibrium adsorption capacities, respectively. Several isotherm equations, namely, the Langmuir, Freundlich, Redlich-Peterson, Toth, Sips^[26] isotherm equations were used to fit the experimental isotherm data of dyes adsorbed on PAC.

Langmuir isotherm equation:

$$q_e = \frac{Q_m K_L c_e}{1 + K_L c_e} \quad (6)$$

Freundlich isotherm equation:

$$q_e = K_F c_e^{1/n_F} \quad (7)$$

Redlich-Peterson isotherm equation:

$$q_e = \frac{a_{RP} c_e}{1 + b_{RP} c_e^g} \quad (8)$$

Sips isotherm equation:

$$q_e = \frac{Q_m (K_S c_e)^{m_S}}{1 + (K_S c_e)^{m_S}} \quad (9)$$

where c_0 is the initial solute concentration; Q_m (mg/g) is the maximum uptake of dyes per unit mass of PAC; K_L (L/mg) is the Langmuir constant related to rate of adsorption; K_F (mg·g⁻¹·L^{1/n_F·mg^{-1/n_F}) and n_F are Freundlich constants which}

give a measure of adsorption capacity and adsorption intensity, respectively; $K_S(L \cdot mg^{-1})^{1/m}$ is Sips constant related to energy of adsorption.

The theoretical model to appropriately describe the adsorption data of the dye-PAC system was chosen from the adsorption capacity (Q_m), correlation coefficient (R^2) and normalized standard deviation (Δq). Each adsorption experiment was performed in triplicate under identical conditions and the mean value was presented.

2.4 Adsorption Thermodynamics

Adsorption thermodynamics such as Gibbs free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS) provide an insight into the mechanism and adsorption behavior of an isolated system. These parameters are respectively calculated by Eqs.(10), (11) and (12):

$$K_d = q_e(W/V) / c_e \quad (10)$$

$$\Delta G = RT \ln K_d \quad (11)$$

$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (12)$$

where $R(8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})$ is the universal gas constant, $T(\text{K})$ is temperature, and K_d is the distribution coefficient for the adsorption^[17].

3 Results and Discussion

3.1 Characteristics of PAC

Fig.2 shows the N_2 adsorption-desorption isotherms of the activated carbons prepared from DPR. It shows that the increment of N_2 adsorption was significant in relative higher pressure range. Type IV isotherms with a hysteresis loop of type H2 indicate that PAC has mesoporosity. And pore size distribution shown in Fig.3 supported the results, confirming that PAC obtained has wide pore size distribution and high mesoporosity. Table 1 lists the physical properties of PAC prepared under optimized conditions, which shows a micropore volume of $0.083 \text{ cm}^3/\text{g}$ compared to a mesopore volume of $0.982 \text{ cm}^3/\text{g}$. It has been revealed from the observation that prepared PAC has high mesoporosity. The probable reason is that an oxygen-limited condition allows a small amount of oxygen to permeate and promotes the volatile matter elimination and consumes surface carbon, destructs microporous structure and makes pore volume and pore size increase.

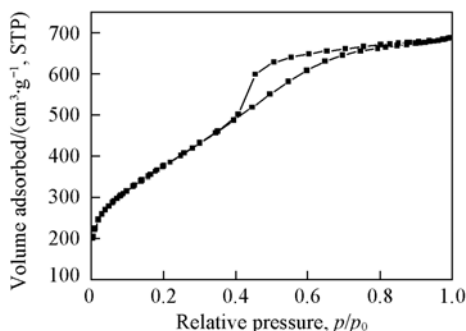


Fig.2 N_2 adsorption-desorption isotherms of PAC at 77 K

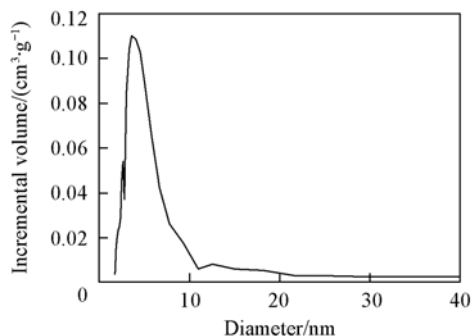


Fig.3 Pore size distribution of PAC

Table 1 Physical properties of PAC prepared under optimized conditions

Yield(%)	29.2
Surface area($\text{m}^2 \cdot \text{g}^{-1}$)	1357
Total pore volume($\text{cm}^3 \cdot \text{g}^{-1}$)	1.065
Micropore volume($\text{cm}^3 \cdot \text{g}^{-1}$)	0.083
Mesopore volume($\text{cm}^3 \cdot \text{g}^{-1}$)	0.982
Average pore diameter/nm	3.158

3.2 Adsorption Kinetics

The effect of contact time on adsorption capacity of PAC for the two selected dyes at different initial concentrations is shown in Fig.4. The adsorption capacity for MB increased with the increase of contact time, and the adsorption reached the equilibrium in about 2 h. The maximum adsorption capacity for MB and AB80 at 303 K were 532.19 and 156.22 mg/g, respectively. The kinetic data were analyzed by means of two kinetic models: pseudo-first order model and pseudo-second order model, respectively. All the kinetic parameters were calculated from the fit of the models with the results shown in Table 2. For the MB adsorption kinetics, the correlation coefficients for the

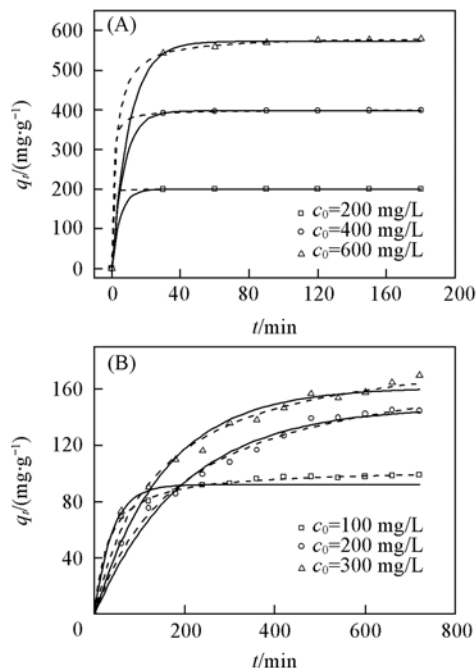


Fig.4 Fit curves of pseudo-first order model (solid line) and pseudo-second order model (dashed line) for MB(A) and AB80(B)

kinetic models are greater than 0.99, which indicates that the kinetic models provided good correlation of the adsorption to the different concentrations of MB onto PAC. The Δq values obtained for the pseudo-second order kinetic model are 0.0115%, 0.068% and 0.3143%, respectively at 200, 400 and 600 mg/L, lower than the corresponding ones obtained for the pseudo-first order kinetic model. For the AB80 adsorption, it

has similar trend but need longer time to reach the equilibrium (12 h). The correlation coefficients and the Δq values obtained from the pseudo-second order kinetic model are better than those obtained from the pseudo-first order kinetic model, respectively (Table 3). It indicates that the pseudo-second order kinetic model was more suitable to describe the adsorption kinetics of the two kinds of dyes onto PAC.

Table 2 Kinetic parameters of MB adsorption on PAC at 303 K

c_0 (mg·L ⁻¹)	q_e (mg·g ⁻¹)	Pseudo-first order model			Pseudo-second order model			
		k_1 /min ⁻¹	R^2	Δq (%)	q_e (mg·g ⁻¹)	k_2 /(g·mg ⁻¹ ·min ⁻¹)	R^2	Δq (%)
200	199.93	0.2047	0.9999	0.0266	200.09	0.0573	0.9999	0.0115
400	397.84	0.1397	0.9999	0.1772	400.15	0.0040	0.9999	0.0680
600	572.67	0.0969	0.9991	1.1296	585.96	6.9033×10 ⁻⁴	0.9999	0.3143

Table 3 Kinetic parameters of AB80 adsorption on PAC at 303 K

c_0 (mg·L ⁻¹)	q_e (mg·g ⁻¹)	Pseudo-first order model			Pseudo-second order model			
		k_1 /min ⁻¹	R^2	Δq (%)	q_e (mg·g ⁻¹)	k_2 /(g·mg ⁻¹ ·min ⁻¹)	R^2	Δq (%)
100	92.05	0.0258	0.9621	5.72	103.23	3.1233×10 ⁻⁴	0.9988	1.08
200	147.68	0.0050	0.9820	8.66	186.47	2.7558×10 ⁻⁵	0.9909	5.17
300	161.15	0.0065	0.9672	13.78	193.91	3.9158×10 ⁻⁵	0.9864	9.72

3.3 Adsorption Isotherms

The adsorption isotherm is important to describe how adsorbates interact with adsorbents. Thus, the experimental equilibrium data for MB adsorption on PAC were calculated from Eq.(4), and fitted with the isotherm models[Eqs.(6)–(9)]. The Langmuir isotherm suggests that adsorption occurred on a homogeneous surface containing sites with equal energy and equal availability for adsorption. Whether the adsorption process is unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$) can be verified by the separation factor (R_L). The Freundlich isotherm is an empirical equation that can be used for heterogeneous systems with interaction between the molecules adsorbed. The parameter K_F value is re-

lated to the adsorption capacity; while $1/n_F$ value is related to the adsorption intensity. The Redlich-Peterson isotherm is a hybrid isotherm featuring both the Langmuir and Freundlich equations. The value of parameter g shows either the Langmuir isotherm ($g=1$) or the Freundlich isotherm ($g=0$) is preferable for the system^[15]. The Sips isotherm is a combination of the Langmuir and Freundlich isotherms, the equation is reduced to the Freundlich equation at low adsorbate concentrations, and the equation provides for the adsorption capacity in the monolayer that is typical of the Langmuir isotherm when the adsorbate concentration is high. The Toth isotherm is another empirical equation developed to improve the fit of the Langmuir isotherm and to describe heterogeneous adsorption systems^[28].

All the isotherm fit curves are present in Fig.5 and Fig.6.

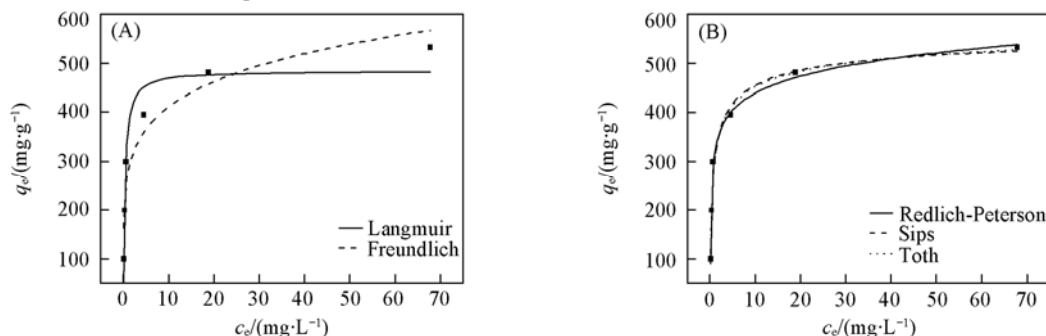


Fig.5 Fit curves of the Langmuir, Freundlich isotherms(A) and Redlich-Peterson, Sips, Toth isotherms(B) for MB adsorption on PAC at 303 K

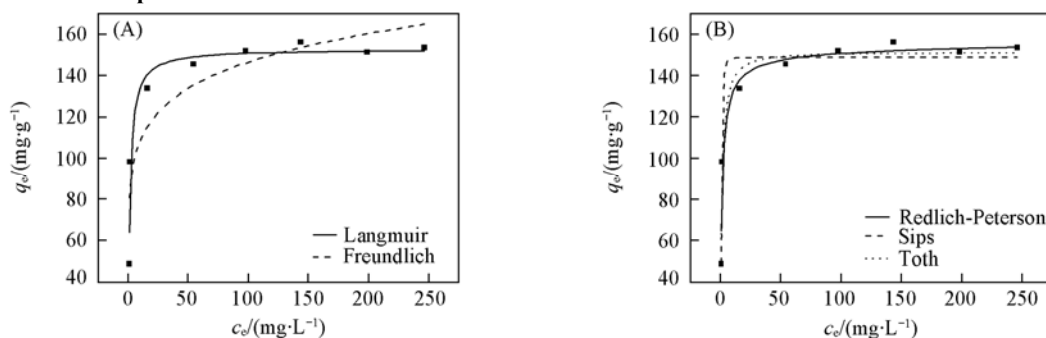


Fig.6 Fit curves of the Langmuir, Freundlich isotherms(A) and Redlich-Peterson, Sips, Toth isotherms(B) for AB80 adsorption on PAC at 303 K

For the Langmuir isotherm, a value of $R_L=5.483 \times 10^{-4}$ indicates the favorability of MB adsorption on PAC. The values of the parameters and correlation coefficient (R^2) for all the isotherms are shown in Table 4. Both Redlich-Peterson and Toth isotherm gave the R^2 values higher than 0.99, but the Toth model presented the lower Δq . Therefore, based on the high R^2 and Δq values observed, Toth model is the most appropriate for describing the adsorption of the MB onto PAC.

Table 4 Adsorption isotherm parameters of MB on PAC

Langmuir	Freundlich	Redlich-Peterson	Sips	Toth
$Q_m=484.90$	$K_f=280.27$	$a_{RP}=3430.5$	$Q_m=579.79$	$Q_m=619.82$
$K_L=3.038$	$n_f=5.9789$	$b_{RP}=9.6759$	$K_S=1.3650$	$n_{T0}=0.3645$
$R_L=0.0005$		$g=0.9007$	$M_S=0.4979$	$b_{T0}=0.2812$
$R^2=0.9256$	$R^2=0.9187$	$R^2=0.9934$	$R^2=0.9883$	$R^2=0.9920$
$\Delta q(\%)=26.13$	$\Delta q(\%)=30.62$	$\Delta q(\%)=5.96$	$\Delta q(\%)=6.12$	$\Delta q(\%)=4.27$

For the adsorption of AB80 on PAC, the R_L is 3.6×10^{-3} (Table 5), indicating favorable adsorption and physical process in the AB80-PAC system. The R_L for MB adsorption is lower than that for AB80 adsorption, indicating that MB is more favorable to adsorb on PAC than AB80. The probable reason is that MB is cationic dye that can be adsorbed easily by PAC with the negative surface charge. The best correlation with an R^2 value of 0.9539 and the lowest Δq value of 4.61 in Sips model (Table 5) may be due to the ability of Sips isotherm on predicting wide adsorbate concentration ranges^[17].

Table 5 Adsorption isotherm parameters of AB80 on PAC

Langmuir	Freundlich	Redlich-Peterson	Sips	Toth
$Q_m=152.98$	$K_f=80.1392$	$a_{RP}=112.4523$	$Q_m=148.75$	$Q_m=151.53$
$K_L=0.6865$	$n_f=7.6371$	$b_{RP}=0.7853$	$K_S=0.7519$	$n_{T0}=1.1699$
$R_L=0.0036$		$g=0.98602$	$M_S=2.9147$	$b_{T0}=1.8807$
$R^2=0.9319$	$R^2=0.7844$	$R^2=0.9204$	$R^2=0.9539$	$R^2=0.9187$
$\Delta q(\%)=13.40$	$\Delta q(\%)=25.57$	$\Delta q(\%)=13.76$	$\Delta q(\%)=4.61$	$\Delta q(\%)=12.87$

3.4 Adsorption Thermodynamics

Based on the dyes adsorption isotherm data which have been calculated from Eq.(4), the value of K_d was calculated from Eq.(10) for each temperature. The values of ΔG , ΔH and ΔS calculated from Eqs.(11) and (12) are listed in Table 6. The ΔH and ΔS parameters can be calculated from the slope and intercept of the plot of $\ln K_d$ vs. $1/T$ (Fig.7). The obtained negative values of ΔG (Table 6) show thermodynamically spontaneous nature adsorption of MB on PAC. However, a

non-thermodynamically spontaneous nature adsorption of AB80 on PAC at low temperature (below 303 K) was proposed. The increase in ΔG value with increasing temperature shows an increase in feasibility of adsorption at higher temperatures. Table 6 shows that the values of ΔH for the dyes adsorption are positive, indicating that the endothermic nature of the adsorption of dyes and also their magnitudes give the information on the type of adsorption, which can be either physical or chemical. Typically, ΔH for physical adsorption ranges from 4 kJ/mol to 40 kJ/mol, while that for chemical adsorption varies from 40 kJ/mol to 800 kJ/mol. Physical adsorption occurs when the intermolecular attractive forces between molecules of adsorbate and adsorbent are greater than those between molecules of the adsorbate itself. Physical adsorption, which may be a monomolecular or multi-molecular layer, occurs rapidly. In contrast, chemisorption involves the formation of chemical bonds between the adsorbate and adsorbent. In this system, the ΔH values show that the adsorptions of MB and AB80 on PAC are in the range of physisorption. The positive ΔS values of 43.48 and 100.68 J/mol suggest an increase in the randomness at adsorbate-solution interface during the adsorption process.

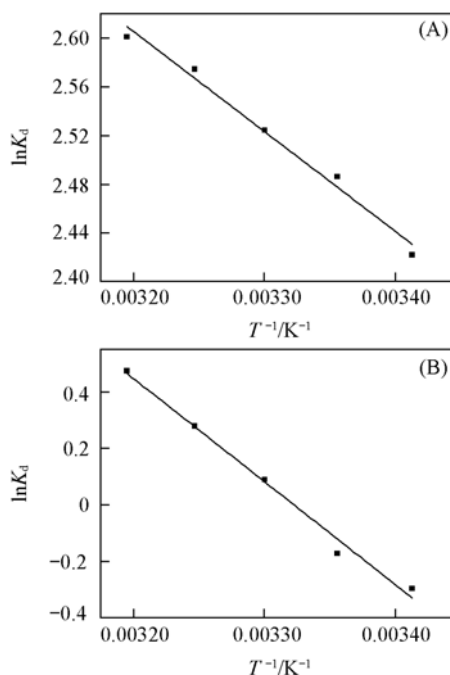


Fig.7 Plots of $\ln K_d$ vs. $1/T$ for MB(A) and AB80(B) adsorption on PAC ($c_0=600$ mg/L)

Table 6 Thermodynamics adsorption parameters for the dyes on PAC

Dye	$\Delta G/(J \cdot mol^{-1})$					$\Delta H/(kJ \cdot mol^{-1})$	$\Delta S/(J \cdot mol^{-1})$
	293 K	298 K	303 K	308 K	313 K		
MB	-5900.34	-6159.67	-6359.27	-6593.12	-6768.85	6.82	43.48
AB80	718.77	424.88	-228.56	-713.39	-1233.14	30.30	100.68

4 Conclusions

DPR has been used to prepare PAC by $ZnCl_2$ oxygen-limited activation. The surface area, total pore volume and mesopore volume of PAC were 1357 m²/g, 1.065 cm³/g and 0.982 cm³/g, respectively. The adsorption kinetic data of the two dyes were well-described by the pseudo-second order

model. The maximum adsorption capacity for MB and AB80 at 303 K were 532.19 and 156.22 mg/g, respectively. Equilibrium adsorption data of MB and AB80 onto PAC can be well-represented by Toth and Sips isotherm models. The calculated thermodynamic parameters, namely, ΔG , ΔH , and ΔS showed that the adsorption of the selected two dyes onto PAC was spontaneous and endothermic under examined conditions. It was considered that the PAC is a fast and effective adsorbent

for removing cationic dye from aqueous solutions.

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