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Effects of acidic treatment of activated carbons on dye adsorption

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Abstract

The effect of acidic treatments of activated carbons on dye adsorption was investigated. The physico-chemical properties of activated carbons were characterised by N_2 adsorption, mass titration, temperature-programmed desorption (TPD), and X-ray photoelectron spectrometry (XPS). It was found that surface chemistry plays an important role in dye adsorption. HNO_3 treatment produces more active acidic surface groups such as carboxyl and lactone, resulting in a reduction in the adsorption of basic dyes. However, HCl treatment decreases active acidic groups and thus enhances the adsorption of larger molecules on activated carbons. For methylene blue, the adsorption shows an order of AC > AC-HCl > AC-HNO_3 while for crystal violet and rhodamine B, the adsorption order is AC-HCl > AC > AC-HNO_3. It was also found that solution pH shows a significant influence on adsorption of methylene blue but little effect on rhodamine B. Kinetic studies indicate that the adsorption of dyes follows the pseudo-second-order model and the adsorption is an endothermic process.

Keywords: Activated carbon; Acid treatment; Dye adsorption; Surface chemistry; Pore structure

1. Introduction

Activated carbons can be used as adsorbents for gaseous or liquid phases as well as supports for catalysts. In activated carbon–liquid phase interactions, it has been known that the adsorption capacity depends on a number of factors namely:

- the physical nature of the adsorbent-pore structure, ash content and functional groups;
- the nature of the adsorbate, its pK_a, functional groups present, polarity, molecular weight and size;
- the solution conditions such as pH, ionic strength and the adsorbate concentration [1].

Currently, textile industry produces a huge quantity of dyed wastewater. The colour and the non-biodegradable nature of the spent dyebaths constitute serious environmental problems. Despite a wide range of wastewater treatment techniques available, there is no single process capable of adequate treatment for these effluents. Adsorption is an efficient method for the removal of dyes from wastewater and activated carbon is one of the most studied adsorptive materials [2–6]. It has been found that the performance of the adsorbents depends on their textural properties (porosity, surface area). The pore size distribution determines the fraction of its structure that can be accessed by a molecule of given size and shape. More recently, some authors started looking at the surface chemistry of activated carbons in order to interpret some results of dye adsorption experiments [4,7]. It was shown that the surface chemistry of the activated carbon could play a key role in dye adsorption performance.

Adsorption and desorption are important for heterogeneous systems. To fully understand the processes, two basic ingredients are required namely, equilibrium and kinetics. The growth of adsorption kinetics is of interest for many aspects of surface chemistry. In the past, research in dye adsorption focussed on equilibrium and a comparison of the adsorption capacity of different adsorbents; only a few reports concentrated on

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kinetics of dye adsorption. In this work, we will discuss the effect of acid treatment of activated carbon on its physical and chemical characteristics and the role of these properties in dye adsorption from aqueous solution as well as adsorption kinetics.

2. Experimental

2.1. Preparation of activated carbon

A commercial activated carbon (AC) (Calgon, USA) was treated with different acidic solutions, such as 2 N HCl and 2 N HNO_3 for about 24 h at room temperature. After the treatment, samples were washed with distilled water and dried in air at 103–105 °C overnight. The ash content was determined by burning off the carbon at 750 °C. The carbon samples treated by acids were then referred to as AC-HCl and AC-HNO_3, respectively.

2.2. Characterisation of the activated carbons

The pH of the aqueous slurry was measured as follows: the slurries were prepared in a ratio of 10 mL of water to 1 g of carbon; this mixture was stirred and the pH was measured several times until a constant value was reached. The pH meter used was microcomputer pH-vision 6071 (Lazar).

The point of zero charge (PZC), which is the pH value required to give zero net surface charge, was determined by a mass titration method proposed by Noh and Schwarz [8]. To measure the PZC of the carbon samples, three different initial pH solutions were prepared using HNO_3 (0.1 M) and NaOH (0.1 M), such that $pH = 3$, 6, and 11. $NaNO_3$ was used as the background electrolyte. For each initial pH, six containers were filled with 20 mL of the solution and different amounts of carbon were added (0.05%, 0.1%, 0.5%, 1% and 10% by weight). The equilibrium pH was measured after 24 h. The plot of pH versus mass fraction shows a plateau and the PZC is identified as the point at which the change of pH is zero. The PZC is then taken as the average of the three asymptotic pH values.

The textural structure was determined by N_2 adsorption/desorption at −196 °C which was conducted using a gas sorption analyser (Quantachrome, NOVA 1200). Samples were degassed for 3 h at 300 °C prior to the adsorption analysis. The BET surface area (S_{BET}), total pore volume (V), and average pore radius (R) were obtained from the adsorption isotherms. The Dubinin–Radushkevich method was used to calculate the micropore volume (V_{micro}) and the mesopore volume (V_{meso}) was determined by subtracting the micropore volume from total pore volume. The XPS measurements were conducted using PHI-560 ESCA system (Perkin Elmer). All spectra were acquired at a basic pressure of 2×10^{-7} Torr with Mg Kα excitation at 15 kV and recorded in $\Delta E =$ constant mode, pass energy 50 and 100 eV.

Temperature-programmed desorption (TPD) experiments were carried out in a vertical tube furnace. Samples with 1 g were placed in a quartz tube and He was flowed as carrier gas. After heated to 110 °C and kept at this temperature for 60 min, the temperature was raised at the rate of 5 °C/min to 800 °C. The gases evolved during the TPD runs were continuous monitored using a gas chromatograph (Shimadzu GC-17A) equipped with a thermal conductivity detector and a carbosphere column.

2.3. Adsorption procedure

Three basic dyes, methylene blue, crystal violet and rhodamine B, were obtained from UNILAB, and AJAX Chemicals. Their chemical structures are shown in Fig. 1. A stock solution at a concentration of 10^{-4} M was prepared. Sorption studies

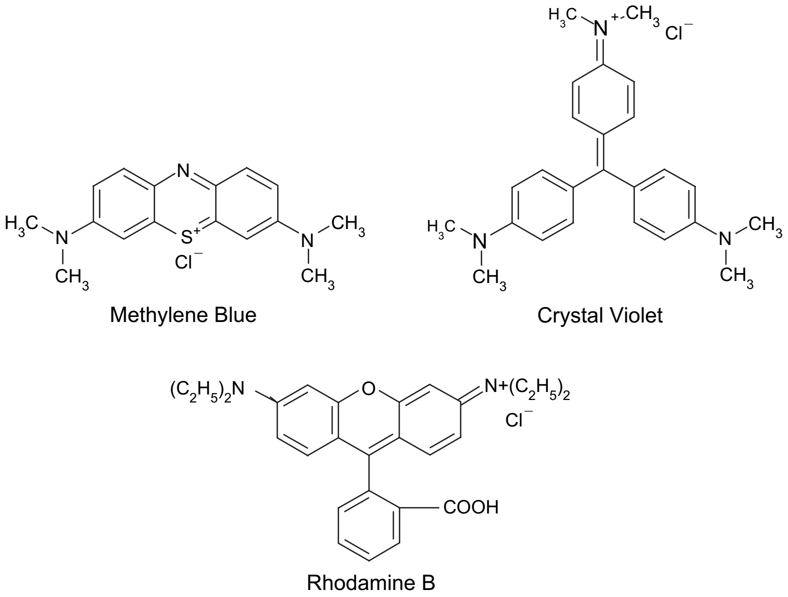

Fig. 1. Chemical structures of tested dyes.

were performed in 250 mL plastic containers with 200 mL of dye solutions. Approximately 5 mg of activated carbon was mixed with 200 mL of dye solutions at various concentrations (1.2×10^{-5}–4.6×10^{-5} M). The samples were placed in an orbital shaker (Sartorius AG) inside a heating hood (Certomat H) maintained at a constant temperature (30–50) ± 0.1 °C. The concentration of dye was determined by a spectrophotometer (Spectronic 20 Genesis, USA), with a wavelength setting at 665, 590 and 556 nm, for methylene blue, crystal violet and rhodamine B, respectively. The amount adsorbed is taken as the change in concentration from the initial value multiplied by the volume.

3. Results and discussion

3.1. Surface and pore structure of activated carbons

Table 1 lists the pore structure variations of the untreated and acid-treated activated carbon samples. It is evident that the original activated carbon (AC) had a high surface area and a well-developed porosity. BET surface area was slightly enhanced due to acid treatment, although the pore volume was relatively unchanged. Acid treatment can remove some mineral matter while changes of surface groups will block the micropores, resulting in little change in pore structure.

3.2. Surface acidity of the activated carbon

The pH of the aqueous slurry and PZC of carbons may give a good indication about the surface oxygen complexes and the electronic surface charges of carbons. This surface charge arises from the interaction between carbon surface and the aqueous solution. The complexes on carbon surface are generally classified as acidic, basic, or neutral. Carboxylic, anhydride, and lactone are acidic groups, while phenolic, carbonyl, quinone and ether groups are neutral or weakly acidic. Basic complexes are mainly pyrone and chromene groups. Based on the slurry pH, the nature of surface oxygen groups on the support and the dominant complexes can be deduced.

The values of pH and PZC for various carbons are shown in Table 2. It is clear that the untreated activated carbon showed basic character. AC-HCl is neutral and AC-HNO_3 is acidic. The pH and PZC of each carbon are very similar, which verifies the conclusion by Noh and Schwart [8] that pH_{slurry} can be taken as equivalent to the PZC of a carbon. The pH results also indicate that acid treatment increased the acidity of the activated carbons. The surface complexes on the carbon have changed and more acidic groups (such as carboxylic) produced.

Table 1
Effect of acid treatment on activated carbon's texture

	Ash (%)	S_{BET} (m^2/g)	V (cm^3/g)	V_{micro} (cm^3/g)	V_{meso} (cm^3/g)	R (Å)
AC	7.44	972	0.53	0.50	0.033	10.86
AC-HCl	5.80	1015	0.55	0.51	0.035	10.78
AC-HNO_3	5.56	987	0.53	0.50	0.036	10.88

Table 2
pH_{slurry} and PZC of various activated carbons

	AC	AC-HCl	AC-HNO_3
pH_{slurry}	8.75	6.58	2.80
PZC	8.60	6.70	2.98

The increase in the acidity of carbon upon acid treatment may be attributed to the removal of inorganic compounds leaving sites on the carbon surface which can chemisorb oxygen in air at room temperature. This would result in more oxygen surface complexes which are more acidic. HNO_3 removed more inorganic constituents (evident from the ash content in Table 1) resulting in more acidic carbon. In addition, HNO_3 as an oxidant may also oxidise some complexes producing acidic groups.

3.3. Surface functional groups

TPD experiments can provide interesting information about the amount, thermal stability, and nature of the surface oxygen groups. During the TPD process the oxygen surface complexes desorb primarily as CO and CO_2. CO_2 proceeds from the decomposition of carboxylic, anhydride (acidic groups), and lactonic groups, whereas CO proceeds from the decomposition of phenolic, carbonyl, quinone, pyrone, and anhydride (acidic) groups. Fig. 2 presents the CO and CO_2 evolution profiles from the carbons.

In general, the desorption profiles are typical of those found on carbons, and the CO_2 complexes, which are responsible for

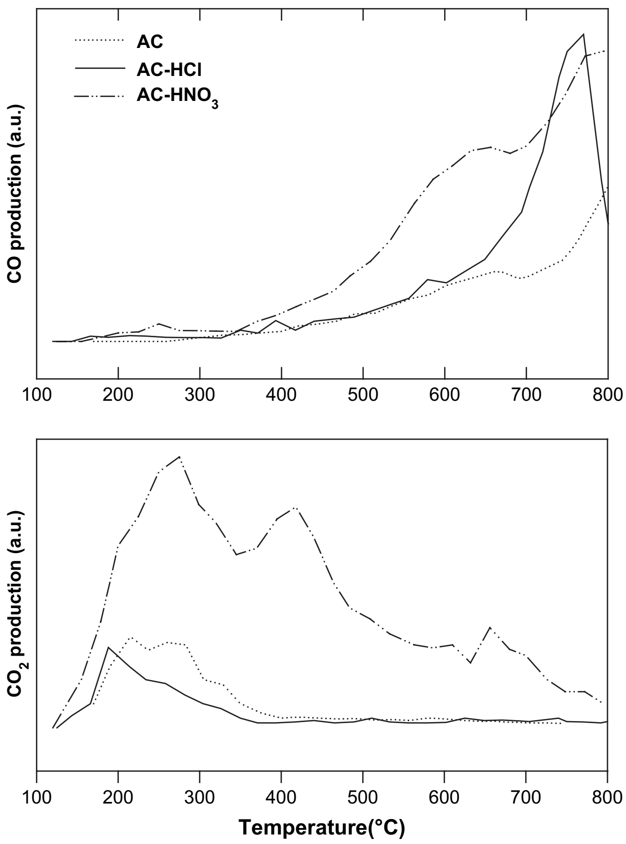

Fig. 2. TPD profiles of untreated and acid-treated carbons.

the acidic sites of the carbon surface, are evolved at much lower temperature than CO complexes. AC treated with HNO_3 generates an intense oxidation that results in the evolution of large amounts of CO_2 and CO. AC-HCl, and AC have comparable amounts of CO_2 complexes, but with different thermal stability. AC and AC-HNO_3 seem to have more stable CO complexes than AC-HCl because no peak is shown up to 800 °C whereas a maximum at 760 °C is observed for AC-HCl. In CO_2 evolution curves AC-HNO_3 shows three peaks at about 280, 400, and 650 °C. For AC and AC-HCl there is a broad peak occurred at 150–300 °C. These results indicate that more and stable carboxylic (CO_2 released at temperatures below 400 °C), anhydride (CO, CO_2 released below 600 °C), lactone groups (CO_2 released around 650 °C) and phenol groups (CO released around 700 °C) formed on AC-HNO_3, which is reflected in pH values. AC treated by HCl, however, has less thermal stability with the surface functional groups attributed to carboxylic and phenol groups. Hence, it can be deduced that some chemical groups may be changed or removed from AC-HCl during the acid washing process.

Fig. 3 shows the C1s signals of activated carbons. The C1s signal maxima on acid-treated carbons are shifted to higher binding energy. This is because of an increase in oxidic species (alcohols, carbonates, or carboxylic) and ether on the carbon surface after acid treatment. The dissolution of peak indicates that three carbon functional groups can be obtained, C–C, C–O and C=O. For AC-HNO_3, C–O and C=O functional groups are much higher than AC and AC-HCl and C=O on AC-HCl is also higher than AC. Therefore, XPS results confirm that more acidic groups such as carboxylic, ether were produced by acid treatment.

3.4. Adsorption of dyes

The dynamic adsorption of three dyes on activated carbons are given in Fig. 4. As shown, activated carbons present a similar adsorption process for three dyes. The adsorption of dyes on various carbons is rapid at the initial period of contact time and then becomes slow and stagnate with the increase in contact time. After 700 h, adsorption of dyes still could not reach equilibrium, suggesting that the adsorption is dominated by diffusion. In general, the mechanism for adsorption of dyes involves the following steps: (1) migration of dye from bulk of the solution to the surface of the adsorbent (AC), (2) diffusion of dye through the boundary layer to the surface of the adsorbent, (3) adsorption of dye at an active site on the surface of AC, and (4) intra-particle diffusion of dye into the interior pores of the AC particle [9].

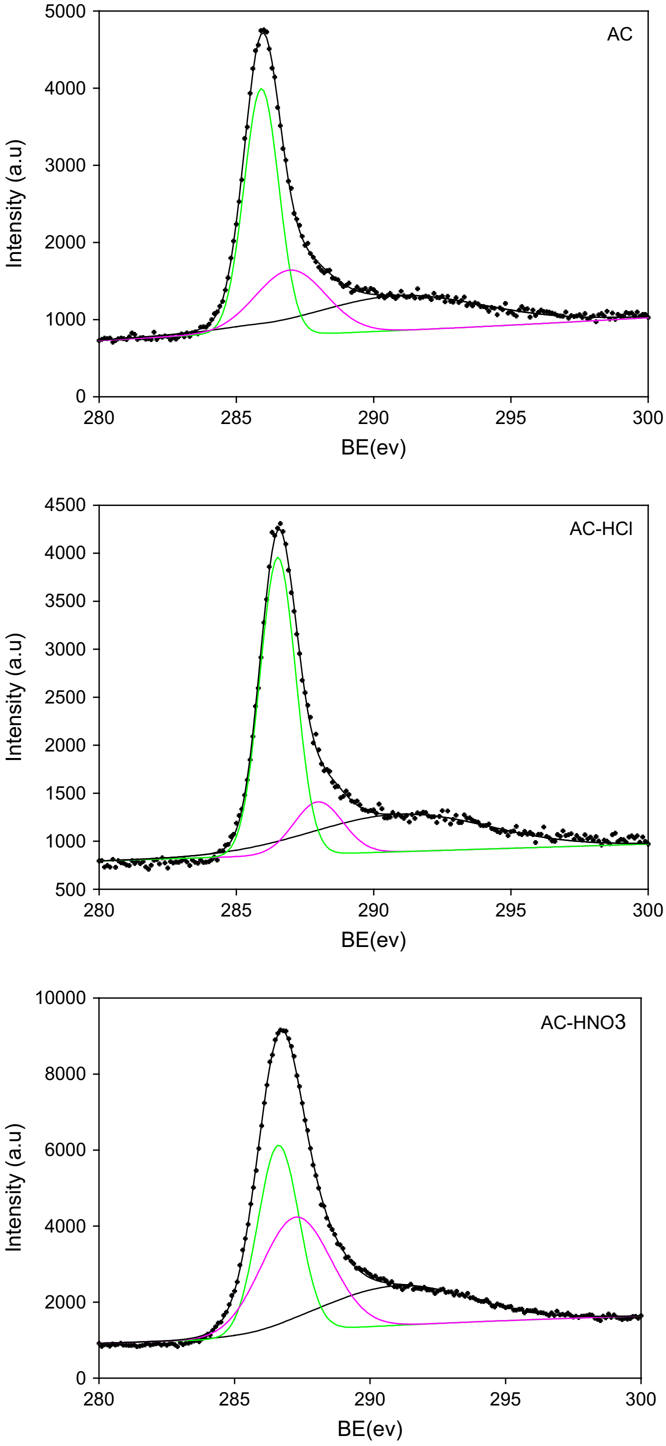

Fig. 3. XPS spectra of C1s on various activated carbons.

For the same activated carbon, it shows varying adsorption capacity for methylene blue, crystal violet and rhodamine B. Generally, activated carbons show the highest adsorption for methylene blue, medium values for crystal violet and the lowest adsorption for rhodamine B. This variation can be attributed to the dye molecular size. For the larger dye molecules, adsorption can only occur at surface and it is difficult for the dyes to enter into the inner smaller pores of carbons. From Fig. 4, it is also shown that activated carbons show a different order in adsorption capacity for the same dye. For methylene blue, adsorption follows an order of AC > AC-HCl > AC-HNO_3 while for crystal violet and rhodamine B, the order is AC-HCl > AC > AC-HNO_3. The difference in adsorption capacity mainly depends on the surface chemistry.

It has been proposed that there are two parallel adsorption mechanisms in the adsorption, the first involving electrostatic interactions between dye molecules and carbon surface groups and the second involving dispersive interactions between dye

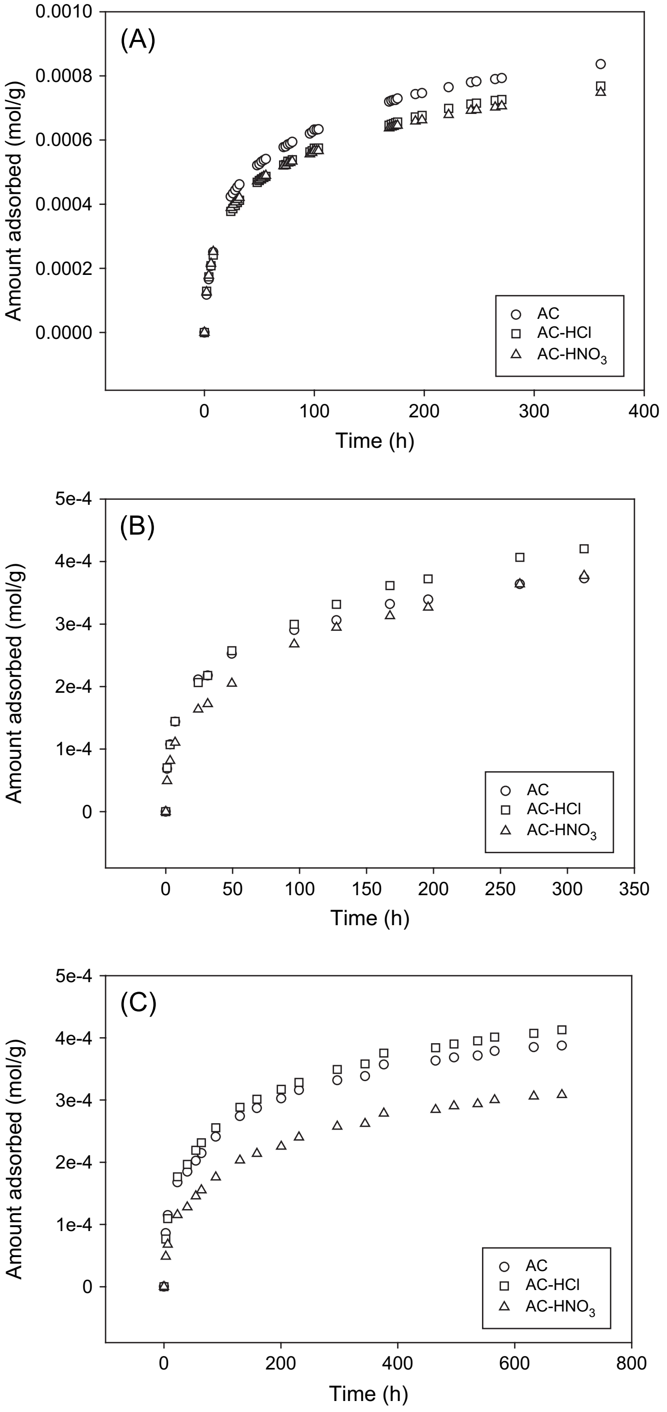

Fig. 4. Adsorption of dyes on activated carbons. (A) Methylene blue, (B) crystal violet and (C) rhodamine B.

molecules and carbon surface layers [4]. For cationic dyes, the electrostatic interactions between dye molecules and carbon surface groups could play a role but the predominant effect is the interaction between the delocalised π-electron of the carbon surface and the free electrons of the dye molecule (aromatic rings and –N=N– or –N=C–C=C– bonds). Therefore, a carbon with the highest acidity shows a lower adsorption for basic dye [4]. In this investigation, basic carbons exhibited higher adsorption to cationic dyes suggesting that dispersive interaction plays a dominant role in the adsorption mechanism.

The effect of solution pH on adsorption is presented in Fig. 5. It is shown that solution pH exerts a significant influence on methylene blue adsorption while it has little effect on rhodamine B adsorption. For methylene blue, higher pH results in higher adsorption. The adsorption can increase from 4×10^{-4} to 14×10^{-4} mol/g at pH = 3 to 10. For rhodamine B, the adsorption at pH = 3 and 5 is much close and shows a bit higher at pH = 10. This adsorption behaviour is because of the different functional groups of dyes. Basically, methylene blue and other cationic dyes produce an intense molecular cation (C^+) and reduced ions (CH^+). Thus, higher pH will make the adsorbent surface negatively charged and result in higher adsorption. Although rhodamine B is a basic dye it contains a carboxyl group and the overall charge is positive.

There are several kinetic models applied for solid–liquid adsorption. The most important model is Lagergren's pseudo-first-order equation [10], which is usually expressed as in Eq. (1)

$$\log(q_e - q_t) = \log(q_e) - \frac{k}{2.303}t \tag{1}$$

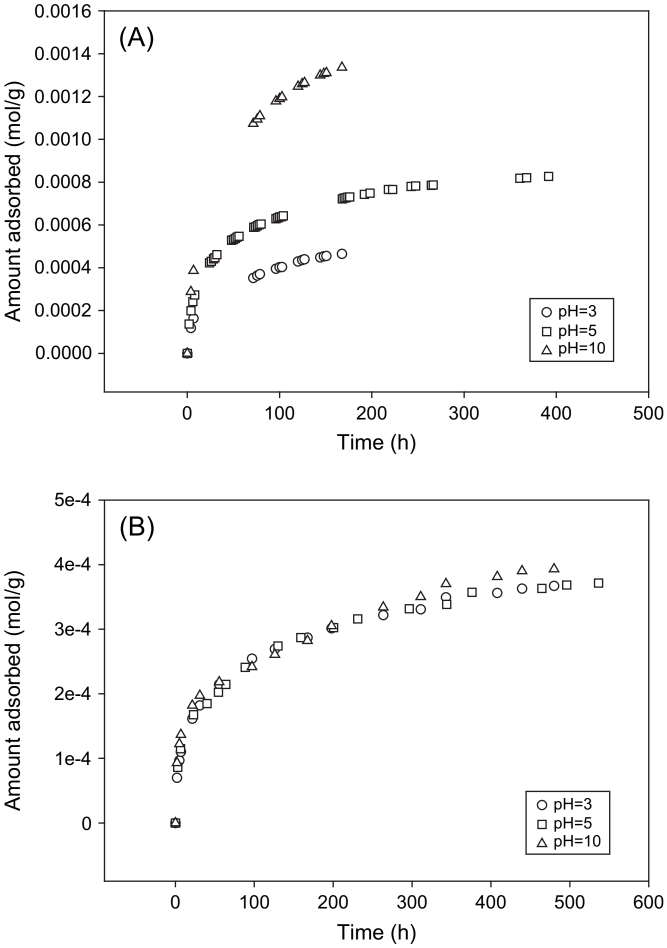

Fig. 5. Effect of solution pH on dye adsorption on AC. (A) Methylene blue and (B) rhodamine B.

where q_t is the amount of dye adsorbed (in mol/g) at various time t, q_e is the equilibrium adsorption capacity and k is the first-order rate constant for the adsorption process (in h^{-1}). However, using this equation, it is necessary to know the equilibrium adsorption. As seen in this investigation, adsorption of three dyes on activated carbon cannot reach equilibrium under the long period of time. Therefore, we will use the kinetic models which will not require knowing the equilibrium adsorption. The first kinetic model is the generalised first-order kinetic equation proposed by Annadurai and Krishnan [11] and cited by Kannan and Sundaram [9].

$$\frac{1}{q_t} = \frac{k_1}{q_e}\frac{1}{t} + \frac{1}{q_e} \tag{2}$$

where q_t is the amount of dye adsorbed (in mol/g) at various time t, q_e is the equilibrium adsorption capacity and k_1 is the first-order rate constant for the adsorption process (in h^{-1}).

Kannan and Vanangamudi also employed the first-order kinetic model based on adsorbate for MB on AC [9], which is given as follows:

$$\log\left(\frac{C_0}{C_t}\right) = \frac{k'}{2.303}t \tag{3}$$

where C_0 and C_t are the concentrations of dye (in M) at time zero and at time t, respectively, and k' is the reaction rate constant.

In addition, Ho [12,13] proposed a pseudo-second-order kinetic model for the adsorption of an adsorbate from an aqueous solution, which is expressed by the following linear equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \tag{4}$$

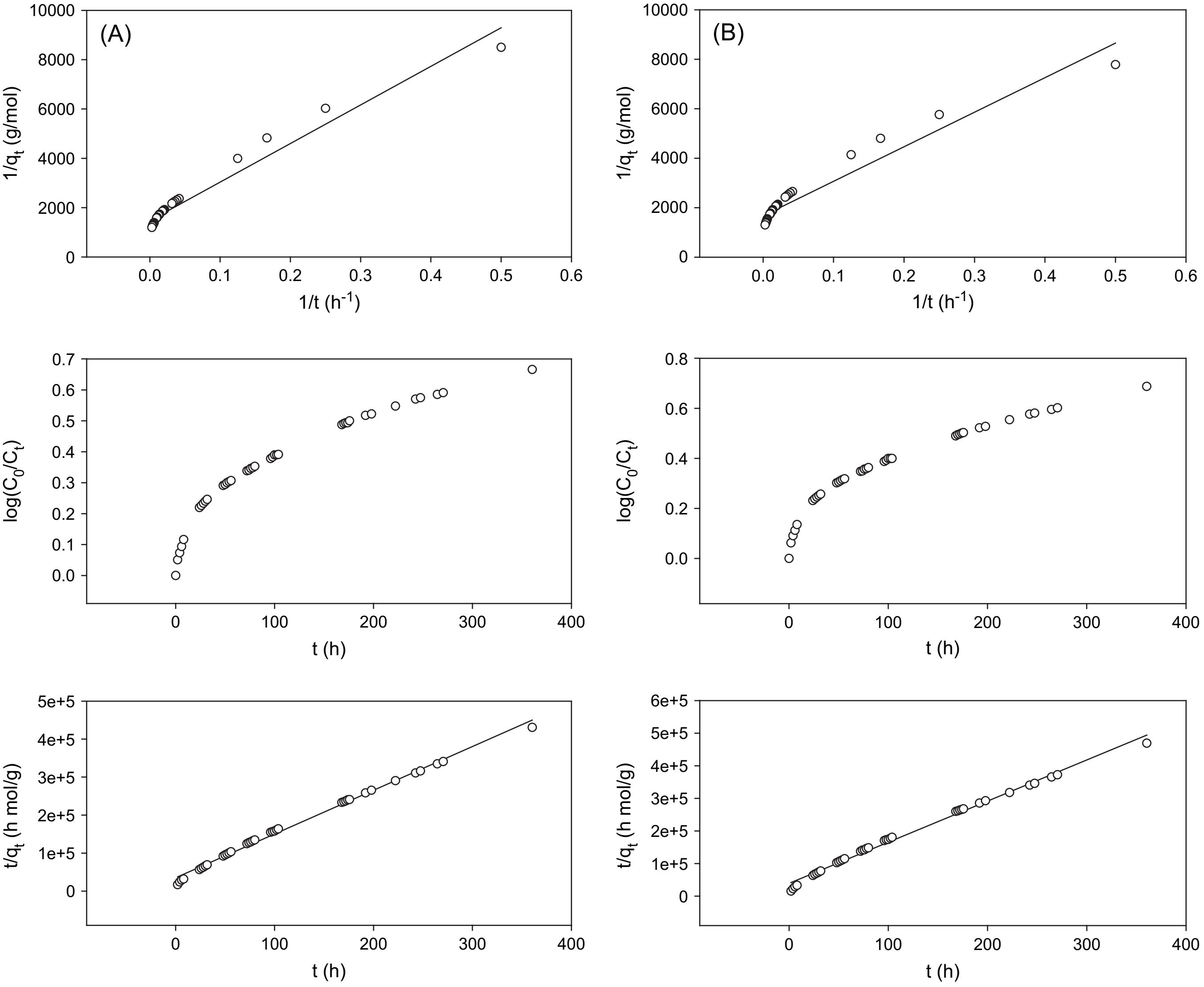

Fig. 6. Comparison of kinetics models. (A) AC, (B) AC-HCl and (C) AC-HNO$_3$.

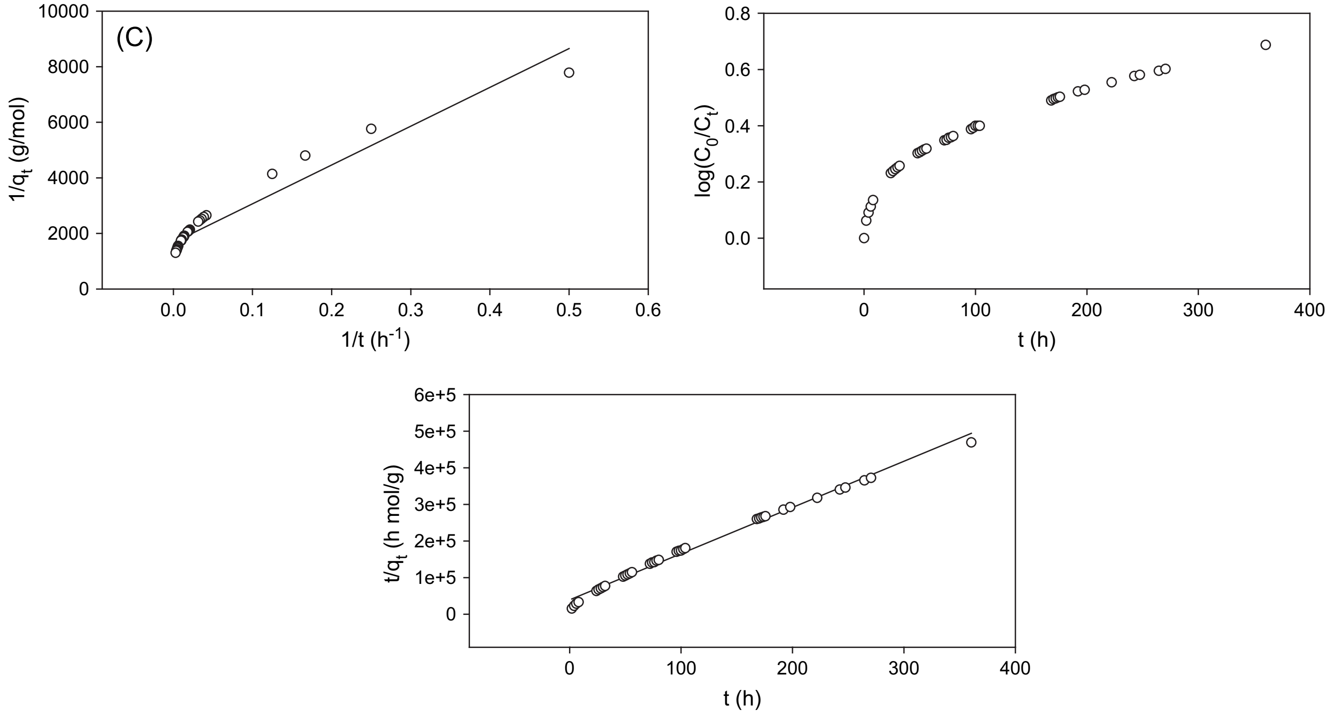

Fig. 6 (*continued*)

where q_t is the amount of dye adsorbed (in mol/g) at various time t, q_e is the maximum adsorption capacity and k_2 is the second-order rate constant for the adsorption process (in h^{-1}).

Fig. 6 and Table 3 present the comparative results using the above kinetic models for methylene blue adsorption on three activated carbons. One can see that the first-order kinetic model either for solid or adsorbate is not good and the correlation ($1/q_t \sim 1/t$ and $\log (C_0/C_t) \sim t$) is not linear. The second-order correlation can best describe the kinetics, given the correlation coefficients around 0.994 and the adsorption capacity is much closer to the experimental value.

Activated carbon usually contains polar functional groups that can be involved in chemical bonding and are responsible for cationic dye adsorption. The reactions could be represented in two ways:

$$-\mathrm{CO}^- + \mathrm{NC}^+(\mathrm{dye}^+) \rightarrow -\mathrm{CO}{-}\mathrm{dye} \tag{5}$$

$$-\mathrm{COO}^- + \mathrm{NCH}^+(\mathrm{dye}^+) \rightarrow -\mathrm{COO}{-}\mathrm{dye} \tag{6}$$

Thus, for the second-order kinetics, the rate expression for the sorption could be described as the driving force between the amount of dye sorbed on active sites at any time and the amount sorbed at equilibrium and the equations should be as follows:

$$\frac{\mathrm{d}[\mathrm{CO}^-]}{\mathrm{d}t} = k_2\{[\mathrm{CO}^-]_e - [\mathrm{CO}^-]_t\}^2 \tag{7}$$

$$\frac{\mathrm{d}[\mathrm{COO}^-]}{\mathrm{d}t} = k_2\{[\mathrm{COO}^-]_e - [\mathrm{COO}^-]_t\}^2 \tag{8}$$

Fig. 7 shows the effect of temperature for the adsorption of three dyes on activation carbon. Usually, temperature has two major effects on the adsorption process. Increasing the temperature is known to increase the rate of diffusion of the adsorbate molecules across the external boundary layer and in the internal pores of the adsorbent particle, owing to the decrease in the viscosity of the solution. In addition, changing the temperature will change the equilibrium capacity of the adsorbent for a particular adsorbate. As can be seen, the three dyes show a similar trend with temperature. Higher temperature will result in higher adsorption indicating that the adsorption is an endothermic process. As stated in the previous section, uptake of dyes from aqueous solution is a diffusion process, which is an

Table 3
Parameters of kinetic models

Samples	Models			R^2
AC	First-order	$k_1 = 10.67$ (h^{-1})	$q_e = 6.81 \times 10^{-4}$ (mol/g)	0.962
	Model 2	$k' = 3.90 \times 10^{-3}$ (h^{-1})		0.881
	Second-order	$k_2 = 37.76$ (g/mol h)	$q_e = 8.68 \times 10^{-4}$ (mol/g)	0.994
AC-HCl	First-order	$k_1 = 8.36$ (h^{-1})	$q_e = 5.98 \times 10^{-4}$ (mol/g)	0.935
	Model 2	$k' = 3.88 \times 10^{-3}$ (h^{-1})		0.884
	Second-order	$k_2 = 40.56$ (g/mol h)	$q_e = 7.92 \times 10^{-4}$ (mol/g)	0.992
AC-HNO_3	First-order	$k_1 = 8.34$ (h^{-1})	$q_e = 5.99 \times 10^{-4}$ (mol/g)	0.954
	Model 2	$k' = 4.26 \times 10^{-3}$ (h^{-1})		0.909
	Second-order	$k_2 = 46.30$ (g/mol h)	$q_e = 7.65 \times 10^{-4}$ (mol/g)	0.993

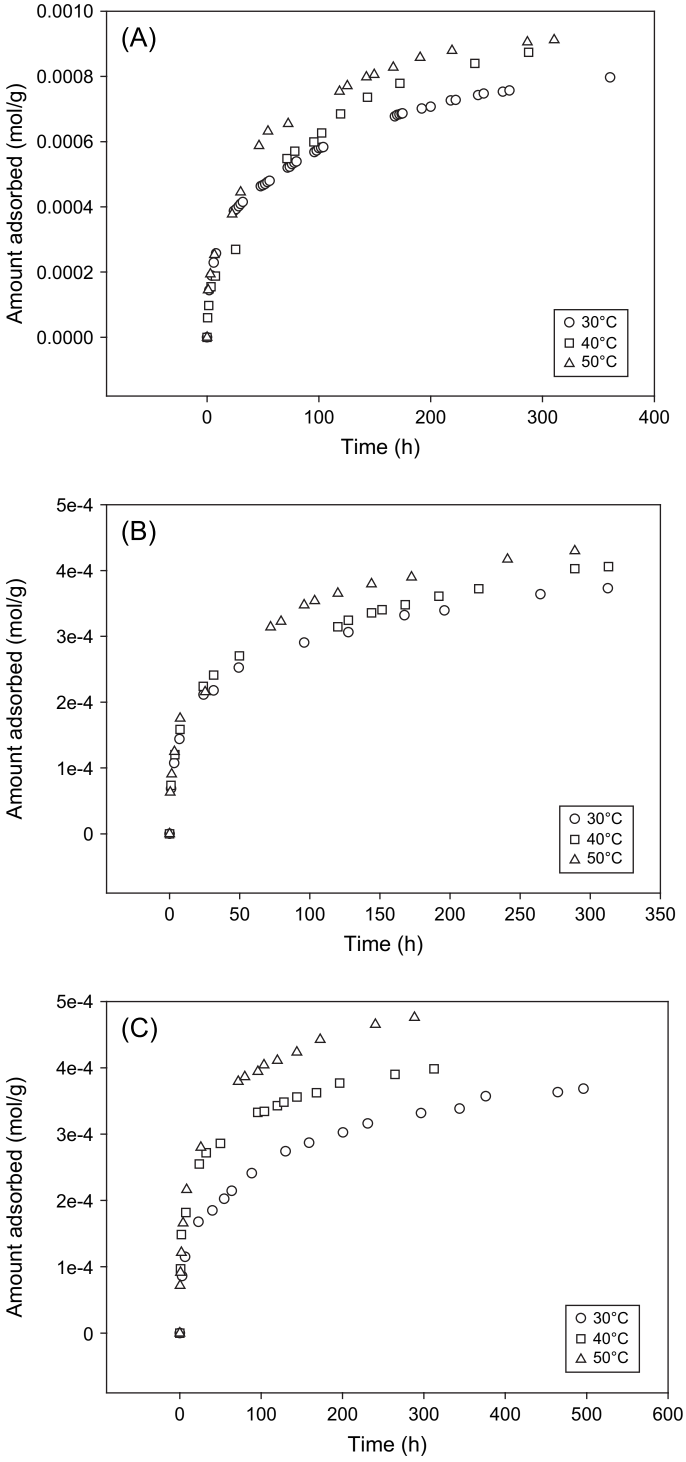

Fig. 7. Effect of temperature on adsorption on AC. (A) Methylene blue, (B) crystal violet and (C) rhodamine B.

endothermic process. It is noted that the temperature seems to have a more remarkable effect on rhodamine B adsorption than methylene blue and crystal violet. This is probably due to the larger molecular size of rhodamine B. Higher temperature will significantly increase the mobility of large dye ions access to the carbon surface and pores.

Table 4 presents the kinetic parameters at different temperatures obtained from the pseudo-second-order kinetics for the three dyes. It is seen that the equilibrium adsorption increases with the increasing temperature while the rate constant does not show significant difference. This is probably due to the complex process of adsorption. The second-order kinetic rate is a lump sum parameter including physical diffusion process and chemical reaction.

Table 4
Kinetic parameters of dye adsorption at different temperatures

Dye	Temperature (°C)					
	30		40		50	
	q_e (mol/g)	k_2 (g/mol h)	q_e (mol/g)	k_2 (g/mol h)	q_e (mol/g)	k_2 (g/mol h)
MB	8.35×10^{-4}	34.65	9.69×10^{-4}	39.55	9.30×10^{-4}	30.84
CV	3.76×10^{-4}	171.22	4.05×10^{-4}	137.59	4.30×10^{-4}	159.25
RB	3.87×10^{-4}	62.95	4.03×10^{-4}	173.54	4.78×10^{-4}	167.59

The thermodynamic parameters such as change in standard free energy (ΔG^0), enthalpy (ΔH^0), and entropy (ΔS^0) were determined using the following equations [14] and are given in Table 5:

$$K_C = \frac{C_A}{C_S} \tag{9}$$

$$\Delta G^0 = -RT \ln K_C \tag{10}$$

$$\ln K_C = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \tag{11}$$

where K_C is the distribution coefficient for the adsorption. C_A is the amount of dye (mol) adsorbed on the adsorbent per dm^3 of the solution at equilibrium, and C_S is the equilibrium concentration (mol/dm^3) of the dye in the solution. T is the solution temperature (K) and R is the gas constant. ΔH^0 and ΔS^0 were calculated from the slope and intercept of van't Hoff plots of $\ln K_C$ versus $1/T$ (see Fig. 8). As could be noted, the adsorption process is spontaneous with the negative values of ΔG^0. The standard enthalpy change (ΔH^0) for the adsorption on activated carbon is positive indicating that the process is endothermic in nature. The positive value of ΔS^0 shows increased disorder at the solid/solution interface during the adsorption of dye. The adsorption increases randomness at the

Table 5
Thermodynamic parameters of dye adsorption on activated carbon

Dye	Temperature (°C)	K_C	ΔG^0 (kJ/mol)	ΔS^0 (J/K mol)	ΔH^0 (kJ/mol)
MB	30	3.63	−3.25	75.2	19.5
	40	4.97	−4.17		
	50	5.86	−4.75		
	30	1.30	−0.67		
CV	40	2.15	−1.99	242.6	73.3
	50	7.96	−5.57		
	30	1.98	−1.71		
RB	40	2.18	−2.02	40.7	10.7
	50	2.57	−2.53		

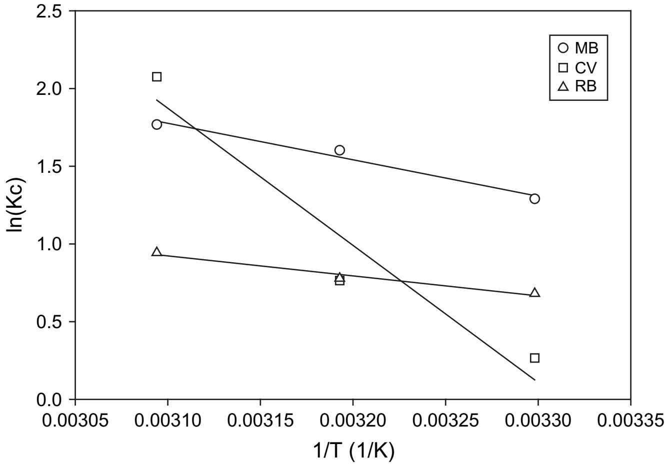

Fig. 8. Relationship between K_C and T for dye adsorption on activated carbon.

solid/solution interface with some structural changes in the adsorbate and adsorbent and an affinity of the adsorbent.

4. Conclusion

Activated carbons treated by some acids have been employed for adsorption of dyes. It is found that acid treatment can change the surface functional groups and pore structure. Acid treatment increases the acidity of activated carbon but the changes in textural structure varies depending on different acids. HNO_3 treatment produces more active acidic surface groups such as carboxyl and lactone, and more homogeneous in pore size, resulting in a reduction in the adsorption of basic dyes. However, HCl treatment decreases active acidic groups, and thus enhances the adsorption of larger molecules on activated carbons. Dynamic adsorption of dyes on activated carbons can be described by a pseudo-second-order kinetic model and thermodynamic analysis shows that the adsorption of dye is an endothermic process. Dye solution pH and temperature will also influence adsorption capacity.

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