

# Preparation of cationic waste paper and its application in poisonous dye removal

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## ABSTRACT

Cationic paper was prepared by reaction of paper with 2,3-epoxypropyltrimethylammonium chloride in aqueous suspension, and tested as low-cost adsorbent for wastewater treatment. The experimental results revealed that anionic dyes (Acid Orange 7, Acid Red 18, and Acid Blue 92) were adsorbed on the cationic paper nicely. The maximum amount of dye Acid Orange 7 adsorbed on cationic paper was 337.2 mg/g in experimental conditions. The effects of initial dye concentration, temperature, and initial pH of dye solution on adsorption capacity of cationic paper were studied. The pseudo-first-order and pseudo-second-order kinetic models were applied to describe the kinetic data. The Freundlich and Langmuir adsorption models were used to describe adsorption equilibrium. The thermodynamic data indicated that the adsorption process of dye on cationic paper occurred spontaneously.

**Key words** | adsorption, cationic paper, dyes, quaternization, waste

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## INTRODUCTION

Acid Orange 7 (AO 7), Acid Red 18 (AR 18), and Acid Blue 92 (AB 92) are very common water-soluble anionic dyes and used widely in the paper and textile industries (Robinson *et al.* 2001). Dyes reduce light penetration and photosynthesis and are known to be pollutants, some even being toxic and carcinogenic for human health (Oh *et al.* 1997). Like other pollutants, anionic dyes that cause a severe threat to humans and the environment have been disposed of mainly in industrial wastewater. Due to their chemical structure, these dyes were resistant to fading on exposure to light or most chemicals. It was very difficult to decompose these dyes once they were released into the aquatic environment. Various techniques were employed for dye removal from wastewater.

There have been several reported methods for the removal of pollutants from effluents. The technologies can be divided into three categories: biological, chemical, and physical (Robinson *et al.* 2001). Biological treatment is often the most economical alternative. However, biological treatment is constrained by sensitivity towards diurnal variation as well as toxicity of some chemicals, and less flexibility in design and operation (Oller *et al.* 2011). Chemical techniques, such as electroflotation and flocculation, are

often expensive, and although the dyes are removed, accumulation of concentrated sludge creates a disposal problem. There is also the possibility that a secondary pollution problem could arise because of excessive chemical use (Verma *et al.* 2012). As a physical method, the major disadvantage of the membrane processes is that they have a limited lifetime before membrane fouling occurs and the cost of periodic replacement is high (Malaeb & Ayoub 2011). Adsorption has been found to be superior to other techniques in terms of initial cost, flexibility, and simplicity of design, ease of operation, and insensitivity to toxic pollutants. Adsorption also did not result in the formation of harmful substances (Crini 2006).

Adsorption techniques employing solid sorbents have been widely used to remove certain classes of chemical pollutants from wastewater. Activated carbon has been the most popular adsorbent for the removal of pollutants. In particular, the effectiveness of adsorption on commercial activated carbons for removal of a wide variety of dyes from wastewaters has made it an ideal alternative to other expensive treatment options. However, activated carbon presents several disadvantages (Mezohegyi *et al.* 2012). It is quite expensive – the higher the quality, the greater the cost – non-selective, and

ineffective against disperse and vat dyes. This led many workers to search for more economic adsorbents.

Due to the problems mentioned above, non-conventional adsorbents, such as bottom ash, de-oiled soya (Gupta 2006), rice hulls, coconut hulls, straw (Robinson *et al.* 2002), and sawdust (Garg *et al.* 2003), have been studied to replace the costly activated carbon. Certain waste products from industrial and agricultural operations represent potentially economical alternative sorbents. Due to the reuse of waste, these waste products could be more environmentally friendly than conventional adsorbents. However, the effectiveness of adsorption on these adsorbents has not been satisfactory (Bhatnagar & Sillanpää 2010). More attention needs to be focused on the modification of low-cost adsorbents to enhance adsorption capacity.

The aim of our research was to develop an efficient adsorbent by modification of low-cost waste paper. As a waste material, a proportion of waste paper has been recycled in the preparation of new paper, with the rest being burned or buried as garbage. However, we believe that waste paper could be used efficiently in other domains, such as wastewater treatment. Because of its low adsorption capacity, normal waste paper cannot be used directly as an adsorbent. In order to improve the adsorption capacity, cationic groups were introduced onto the surface of paper by quaternization (Ding *et al.* 2012). Via electrostatic interaction, anionic dye was adsorbed easily on the cationic surface of the paper. By this simple modification, the waste paper could be used as a low-cost, environmentally friendly, and efficient adsorbent to replace conventional adsorbents.

## MATERIALS AND METHODS

### Materials

Filter paper was purchased from HangZhou XinHua Paper Industry Co., Ltd. The ash content was less than 0.15% of weight. Acid Orange 7 (98%), Acid Red 18 (indicator grade), and Acid Blue 92 (99%) were purchased from Acros Organics Co., Ltd. AO 7, AB 92, and AR 18 were dissolved in deionized water (pH = 6.0) to produce stock solutions. Sodium hydroxide (AR), epichlorohydrin (AR), acetic acid (AR), ethanol (AR), ether anhydrous (AR), trimethylamine aqueous solution (33%) and H<sub>2</sub>SO<sub>4</sub> (98%) were all purchased from Sinopharm Chemical Reagent Co., Ltd. All the reagents were used without further purification.

### Synthesis of 2,3-epoxypropyltrimethylammonium chloride (EPTMAC)

The synthesis process of EPTMAC was described as follows (Yan *et al.* 2009). In brief, 20 g of NaOH aqueous solution (40 wt%) was added to 20 mL of trimethylamine aqueous solution drop by drop. The overflowed trimethylamine gas was introduced into a flask which contained 80 mL of epichlorohydrin, and the mixture was stirred for 6 h in a water-ice bath. The crystal deposited from the mixture was collected by vacuum filtration and then washed several times with ether. The white product was sealed and preserved in a bottle. Fourier transform infrared spectroscopy (FT-IR): 1,264.73 cm<sup>-1</sup> (epoxy ether bond); <sup>13</sup>C-NMR: 54.1 ppm (<sup>+</sup>N-CH<sub>3</sub>), 68.9 ppm (CH<sub>2</sub>-N<sup>+</sup>), 45.2 ppm (OCH<sub>2</sub>), 46.0 ppm (OCH).

### Quaternization of filter paper

One gram of filter paper was torn into small pieces (1 ~ 2 mm) and immersed in 50 mL of NaOH aqueous solution (18%). The mixture was stirred at ambient temperature for 15 h to activate the filter paper. The treated paper was collected by filtration and added directly to 40 mL of EPTMAC aqueous solution. The mixture was stirred for 24 h at ambient temperature (the mass ratio of EPTMAC to filter paper was 2.8:1) (Yan *et al.* 2009). After the complete reaction, the product (cationic paper) was collected by vacuum filtration and neutralized with acetic acid solution (10%). Then the product was washed with ethanol three times and dried in an oven at 55 °C.

### Characterization

FT-IR spectra were recorded on an EQUINOX55 spectrometer (Bruker, Germany) using KBr pellets. <sup>13</sup>C-NMR spectra were measured on an AVANCE 300 spectrometer (Bruker, Switzerland). Elemental analysis was carried out by a VARIO ELIII analyzer (Elemental Analysis System Co. Ltd, Germany).

### Batch adsorption studies

The dye solutions with different initial concentrations were prepared by diluting the stock solution of each dye with deionized water (pH = 6.0). The adsorption experiments were carried out at 20 ± 1 °C in a thermostated shaker. The initial pH of the dye solution was adjusted to the required value with 0.01N HCl and NaOH solution. 0.1 g of cationic paper and 50 mL of dye solution were mixed in

a 100-mL flask, and then the flask was shaken for 3 h to attain adsorption equilibrium. After that, a 0.5-mL sample was withdrawn from the flask and diluted with deionized water. Then, the pH value of the sample was adjusted to 6.0 and the sample was centrifuged at 6,000 rpm for 10 min. After centrifugation, the dye concentration of the supernatant liquid was analyzed using UV-vis spectrophotometer. In kinetic experiments, a 0.5-mL sample was taken from the flask for analysis of the residual dye concentration at regular intervals (Gupta 2006). All the experiments were carried out in triplicate. The maximum adsorption wavelengths of AO 7, AB 92, and AR 18 were 484, 571, and 506 nm, respectively.

## RESULTS AND DISCUSSION

Because the composition is the same, filter paper was chosen as the simulated material of waste paper in our study. The main component of the filter paper was cellulose. Under alkaline conditions, quaternization reaction occurred between the hydroxyl group of cellulose and EPTMAC. Via quaternization reaction, plenty of quaternary ammonium salt groups were introduced onto the surface of the paper, and the cationic paper was formed.

### FT-IR

The FT-IR spectra of filter paper and cationic paper are shown in Figure 1. In the FT-IR spectrum of filter paper, the bands at 3,430 and 1,330  $\text{cm}^{-1}$  are assigned to the

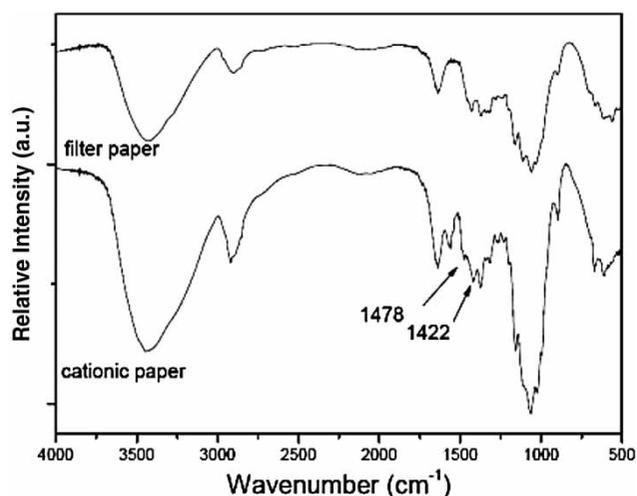


Figure 1 | FT-IR spectra of filter paper and cationic paper (a.u. = arbitrary units).

stretching vibration and bending vibration of  $-\text{OH}$  groups, respectively; the bands at 2,900 and 1,375  $\text{cm}^{-1}$  correspond to the stretching vibration and bending vibration of  $-\text{CH}_2-$  groups, respectively; the band at 1,160  $\text{cm}^{-1}$  corresponds to the stretching vibration of  $\text{C}-\text{O}-\text{C}$  groups. These are the characteristic bands of cellulose (Sun *et al.* 2004), which confirm that the main composition of filter paper is cellulose. Compared with filter paper, the FT-IR spectrum of cationic paper showed a new band at 1,478  $\text{cm}^{-1}$ , which corresponded to the methyl groups of ammonium (Loubaki *et al.* 1991). Furthermore, the band at 1,422  $\text{cm}^{-1}$  was assigned to the  $\text{C}-\text{N}$  stretching vibration (Kacurakova *et al.* 1994; Pal *et al.* 2005). Hence, the FT-IR spectra provide evidence of the introduction of the quaternary ammonium salt groups on paper.

### Elemental analysis

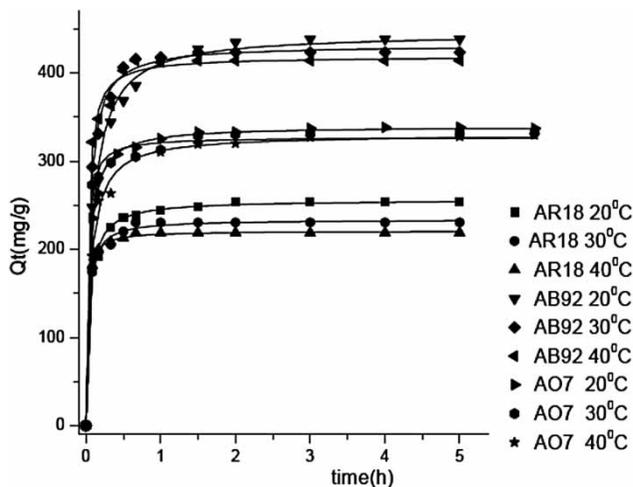
Elemental analysis of filter paper and cationic paper was carried out. The content of carbon in cationic paper decreased by 3.2% compared with that in filter paper, while the content of nitrogen increased nearly 12 times. These results were attributed to the introduction of the quaternary ammonium salt groups on paper.

### Effect of contact time

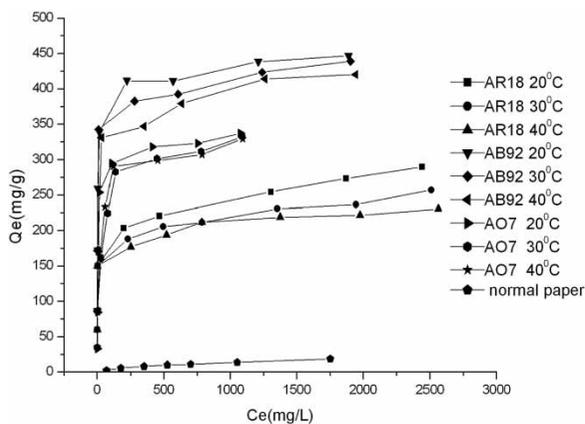
The effect of contact time on adsorption of AO 7, AR 18, and AB 92 on cationic paper was investigated, and the results are shown in Figure 2. The amount of dye adsorbed on cationic paper increased with the increase of contact time from 0 to 3 h. After 3 h the amount of dye adsorbed on cationic paper did not increase further and the adsorption equilibrium was reached. The same experiments were performed at 30 and 40  $^{\circ}\text{C}$  and the results were found to be almost similar. Therefore, adsorption experiments were all carried out for 3 h in the following studies to make sure that the equilibrium state was reached.

### Effect of initial dye concentration

The initial concentration of dye was an important driving force to overcome the mass transfer resistances between the aqueous and solid phase (Aksu 2005). Thus, high initial concentration of dye could enhance the adsorption capacity of absorbent. The effect of initial dye concentration on adsorption of AO 7 on cationic paper was investigated from 70.1 to 1,751.6  $\text{mg/L}$ , and the results are shown in Figure 3. There was an obvious increase in the amount of



**Figure 2** | Effect of contact time on adsorption of dyes on cationic paper (pH = 6.0; initial dye concentration  $C_0$  (AR18) = 1,813.4 mg/L,  $C_0$  (AO7) = 1,751.6 mg/L,  $C_0$  (AB92) = 2,086.8 mg/L).



**Figure 3** | Effect of initial dye concentrations on adsorption capacities of cationic paper (pH = 6.0).

dye adsorbed on cationic paper, while the initial dye concentration increased from 70.1 to 700.6 mg/L. From 700.6 to 1,751.6 mg/L, the amount of dye adsorbed on cationic paper increased slightly. The saturation of adsorption was reached gradually with the increase of dye concentration. Similar results were obtained at 30 and 40 °C, and the amount of dye adsorbed on cationic paper decreased with the increase in temperature.

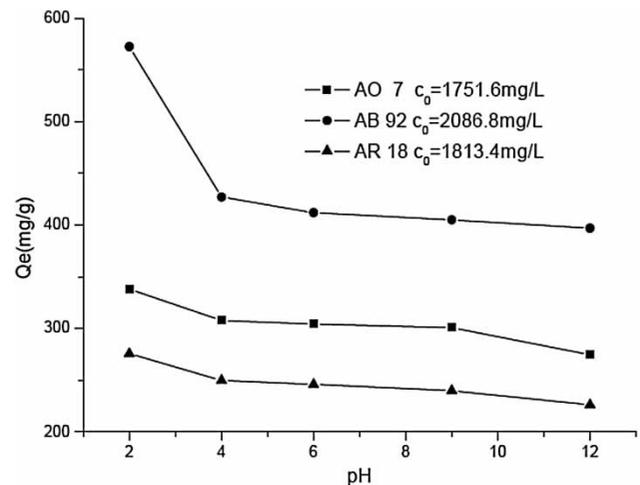
The adsorption experiments of AB 92 and AR 18 were also studied. In the range of experimental concentration, the maximum amounts of AO 7, AB 92, and AR 18 adsorbed on cationic paper were 337.2, 446.5, and 289.5 mg/g at 20 °C, respectively. The adsorbed amounts of AO 7, AB 92, and AR 18 were different, which might be due to the different properties of dyes such as molecule

weight and molecular structure. The experimental results showed that other anionic dyes could also be adsorbed on cationic paper.

Adsorption experiments with normal filter paper were studied. While the initial concentration of AO 7 increased to 1,751.6 mg/L, the adsorption capacity of normal filter paper was only 18.6 mg/g. Contrasted with normal filter paper, the adsorption capacity of cationic paper was greater under the same conditions. This result was attributed to the introduction of cationic groups on the surface of paper.

### Effect of initial pH of dye solution

The effect of initial pH of dye solution on adsorption capacity of cationic paper was investigated at 20 °C, and the results are shown in Figure 4. In this series of experiments, the initial pH of dye solution was adjusted to the required value with 0.01N HCl and NaOH solutions, and the ionic strength of dye solution was controlled with NaCl solution. The amount of dye adsorbed on cationic paper decreased when the pH of dye solution changed from 2 to 12, and the maximum amounts of AO 7, AB 92, and AR 18 adsorbed were 338.1, 572.3, and 275.5 mg/g at pH 2.0. The adsorption capacity of cationic paper was higher at low pH, which might be due to electrostatic interaction between the cationic groups of paper and anionic dyes (Hu 1996; Aksu & Tezer 2000). The lower amount of dye adsorbed in alkaline conditions might be due to the presence of excess  $\text{OH}^-$  ions, which competed with anionic dyes for adsorption sites (Arami *et al.* 2008). Furthermore, the increase of solubility of dye in alkaline conditions



**Figure 4** | Effect of initial pH of dye solution on adsorption capacity of cationic paper ( $T = 20$  °C, initial dye concentration  $C_0$  (AO7) = 1,751.6 mg/L,  $C_0$  (AB92) = 2,086.8 mg/L,  $C_0$  (AR18) = 1,813.4 mg/L).

could result in the decrease of absorption capacity (Zhou & Banks 1993). Due to the use of NaCl, the ionic strength of dye solution in this study was greater than normal dye solution prepared with deionized water directly. Thus the adsorption capacity of cationic paper in this dye solution was slightly lower at pH 6.0.

### Adsorption isotherms

The Langmuir (Langmuir 1918) and Freundlich (Freundlich 1906) models have been used commonly to describe the adsorption equilibrium at a constant temperature. The well-known expression of the Langmuir model is given as below:

$$q_{\text{eq}} = \frac{Q_0 b c_{\text{eq}}}{1 + b c_{\text{eq}}} \quad (1)$$

where  $q_{\text{eq}}$  (mg/g) and  $c_{\text{eq}}$  (mg/L) are the adsorbed amount of dye per unit weight of adsorbent and unadsorbed concentration of dye at equilibrium, respectively.  $Q_0$  and  $b$  are Langmuir constants related to maximum adsorption capacity (monolayer capacity) and bonding energy of adsorption, respectively, which are functions of the characteristics of the system.

The Freundlich equation based on adsorption onto a heterogeneous surface is given as below:

$$q_{\text{eq}} = K_F c_{\text{eq}}^{1/n} \quad (2)$$

$K_F$  and  $n$  are the Freundlich characteristic constants, which relate to adsorption capacity and adsorption intensity, respectively.

The adsorption constants and correlation coefficients evaluated from Langmuir and Freundlich models are listed in Table 1. The correlation coefficients for the Langmuir model are quite high ( $R^2 > 0.99$ ), and the theoretical adsorption capacities ( $Q_0$ ) evaluated from the Langmuir model are consistent with the experimental data ( $q_{\text{e,exp}}$ ). These indicate that the adsorption of AO 7 on cationic paper fitted the Langmuir model well and monolayer coverage was formed on the surface of adsorbent at high  $C_{\text{eq}}$ . Similar results were also obtained from the adsorption of AR 18 and AB 92 on cationic paper. The adsorption capacity ( $K_F$ ) evaluated from the Freundlich model deviated from the experimental data ( $q_{\text{e,exp}}$ ) and the correlation coefficients for the Freundlich model were low. These indicated that the Freundlich model was not suitable for describing the adsorption of dyes on cationic paper.

### Adsorption thermodynamic

The thermodynamic parameters such as free energy ( $\Delta G^0$ ), enthalpy ( $\Delta H^0$ ), and entropy ( $\Delta S^0$ ) changes were estimated by the following equations (Namasivayam & Yamuna 1995):

$$K = b \quad (3)$$

$$\Delta G^0 = -RT \ln K \quad (4)$$

$$\log K = \frac{\Delta S^0}{2.303R} - \frac{\Delta H^0}{2.303RT} \quad (5)$$

where  $K$  is the equilibrium constant corresponding to Langmuir constant  $b$ ,  $T$  is the solution temperature (K) and  $R$  is the gas constant.

**Table 1** | Langmuir and Freundlich isotherm constants for each dye adsorption

Sample	$q_{\text{e,exp}}$ (mg/g)	Langmuir			Freundlich		
		$Q_0$ (mg/g)	$b$ (L/mg)	$R^2$	$K_F$ [(mg/g)/(mg/L) <sup>n</sup> ]	$n$	$R^2$
AO 7 20 °C	337.2	339.0	0.0489	0.999	55.1	3.42	0.630
AO 7 30 °C	332.0	331.1	0.0404	0.998	52.6	3.43	0.915
AO 7 40 °C	329.4	325.7	0.0556	0.998	63.1	3.78	0.914
AR 18 20 °C	289.5	286.5	0.0150	0.994	84.9	6.36	0.802
AR 18 30 °C	256.9	252.5	0.0140	0.994	87.2	7.33	0.759
AR 18 40 °C	230.2	229.9	0.0204	0.998	87.2	7.85	0.730
AB 92 20 °C	446.5	446.4	0.0770	0.999	142.2	5.80	0.734
AB 92 30 °C	439.2	438.6	0.0429	0.999	125.5	5.49	0.740
AB 92 40 °C	420.3	421.9	0.0337	0.998	110.6	5.17	0.833

The values of  $\Delta G^0$ ,  $\Delta H^0$ , and  $\Delta S^0$  were calculated by the above equations, and listed in Table 2. The negative values of  $\Delta G^0$  indicate that the adsorption of each dye on cationic paper was spontaneous. The negative value of  $\Delta H^0$  for AB 92 adsorption indicated that the adsorption of AB 92 was an exothermic process. The negative value of  $\Delta S^0$  for AB 92 adsorption indicated that the randomness decreased at the solid-solution interface during the adsorption of AB 92 on cationic paper. A similar situation has been reported for the adsorption of reactive dye onto chemical cross-linked chitosan beads (Chiou & Li 2003). The positive value of  $\Delta H^0$  for AO 7 and AR 18 adsorption revealed that the adsorption of AO 7 and AR 18 was endothermic. The positive value of  $\Delta S^0$  for AO 7 and AR 18 adsorption suggests the increased randomness at the solid-solution interface during the adsorption of AO 7 and AR 18 onto cationic paper. A similar situation had been reported by Gupta (2006).

### Adsorption dynamics

In order to investigate the mechanism of adsorption, the pseudo-first-order and pseudo-second-order models were used to describe kinetic data (Ho 2004, 2006). The pseudo-

first-order model of Lagergren is given as below:

$$\log(q_e - q) = \log q_e - \frac{k_1}{2.303}t \quad (6)$$

where  $q_e$  and  $q$  (mg/g) are the amounts of adsorbed dye on adsorbent at equilibrium and at time  $t$ , respectively, and  $k_1$  ( $\text{h}^{-1}$ ) is the rate constant of pseudo-first-order model.

The equations of the pseudo-second-order model are expressed as below:

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (7)$$

and

$$h = k_2 q_e^2 \quad (8)$$

where  $k_2$  (g/mg h) is the rate constant of pseudo-second-order adsorption and  $h$  (mg/g h) is the initial adsorption rate.

The rate constants, adsorption capacities at equilibrium, and correlation coefficients were calculated from pseudo-first-order and pseudo-second-order models and listed in Table 3. The theoretical data ( $q_{e,cal}$ ) of the

**Table 2** | Thermodynamic parameters for each dye adsorption

Sample T (°C)	AO 7			AR 18			AB 92		
	20	30	40	20	30	40	20	30	40
$\Delta G^0$ (kJ/mol)	-23.8	-24.1	-25.7	-22.6	-22.8	-24.5	-27.0	-26.0	-26.2
$\Delta H^0$ (kJ/mol)	4.75			11.6			-119.4		
$\Delta S^0$ (J/mol K)	96.4			114.8			-300.9		

**Table 3** | Kinetic constants of pseudo-first-order and pseudo-second-order models for AO 7, AR 18, and AB 92 adsorption at different temperatures

Sample	$q_{e,exp}$ (mg/g)	Pseudo-first-order			Pseudo-second-order			
		$q_{e,cal}$ (mg/g)	$k_1$ (1/h)	$R^2$	$q_{e,cal}$ (mg/g)	$k_2$ (g/mg h)	$H$ (mg/g h)	$R^2$
AO 7 20 °C	337.2	73.7	1.46	0.952	340.1	0.0685	7,922	1.000
AO 7 30 °C	332.0	62.5	1.56	0.953	334.4	0.0773	8,639	1.000
AO 7 40 °C	329.4	75.1	0.90	0.881	333.3	0.0367	4,084	1.000
AR 18 20 °C	254.3	64.6	0.33	0.905	257.1	0.0834	5,511	1.000
AR 18 30 °C	230.5	72.1	0.70	0.949	232.0	0.207	11,132	1.000
AR 18 40 °C	218.7	45.3	0.79	0.970	219.3	0.410	19,736	1.000
AB 92 20 °C	438.4	203.5	0.38	0.995	448.4	0.0252	5,074	1.000
AB 92 30 °C	423.3	152.2	0.70	0.928	427.4	0.0776	14,243	1.000
AB 92 40 °C	413.9	143.5	0.83	0.970	416.7	0.114	19,802	1.000

pseudo-first-order model deviated from the experimental data ( $q_{e,exp}$ ), and the values of correlation coefficients were low. These indicated that the pseudo-first-order model was not applicable in this case.

The theoretical data ( $q_{e,cal}$ ) of the pseudo-second-order model were consistent with the experimental data ( $q_{e,exp}$ ) and the values of correlation coefficients were close to unity at all temperatures studied. These results indicate that the pseudo-second-order model was suitable for describing the adsorption of dyes on cationic paper. The rate constant ( $k_2$ ) for AB 92 and AR 18 adsorption increased as the temperature increased from 20 to 40 °C. The rate constant ( $k_2$ ) for AO 7 adsorption increased as the temperature increased from 20 to 30 °C and started to decrease with further increase in temperature. A similar trend has been reported for the adsorption of Remazol black B by *Rhizopus arrhizus* (Aksu & Tezer 2000).

## CONCLUSIONS

Via quaternization, the cationic groups were introduced onto the surface of paper. This cationic paper could remove anionic dyes from aqueous solution more efficiently than normal paper. The maximum amounts of AO 7, AB 92, and AR 18 adsorbed on cationic paper were 337.2, 446.5, and 289.5 mg/g at pH 6.0, respectively. The adsorption equilibrium could be reached within 3 h at 20 °C. The adsorption capacity of this low-cost adsorbent was enough to remove dye pollution from the aquatic environment. It was found that the adsorption capacity was affected by the initial concentration of dye, temperature, and initial pH of dye solution. The adsorption of dyes on cationic paper fitted the Langmuir model well and pseudo-second-order model was suitable for describing the kinetic data. The thermodynamic data indicated that the adsorption of dye on cationic paper was spontaneous. The main synthesis material of this adsorbent in this research was low-cost waste paper. Thus this research could contribute towards developing an environmentally friendly and low-cost dye adsorbent to substitute for conventional adsorbent such as activated carbon.

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