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Study of adsorption behavior using activated carbon for removal of colored impurities from 30% caprolactam solution produced by means of SNIA-toluene-technology

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Abstract−We studied the adsorption removal of the colored impurities from caprolactam solution by granular activated carbons. It was observed that removal was favored at lower pH (pH 3.84 or below) and higher temperature. The effects of concentration, dosage of activated carbons, contact time have been also reported. Uptake of colored impurities was very rapid in the first 100 minutes and reached equilibrium after 24 h. The batch adsorption kinetics was found to follow the pseudo-second-order model and the rate constants of adsorption for all these kinetic models have been calculated. Three isotherm expressions Langmuir, Freundlich and Trinomial were shown to fit with the experimental results successfully. The mass transfer coefficient β and the effective diffusion coefficient in aqueous phase D_{eff} was calculated under a temperature 35-80 °C. The value of the mean free energy of adsorption E signifies that the adsorption of colored impurities onto activated carbon has a physical nature.

Key words: Colored Impurities, Caprolactam Solution, Activated Carbon, Adsorption Kinetics, Diffusion

INTRODUCTION

Caprolactam is one of the most important materials in the petroleum chemistry industry. It is mainly used to polymerize the fibers of nylon-6 and engineering plastics. There are generally four ways to produce caprolactam in industry. The materials we treated in this paper are produced by means of toluene, a technology developed by Italy SNIA Co. Ltd. Just as this technology process has the following characters--many more kinds of raw materials, larger expenditure, complicated technology, much longer technological process and rather more chemical reactions--so there are a many impurities appearing during the process of production. According to the research work by others, through gas chromatographic identification the composition of the impurities in the solution of caprolactam consists of alcohols, ketones, acids, esters, amide, oximes, and so on. Among those there are also many unknown compositions that we cannot identify [Eppert et al., 1990; Czerw et al., 1981; Jodra et al., 1981; Kontoyannis et al., 1995; Jodra et al., 1981]. These impurities especially the colored impurities exhibit a negative influence on the quality and quantity of the caprolactam and its polymers produced. They will affect the rate of polyreaction, and reduce the viscosity and the relative molecule mass of the polymers. Thus they will determine the strength, color and luster, life span of the ultimate products [Kontoyannis et al., 1995]. Therefore, the decolorization of the caprolactam solution is absolutely necessary to the guarantee of product quality. Presently, the refining of caprolactam is a long and energy-consuming process. Although all of the following processes, such as neutralization, extraction, hydrofining, dehydration, sodium hydroxide-heat-treating, evaporation, distillation, rectification, and ion exchange are used in the refining of caprolactam, the first-rate product cannot be gained; especially, a composition having the maximum UV adsorption at 290 nm cannot be removed utterly. Considering that the activated carbon is an economical and effective adsorbent for industrial separation and purification, and the fact that it has been widely used in the water treatment to remove heavy metals, organic and inorganic impurities, we investigated the ability of activated carbon to remove colored impurities from the caprolactam solution.

Moreover, in order to provide a more dependable basis in theory for the technology design of the production, this paper studied the adsorption kinetics during the process of decolorization. For this study, all colorants that have maximum UV adsorption at 290 nm are treated as a single substance, termed as colored impurities. Both kinetic and equilibrium results were obtained from the batch adsorption experiments.

The work can be considered the starting point for further studies in which column operation will be optimized.

EXPERIMENTAL

1. Adsorbent

The activated carbon employed in this work was made in Tianjin Tianda Co. Ltd. (China). For its use in the experiments, the activated carbon was first screened to a series of particle sizes and then washed thoroughly in distilled water to remove fines, dried at 105 °C and stored in plastic containers for further studies.

2. Adsorbate

The 30% caprolactam solution coming from Shijiazhuang Chemical & Chemical fiber Co. Ltd. with original pH 9.83 was used in all the experiments.

3. Adsorption Experiments

In order to obtain both the kinetic and equilibrium data of the decolorization process, we carried out a study of batch adsorption. Adsorption experiments were made by mixing 500 ml of the colored caprolactam solution and 500 ml distilled water with various amounts of the adsorbents in 1,000 ml agitated vessels (150 rpm). For following the history of the concentration of the colored impurities and establishing the time needed to reach equilibrium, the cap-

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rolactam solution samples at specified time intervals were taken and inspected. The intensity of the color of the solution, considered as the total contribution of the different compounds, was determined by the UV-absorbance method, and the amount of the impurities adsorbed was calculated as the difference between initial color and present color in the liquid sample.

The different concentration of colored impurities was prepared by diluting the original caprolactam solution with the distilled water according to appropriate proportion.

The pH of the solution was adjusted using HCl and NaOH.

4. Analysis

Assuming that there is a linear behavior between light absorbance and the colored impurities concentration, the concentration of the impurities in the liquid and solid phase (C and q) can be calculated according to [Jorge et al., 2002]:

$$C=\frac{m_{caprolactam\ solution}\cdot A_{caprolactam\ solution}}{m_{caprolactam\ solution}}=A_{caprolactam\ solution} \tag{1}$$

$$\begin{aligned} q&=\frac{[\text{Colored impurities}]_{AC}}{m_{AC}} \\ &=\frac{[\text{Initial colored impurities}]_{caprolactam\ solution}-[\text{Final colored impurities}]_{caprolactam\ solution}}{m_{AC}} \\ &=\frac{m_{caprolactam\ solution}}{m_{AC}}(A_0-A_{caprolactam\ solution}) \end{aligned} \tag{2}$$

where $m_{caprolactam\ solution}$ and m_{AC} are the weights of caprolactam solution and activated carbon, respectively, and A is the value of the absorbance measured in the liquid.

Although there are many kinds of colored impurities in the caprolactam solution, the light absorbance values of the liquid samples, that is C and q, mirror accurately the total color charge in both solid and liquid phase for what we care about is only the composition having the maximum UV adsorption at 290 nm. Adsorption isotherms were carried out at the initial pH=9.83 and different temperatures (35 °C, 45 °C, 65 °C, 80 °C).

ADSORPTION THEORY AND MATHEMATICAL MODEL

1. Adsorption Isotherm

Equilibrium behavior of the adsorption system is an essential requirement for modeling of system kinetics. Adsorption data are usually described by adsorption isotherms. These isotherms relate impurities uptake per unit weight of adsorbent q_e to the equilibrium adsorbate concentration in the bulk fluid phase C_e. The following are the isotherm models usually used to fit with the adsorption equilibrium data:

$$q_e=\frac{q_s bC_e}{1+bC_e}\quad \text{Langmuir} \tag{3}$$

$$q_e=K_F C_e^{n_F}\quad \text{Freundlich} \tag{4}$$

$$q_e=a_1C_e^3+a_2C_e^2+a_3C_e+a_4\quad \text{Trinomial} \tag{5}$$

$$\ln q_e=\ln q_m-\lambda\theta^2\quad \text{Dubinin-Radushkevich} \tag{6}$$

where q_s and b are Langmuir constants related to adsorption capacity and energy of adsorption, respectively. K_F relates to sorption capacity and n_F to sorption intensity, θ (Polanyi's Potential) is RT ln(1+1/C_e), q_m is the adsorption capacity.

All of the isotherm formulas can be used for analysis of equilibrium batch experiment data.

2. Effective Diffusion in Aqueous Phase

Considering that the D_{eff} may include molecular, pore, and/or surface diffusion processes involving external mass transfer, internal pore mass transfer, and surface diffusion [Phillip and Sophie, 2003], we follow McKay's method for D_{eff} evaluation, where it was commented that the D_{eff} depends on several parameters including particle radius, particle porosity, adsorbent mass, adsorbent density, solution volume, isotherm constants, and the extent of adsorption time [McKay, 2001].

$$\frac{\partial C}{\partial t}=\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 D_{eff}\frac{\partial C}{\partial r}\right) \tag{7}$$

Assuming that the effective diffusion coefficient is constant, we gain the solute material balance

$$D_{eff}\left(\frac{\partial C}{\partial r^2}+\frac{2}{r}\frac{\partial C}{\partial r}\right)=\frac{\partial C}{\partial t} \tag{8}$$

The initial and boundary integration conditions for Eq. (10) are usually given as

$$\begin{aligned} &r=R,\ t=0,\ C(r,0)=C_0 \\ &0\le r\le R,\ t=t,\ C(r,t)=Ct,\ \left(\frac{\partial C}{\partial r}\right)_{r=0}=0,\ \left(\frac{\partial C}{\partial t}\right)_{r=0}=0 \end{aligned} \tag{9}$$

In these boundary conditions, C_0 is the initial concentration of colored impurities in the solution at time t=0, and C^* is the equilibrium concentration of colored impurities in the solution at time t=∞. When activated carbon particle has a uniform average surface concentration maintained constant, the total amount of diffusing substance entering or leaving the sphere is given

$$\frac{C_0-C_t}{C_0-C^*}=1-\frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp\left(-\frac{D_{eff}n^2\pi^2 t}{R^2}\right) \tag{10}$$

The concept of a constant surface concentration may be envisaged as an adsorption system where the amount adsorbed is low and the bulk concentration is only marginally affected. The colored impurities concentration C and the absorption amounts of the absorbent q are also fitted

$$\frac{C_0-C_t}{C_0-C^*}=\frac{q_t}{q_\infty} \tag{11}$$

Supposing, $\alpha=q_t/q_\infty$ then the approximate solution of Eq. (10) is

$$\alpha=\sqrt{1-e^{-\frac{D_{eff}\pi^2}{R^2}t}} \tag{12}$$

It can also be rewritten in the following form

$$2.303\lg(1-\alpha^2)=-\frac{D_{eff}\pi^2}{R^2}t \tag{13}$$

RESULTS AND DISCUSSION

1. Effect of Initial Concentration

Fig. 1 illustrates the adsorption of colored impurities for differ-

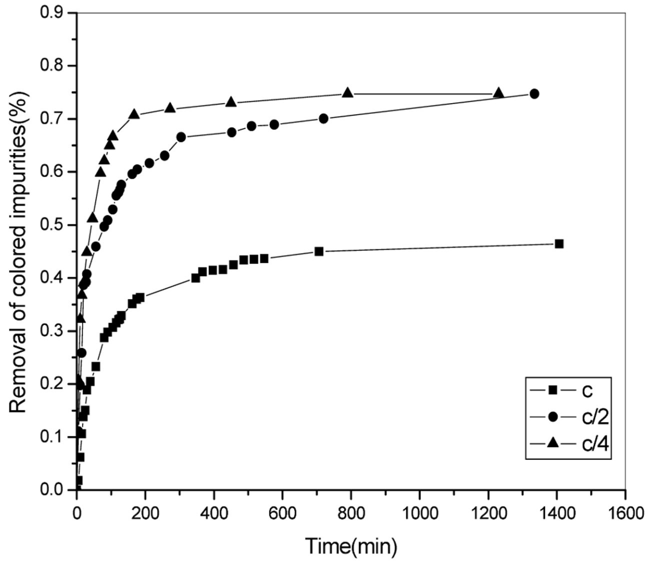

Fig. 1. Influence of initial concentration of colored impurities on percent adsorbate removal by AC at 65 °C.

ent initial concentrations of caprolactam solution at 65 °C and pH 9.83 as a function of contact time. The adsorption of colored impurities onto AC increases with the increment of contact time and thereafter levels off. The removal of colored impurities on AC has been shown to increase with time and attains a maximum value at about 1,200 min, and thereafter, it remains almost constant. On changing the initial concentration of the caprolactam solution, the equilibrium time becomes short as the concentration is decreased. From Fig. 1, one can see that the amount of adsorbate attained on the solid phase increases with increasing initial concentrations. However, the percentage removal of the colored impurities decreases, and with the initial concentration even smaller, the percentage removal reaches almost the maximum and does not change anymore.

2. Effect of Initial pH on Adsorption

The effect of pH on the removal of colored impurities by AC is shown in Fig. 2. From Fig. 2, it can be shown that the solution pH plays a very important role in the adsorption of colored impurities. The percent removal of the colored impurities increases as pH is decreased. And a sharp decrease in the removal rate was observed between pH 11.00 and 13.85 or above. In the meantime a sharp in-

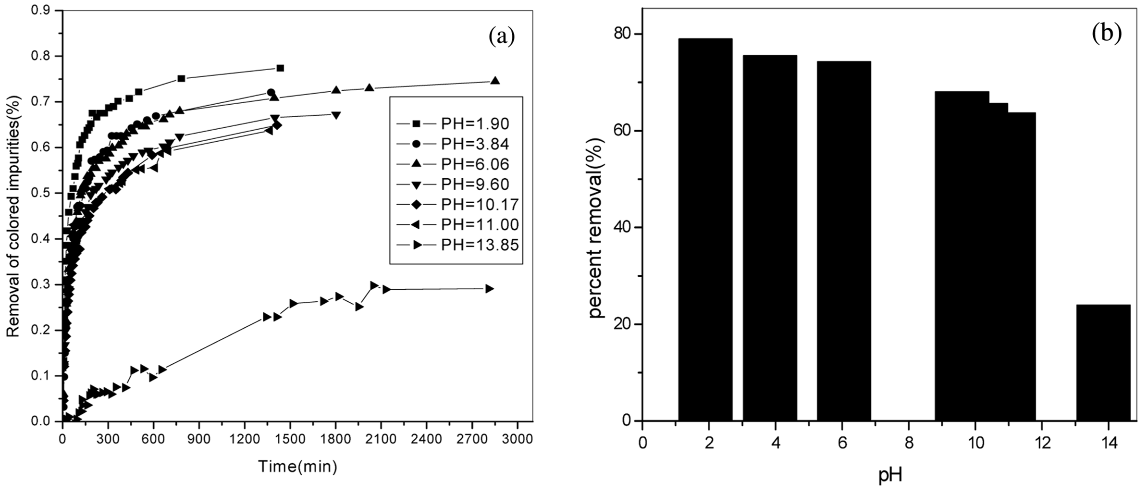

Fig. 2. Influence of initial pH on percent adsorbate removal by AC at 65 °C.

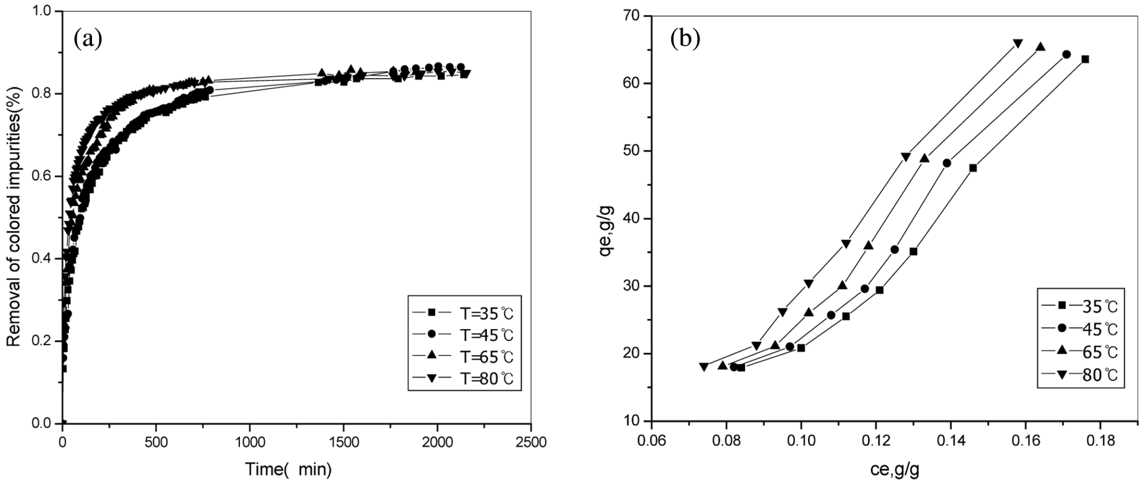

Fig. 3. Influence of different temperatures on percent adsorbate removal by AC.

crease in the removal rate was also observed between pH 3.84 and 1.90 or below. All these indicate that the adsorption capacity of the adsorbent is strongly pH dependent.

3. Adsorption Isotherms

Fig. 3 shows the influence of different temperatures on percent removal by AC. From the figure we can see that, with the temperature rising from 35 to 80, the percent removal of colored impurities is increased from 78.90 to 82.72 when contact time is 12 h, and the q_e is changed from 43.00 $g\cdot g^{-1}$ to 56.17 $g\cdot g^{-1}$ when C_e is 0.14 $g\cdot g^{-1}$. This indicates that the adsorption is highly dependent on temperature and contact time and it also mirrors that the adsorption of colored impurities onto AC is an endothermic reaction. It was also revealed that uptake of colored impurities was very rapid in the first 100 minutes and was reached equilibrium after 24 h. Fig. 3 b) also reflects that the adsorption isotherms of colored impurities onto AC are not Langmuir-type; this can be further confirmed by the fact that the parameter values q_s and b are calculated as less than 0.

Fig. 4 presents equilibrium data for adsorption of colored impurities in caprolactam solution onto activated carbon at 35 °C, 45 °C, 65 °C, 80 °C, respectively. From the plots testing the isotherm equations, we found that the experimental points basically fit to these three isotherms, and the results are presented in Table 1. The Freundlich isotherm yielded a better fit. The best fit among the three isotherms was the Trinomial equation. But the improvement of the fit provided by this equation is accompanied by the loss of significance of the new parameters. However, another important and well-fitted adsorption isotherm is Dubinin-Radushkevich. The values of the parameters of the three isotherms were calculated from the slope and the intercept of the linear plot of their isotherm equations, and the results are reported in Table 1. It was observed that Freundlich constants K_F and n_F were influenced by temperature. Generally, an increase in temperature results in an increase in both K_F and n_F. A higher value for K_F indicates higher affinity for the adsorbate, but the values of $n_F>1$ indicate unfavorable adsorption. Upon investigating further, we found that K_F has the highest value at 65 °C, which indicates the intensity of adsorption is the most strong at this temperature. And the value of $n_F=1.8949<n_F=1.91389$(45 °C)$<n_F=1.9306$ (35 °C) also shows the process at 65 °C is more favorable. From Table 1 we can also see that the constant λ of D-R equation was almost independent of temperature, from 0.0686 mol^2kJ^{-2} to 0.0786 mol^2kJ^{-2}. Whereas q_m was changed between 397.50 and 429.69 g g^{-1} with an increase in temperature from 308.15 to 353.15 K. The mean free energy of adsorption (E), defined as the free energy change when one mole of adsorbate is transferred from infinity in solution to the surface of the solid, was calculated by using the following equation [Tony and Pant, 2004]:

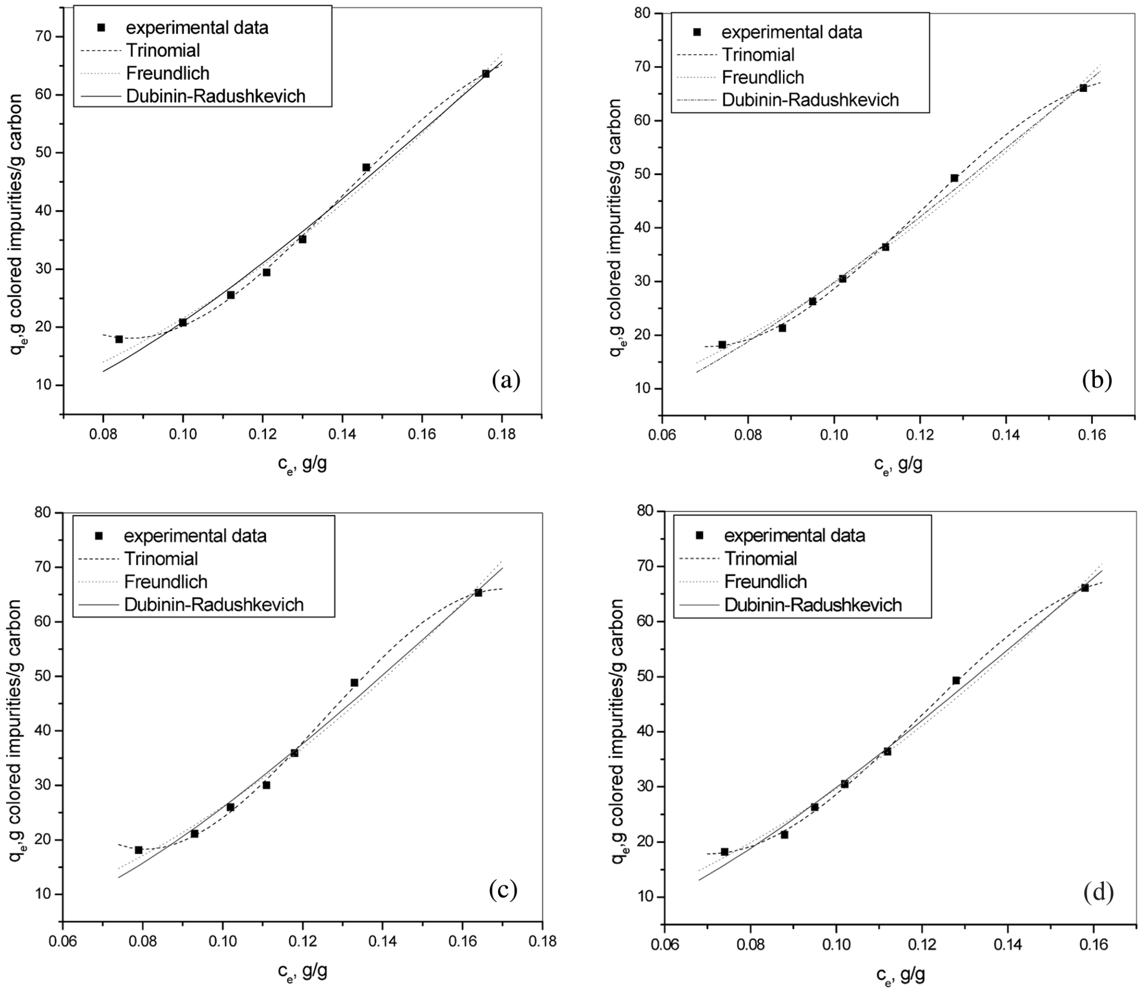

Fig. 4. Equilibrium isotherm for adsorption of colored impurities on AC at (a) 35 °C (b) 45 °C (c) 65 °C (d) 80 °C.

Table 1. Parameter and R^2 values of the isotherm equations tested under the temperature 35 °C, 45 °C, 65 °C, 80 °C

Isotherm model		Parameters values				R^2
Langmuir: $q_e=\frac{q_s bC_e}{1+bC_e}$	35 °C	$q_s=-44.73$	$b=-3.36$			0.9822
	45 °C	$q_s=-47.20$	$b=-3.41$			0.9712
	65 °C	$q_s=-49.30$	$b=-3.51$			0.9716
	80 °C	$q=-56.07$	$b=-3.46$			0.9778
Trinomial: $q_e=a_1C_e^3+a_2C_e^2+a_3C_e+a_4$	35 °C	$a_1=-80382.1$	$a_2=33775.3$	$a_3=-4041.0$	$a_4=166.94$	0.9987
	45 °C	$a_1=-119165.7$	$a_2=47168.4$	$a_3=-5459.7$	$a_4=214.6$	0.9969
	65 °C	$a_1=-133290.8$	$a_2=50124.8$	$a_3=-5483.1$	$a_4=204.4$	0.9985
	80 °C	$a_1=-104840.7$	$a_2=37630.1$	$a_3=-3741.2$	$a_4=131.3$	0.9990
Freundlich: $q_e=K_F C_e^{n_F}$	35 °C	$K_F=1835.95$	$n_F=1.9306$			0.9874
	45 °C	$K_F=1920.49$	$n_F=1.9138$			0.9813
	65 °C	$K_F=2047.95$	$n_F=1.8949$			0.9841
	80 °C	$K_F=1849.45$	$n_F=1.7953$			0.9896
D-R: $\ln q_e=\ln q_m-k\left\{RT\ln\left(1+\frac{1}{C_e}\right)\right\}^2$	35 °C	$q_m=406.86$	$k=7.86\times10^{-8}$			0.9823
	45 °C	$q_m=417.96$	$k=7.68\times10^{-8}$			0.9799
	65 °C	$q_m=429.69$	$k=7.44\times10^{-8}$			0.9851
	80 °C	$q_m=397.50$	$k=6.86\times10^{-8}$			0.9915

$$E=-\frac{1}{\sqrt{2\lambda}} \tag{14}$$

The calculated value of E was 2.52-2.70 $kJmol^{-1}$. Considering that the energy range of physical adsorption due to weak van der Waals forces is $E<8$ $kJmol^{-1}$, we may deduce that the adsorption of colored impurities in the caprolactam solution onto activated carbon has a physical nature.

4. Effect of Dose of Activated Carbon

Fig. 5 shows the removal of colored impurities as a function of AC dosage in the caprolactam solution. The AC dosage was varied from 7.000 g to 35.000 g. The experimental results revealed that the removal efficiency of colored impurities increases up to an optimum dosage beyond which the removal efficiency does not change anymore. It maybe concluded that the removal efficiency increases with the increment of adsorbent dose but adsorption density decreases. The decrease in adsorption density can be attributed to the fact that some of the adsorption sites increase with increasing adsorbent and this results in the increase in removal efficiency. As expected, the equilibrium concentration decreases with increasing adsorbent for a given initial concentration. For a fixed initial solute concentration, increasing the adsorbent dose provides a greater surface area or adsorption sites.

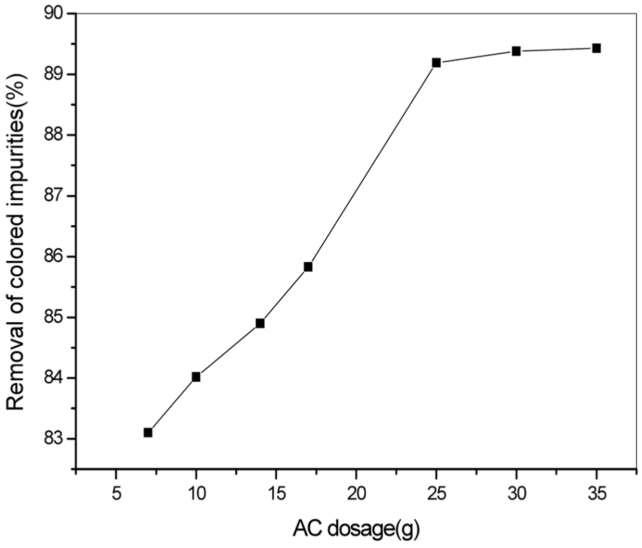

Fig. 5. Influence of different AC dosages on percent adsorbate removal at 65 °C.

5. Kinetics of Adsorption

The models of adsorption kinetics correlate the solute uptake rate, so these models play a very important role in the adsorption process design. There are various models to analyze the kinetics of the sorption process. The simplest reaction model correlating the rates of reaction was a first-order reaction model. Lagergren, Ho and McKay, and Namasivayam and Kardivelu all suggested using the following rate equation for the sorption of solutes from a liquid solution,

$$\frac{dq}{dt}=k_{ad\,1}(q_e-q) \tag{15}$$

Integrating Eq. (15) for the boundary conditions t=0 to t=t and q=0 to q=q gives

$$\ln\frac{q_e}{(q_e-q)}=k_{ad\,1}t \tag{16}$$

Eq. (16) can be rearranged to obtain a linear form

$$\ln(q_e-q)=\ln q_e-k_{ad\,1}t \tag{17}$$

Where q_e is the amount of colored impurities adsorbed at equilibrium, $g\cdot g^{-1}$; q the amount of colored impurities adsorbed at time t, $g\cdot g^{-1}$; and $k_{ad\,1}$ is the mass transfer rate constant of pseudo-first adsorption, min^{-1}. Another useful model for analysis of sorption kinetics is pseudo-second-order. The rate law for this system is expressed as

$$\frac{dq}{dt}=k_{ad2}(q_e-q)^2 \tag{18}$$

Integrating Eq. (18) for the boundary conditions t=0 to t=t and q=0 to q=q gives

$$\frac{1}{(q_e-q)}=\frac{1}{q_e}+k_{ad2}t \tag{19}$$

Eq. (19) can be rearranged to obtain a linear form:

$$\frac{t}{q}=\frac{1}{k_{ad2}q_e^2}+\frac{1}{q_e}t \tag{20}$$

The plot of t/q versus t gives a straight line with slope of k_{ad2} and intercept of $1/q_e$.

Two kinetic models for sorption from liquid solution, represented above (first-order and second-order models), were derived and used in the literature without any assumptions or specialization of process conditions. Plots for Eqs. (17) and (20) were made for colored impurities absorbed on AC at different temperatures. Approximately, linear fits were observed for all temperatures indicating that sorption reaction can be approximated to pseudo-first-order and pseudo-second-order kinetics. For the pseudo-first-order kinetic model, the smallest correlation coefficient in this case was 0.9898. But in general, the pseudo-second-order kinetic model is even better than the pseudo-first-order kinetic model, for which the smallest correlation coefficient is 0.9961.

The constants k_{ad1} and k_{ad2} are calculated from the figures and represented in Table 2. It can be observed that the constants change with the temperature. The higher the temperatures, the larger the constants. From Table 2, we can also see that although the correlation coefficients for pseudo-first-order model are found to be higher than 0.98, the calculated equilibrium adsorption capacities do not agree with experimental values. This indicates that adsorption of colored impurities onto AC is not an ideal pseudo-first-order reaction. But the plots of t/q versus t show a good agreement of experimental data with the pseudo-second-order kinetic model for which the smallest correlation coefficients (r^2) is above 0.996, and the calculated q_e values agree well with the experimental data. It indicates that the adsorption of colored impurities from the caprolactam solution on AC obeys pseudo-second -order kinetic model. P.K. Malik reported similar findings for the dye removal from wastewater using activated carbon developed from sawdust [Malik, 2004]. The adsorption of Congo Red on activated carbon prepared from agriculture waste is also found having similar results [Namasivayam and Kavitha, 2002]. From Fig. 6, we can clearly observe that the variation in rate was not proportional to the first power of concentration, and the relationship between initial solute concentration and the rate of adsorption was also not linear. This might indicate that the process is not strict surface adsorption, and perhaps the pore diffusion limits the adsorption process to some extent [Tony and Pant, 2004].

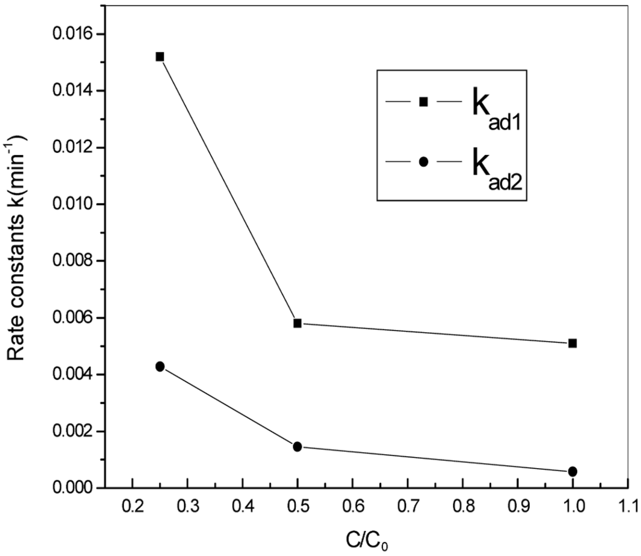

Fig. 6. Plots of rate constants under different initial concentrations.

6. Mass Transfer Analysis

In order to interpret the experimental data from a mechanistic viewpoint, it is essential to identify the steps involved during adsorption. The kinetics of bulk transport of the solute is generally investigated by using the following mass transfer model suggested by McKay et al. [McKay, 1981]:

$$\ln\left(\frac{C_t}{C_0}-\frac{1}{1+\tilde{m}K}\right)=\ln\frac{\tilde{m}K}{1+\tilde{m}K}-\frac{1+\tilde{m}K}{\tilde{m}K}\beta S_s t \tag{21}$$

where C_0 is the initial solute concentration; C_t is the adsorbate concentration after time t; K is the constant obtained by multiplying the Langmuir constant q_s and b; β is the mass transfer coefficient; and $\tilde{m}$ is the mass of adsorbent per unit volume of particle free adsorbate solution. S_s is the outer surface of the adsorbent per unit volume of particle free slurry. They are calculated as $\tilde{m}=W/V$, $S_s=6\tilde{m}/$

Table 2. Pseudo-first- and pseudo-second-order adsorption rate constants and the calculated and experimental q_e values for adsorption of colored impurities on activated carbons

		Pseudo-first-order				Pseudo-second-order		
		q_e (Exp)	k_{ad1} (min^{-1})	q_e (Cal)	R^2	k_{ad2} (min^{-1})	q_e (Cal)	R^2
Temperature	35 °C	47.5	6.4×10^{-3}	33.6	0.9967	3.98×10^{-4}	49.3	0.9961
	45 °C	48.2	6.1×10^{-3}	32.1	0.9898	4.10×10^{-4}	50.0	0.9979
	65 °C	48.8	1.07×10^{-2}	35.0	0.9924	5.76×10^{-4}	51.9	0.9989
	80 °C	49.3	1.13×10^{-2}	29.2	0.9925	8.33×10^{-4}	51.6	0.9997
Different initial concentrations	$C/C_0=1$	30.5	5.1×10^{-3}	17.5	0.9895	5.75×10^{-4}	31.9	0.9993
	$C/C_0=0.5$	24.1	5.8×10^{-3}	10.9	0.9912	1.46×10^{-3}	24.5	0.9990
	$C/C_0=0.25$	13.0	1.52×10^{-2}	8.2	0.9966	4.28×10^{-3}	13.3	0.9986

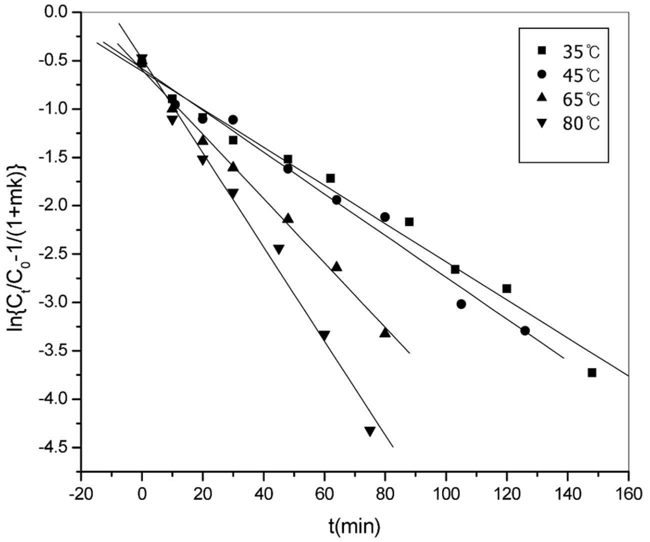

Fig. 7. Plots of estimation of mass transfer coefficients for adsorption of colored impurities on activated carbons.

Table 3. Mass transfer coefficients (β)

Temperature (°C)	$\tilde{m}$ ($g\cdot g^{-1}$)	K ($g\cdot g^{-1}$)	S_s (cm^{-1})	β ($cm\cdot s^{-1}$)
35	0.01	144.77	0.76	2.55×10^{-4}
45		146.72		2.81×10^{-4}
65		153.42		4.42×10^{-4}
80		166.73		6.67×10^{-4}

$(1-\varepsilon_p)d\rho$, respectively. Here d is the AC diameter; ρ is the density of adsorbent; and ε_p is the porosity of adsorbent particles. The plots of $\ln((C_t/C_0)-(1/1+\tilde{m}K))$ versus t (Fig. 7) result in a straight line of slope $(1+\tilde{m}K/\tilde{m}K)\beta S_s$ and the values of mass transfer coefficients β as calculated are listed in Table 3. For the adsorption of various adsorbates onto adsorbents, the β values obtained in this study are lower than those reported in the literature As(III)-activated alumina (7.2×10^{-3}-1.1×10^{-2} $cm\cdot s^{-1}$), benzaldehyde-carbon (9×10^{-3} $cm\cdot s^{-1}$) and phenol-carbon (3.9×10^{-3} $cm\cdot s^{-1}$) [Tony and Pant, 2004]. This can be explained by the fact that larger organic molecules will restrict their motilities in the solution. So the colored impurities in the caprolactam solution move with difficulty since these are larger organic molecules. The lower β values suggest that the velocities of mass transfer of all the solutes from solution to the adsorbent phase are quite slow. Thus the step of bulk transport, i.e., the transport of ingoing solute to the external surface of the adsorbent via the process known as film diffusion may be the key step in determining the rate. By the way, the good linear nature of Fig. 7 confirms the validity of the diffusion model for the adsorption system. Also, the results in Table 3 show that the mass transfer coefficients increase with the temperature. It indicates that the mass transfer of colored impurities in the caprolactam solution at lower temperature is more important than at higher temperature. On comprehensive consideration, it may be suggested that the adsorption mechanism of colored impurities onto AC is fairly complex and perhaps both, the film diffusion as well as pore diffusion, contribute to the rate determining step.

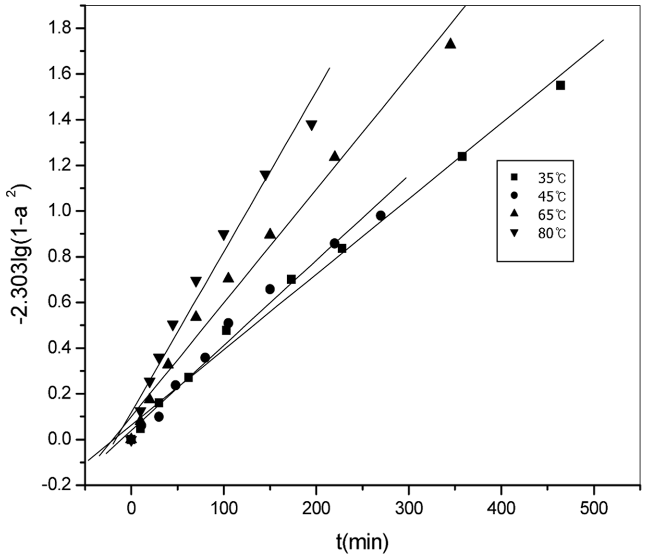

Fig. 8. [$-2.303\lg(1-\alpha^2)$] versus time plots at different temperatures for the adsorption of colored impurities on AC.

Table 4. Effective diffusion coefficient in aqueous phase at different temperature

T (°C)	35	45	65	80
D_{eff} (cm^2/s)	1.92×10^{-7}	2.17×10^{-7}	2.90×10^{-7}	4.10×10^{-7}

7. Effective Diffusion Coefficient in Aqueous Phase

For the convenience of analysis, we rewrite the Eq. (15) in the following form:

$$2.303\lg(1-\alpha^2)=-kt \tag{22}$$

$$k=\frac{D_{eff}\pi^2}{R^2} \tag{23}$$

In order to distinguish whether the adsorption process is controlled by film diffusion or particle diffusion, the linearity of [$-2.303\lg(1-\alpha^2)$] versus time was tested, and the values of D_{eff} are listed in Table 4. From Fig. 8, we can see that, although the plots of [$-2.303\lg(1-\alpha^2)$] versus time at different temperatures show fairly good linearity, they do not pass through the origin, indicating that, in the studied solute concentration range, external transport mainly governs the rate-limiting process. The observation is again in conformity with the prediction of Zogorski and Mitali Sarkar [Mitali Sarkar et al., 2003].

From Table 4, we can also see that D_{eff} values increase as temperature is increased, which illustrates the higher efficiency in removing the colored impurities from solution. The reason may be that, under higher temperatures, the viscosity of the solution decreases and the apparent rate of molecule motion speeds up, both of which result in the increment of the diffusion rate inside the pores.

CONCLUSION

In this work a detailed experimental and theoretical analysis of the sorption of colored impurities on activated carbons is presented.

On the basis of the present study, the following conclusions can be drawn:

Activated carbon is an effective adsorbent for the removal of colored impurities from the caprolactam solution. The adsorption is highly dependent on temperature, contact time, adsorbent dose and pH. The higher the temperature, the higher the removal percentage. The equilibrium of the adsorption is reached after 24 h. The most ideal pH for adsorption of colored impurities on activated carbon is 3.84 or below.

The equilibrium data fit well in the D-R, Freundlich model of adsorption, showing the mechanism of adsorption removal of colored impurities on activated carbon is very complex where either film diffusion or intra-particle diffusion could contribute to the rate determining step. But the study of equilibrium data at different temperatures has illustrated that the equation that describes the equilibrium the best is the Trinomial isotherm:

$$q_e=a_1C_e^3+a_2C_e^2+a_3C_e+a_4$$

The adsorption kinetics of colored impurities by activated carbon follows the pseudo-second-order model. Kinetic studies have permitted us to conclude that the adsorption mechanism of colored impurities onto AC is fairly complex and perhaps both the film diffusion as well as pore diffusion contribute to the rate determining step.

Meanwhile, the mean free energy of adsorption was calculated as 2.52-2.70 $kJmol^{-1}$. It signifies that the adsorption of colored impurities onto activated carbon has a physical nature.

NOMENCLATURE

α : represents q_t/q_∞
β : mass transfer coefficient $[cm.s^{-1}]$
ε_p : porosity of adsorbent particles
θ : Polanyi's Potential
λ : Dubinin-Radushkevich constants
ρ : density of adsorbent $[g/cm^3]$
A : absorbance value
b : Langmuir constant
C_e : equilibrium concentration of colored impurities $[g \cdot g^{-1}]$
C_0 : initial concentration of colored impurities $[g \cdot g^{-1}]$
C^* : equilibrium concentration of colored impurities in the solution at time $t=\infty$ $[g \cdot g^{-1}]$
C, C_t : concentration of colored impurities at time t $[g \cdot g^{-1}]$
d : diameter [cm]
D_{eff} : effective diffusion coefficent $[cm^2/s]$
k : represents $D_{eff}\pi^2/R^2$
$k_{ad\,1}$: the rate constant of pseudo-first adsorption $[min^{-1}]$
$k_{ad\,2}$: the rate constant of pseudo-second adsorption $[min^{-1}]$
K_F : Freundlich constants
K : constant obtained by multiplying the Langmuir constant q_s and b $[g \cdot g^{-1}]$
m : weight [g]
$\tilde{m}$: mass of adsorbent per unit volume of particle free adsorbate solution [g/ml]
n_F : Freundlich constants
q : colored impurities concentration in the solid phase $[g \cdot g^{-1}]$
q_s : Langmuir constants $[g \cdot g^{-1}]$
q_t : amount of colored impurities adsorbed at time t $[g \cdot g^{-1}]$
q_m : Dubinin-Radushkevich constants $[g \cdot g^{-1}]$
q_e : amount of colored impurities adsorbed at equilibrium $[g \cdot g^{-1}]$
q_∞ : the amount of colored impurities adsorbed at time $t=\infty$ $[g \cdot g^{-1}]$
r : dimension [m]
R : particle radius [m]
S_s : the outer surface of the adsorbent per unit volume of particle free slurry $[cm^{-1}]$
V : volume [ml]

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