

# Removal of Coloured Impurities from Caprolactam Solution by Adsorption onto Activated Carbon: Equilibrium and Thermodynamic Studies

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**ABSTRACT:** A large number of impurities appear during the production of caprolactam. Such impurities — especially coloured impurities — having a maximum UV absorbance at a wavelength of 290 nm, make it quite difficult to isolate the high-purity product. In order to improve the purification technology, the removal of the coloured impurities from caprolactam solution by adsorption onto activated carbon was studied with good results. The thermodynamic and mass-transfer behaviours of the adsorption process were also examined in this study with the values of  $D_i$ ,  $k_{ad}$ ,  $E_a$  and  $E^\#$  being calculated. The magnitudes of the thermodynamic parameters  $\Delta G^0$ ,  $\Delta H^0$  and  $\Delta S^0$  were also evaluated. A negative  $\Delta G^0$  value confirmed the feasibility of the method and the spontaneous nature of the adsorption process. The positive value of  $\Delta H^0$  indicated the endothermic nature of the process while the positive value of  $\Delta S^0$  indicated an increase in the degrees of freedom of the adsorbed species. The value of  $\Delta H_{iso}$  increased with the extent of adsorption and showed a linear relationship when plotted against  $\ln q$ .

## INTRODUCTION

Caprolactam is one of the most important materials of petroleum processing and the chemical industry. It is mainly used to polymerize the fibres of nylon-6 and engineering plastics. There are generally four ways of producing caprolactam industrially. The materials studied in the present work were produced by means of toluene, a technology developed by Italy SNIA Co. Ltd. Because of the technology employed, quite a number of impurities appear during the production process, including many whose compositions have yet to be established (Eppert *et al.* 1990; Czerwiński *et al.* 1981; Jodra *et al.* 1981a,b; Kontoyannis *et al.* 1995). These impurities, especially those which are coloured, exert a negative influence on the quality and quantity of the caprolactam produced and its polymers. Through their influence on the rates of polymerization and the reduction in the viscosities and relative molecular masses of the polymers, they determine the strength, colour, lustre and lifespan of the ultimate products (Kontoyannis *et al.* 1995). Hence, decolourization and purification of the caprolactam solution is absolutely essential to guarantee the product quality. However, at present, the technology employed for refining caprolactam involves a long and energy-consuming process. Although processes such as neutralization, extraction, hydro-refining, dehydration, heat treatment, evaporation, distillation, rectification and ion exchange are employed, it has not proved possible to obtain a high-purity product since the composition having the maximum absorbance at 290 nm, in particular, is not completely eliminated.

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Since activated carbon is an economical and effective adsorbent for industrial separation and purification processes, and has been widely used in water treatment to remove heavy metals, organic and inorganic impurities (Garca Agudo *et al.* 2002; Ferreira *et al.* 2004; Acemioğlu 2004; Sarkar *et al.* 2003; Mohan *et al.* 2001, Srivastava *et al.* 1996; Singh and Pant 2004), we have investigated the ability of activated carbon to remove coloured impurities from aqueous caprolactam solutions.

For this study, all colorants having the maximum absorbance at 290 nm were treated as a single substance and are termed as coloured impurities below. The equilibrium results were obtained from batch adsorption experiments. However, because the system studied is multi-component, the thermodynamic analysis employed cannot be considered as fully rigorous. However, despite these limitations, the results obtained are of significance since they provide the necessary knowledge for an understanding of the adsorption mechanism and process. The work can be considered as the starting point for further studies in which column operations will be optimized.

## MATERIALS AND METHODS

### Materials

A commercial activated carbon manufactured by the Tianjin Tianda Co. Ltd. (P. R. China) was employed in this work. Prior to being used in the adsorption studies, the activated carbon was screened to provide a series of particle sizes and then washed thoroughly in distilled water to remove fines, dried at 105°C and then stored in plastic containers.

The 30% caprolactam solution was obtained from the Shijiazhuang Chemical & Chemical Fiber Co. Ltd. (P. R. China), the original solution with a pH value of 9.83 being used in all subsequent experiments. All other chemicals employed were of analytical grade.

### Methods

Batch methods were employed to obtain both kinetic and equilibrium data for the decolourization process. Adsorption experiments were undertaken by mixing 500 ml of the coloured caprolactam solution and 500 ml of distilled water with various amounts of the adsorbents in 1000-ml volume vessels and agitating the resulting mixture at 150 rpm. Samples of the caprolactam solution were taken at specified time intervals and analyzed to measure the influence of the concentration of the coloured impurities and to establish the time needed to attain equilibrium. The intensity of the solution colour, considered as being the total contribution of a number of different compounds, was determined by a UV absorbance method, while the amount of impurities adsorbed was calculated as being the difference between initial and final colour of the liquid sample.

Assuming that a linear relationship exists between the light absorbance of the caprolactam solution and the concentration of coloured impurities, the concentration of impurities in the liquid and solid phases (C and q) can be calculated from the relationship (Garca Agudo *et al.* 2002):

$$C = \frac{m_{\text{caprolactam solution}} \cdot A_{\text{caprolactam solution}}}{m_{\text{caprolactam solution}}} = A_{\text{caprolactam solution}} \quad (1)$$

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

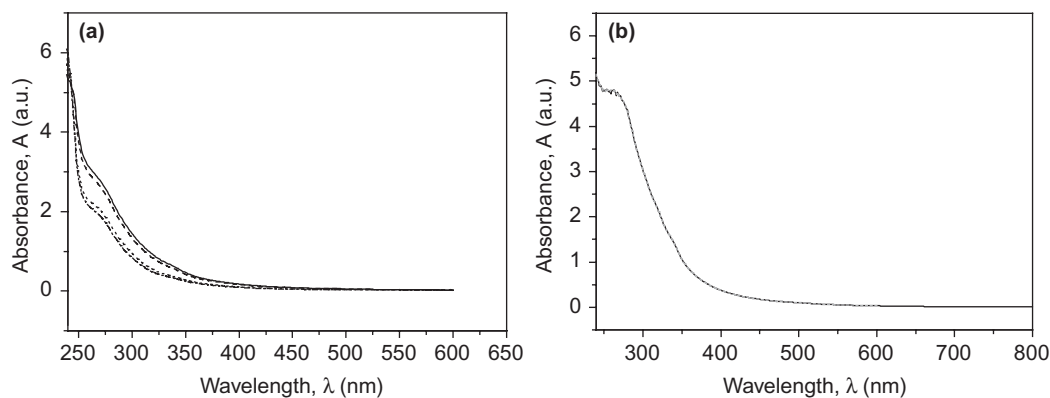
where  $m_{\text{caprolactam solution}}$  and  $m_{AC}$  are the weights of caprolactam solution and activated carbon, respectively, and  $A$  is the value of the measured absorbance of the liquid.

Although there were quite a number of various kinds of coloured impurities in the caprolactam solutions, the values of the light absorbance of the liquid samples, i.e.  $C$  and  $q$ , mirror accurately the total colour change in both the solid and liquid phases. Adsorption isotherms were measured at different temperatures (35°C, 45°C, 65°C, 80°C) and an initial pH value of 9.83 for the caprolactam solution. After treatment with activated carbon under different conditions, the caprolactam solution was analyzed spectroscopically using a UV spectrophotometer (Cary 5000, UV-vis-NIR) and by HPLC methods (Agilent 1100).

## RESULTS AND DISCUSSION

### Spectral and chromatographic analyses

The results of the spectral and HPLC analyses of caprolactam solutions treated with activated carbon under different conditions are depicted in Figures 1 and 2. The spectra depicted in Figure 1 show that the light absorbance,  $A$ , decreased as the temperature increased. This indicates that the coloured impurities exhibited a higher percentage removal at higher temperatures. In addition,



**Figure 1.** Spectra of caprolactam solutions before and after adsorption at different temperatures by activated carbon. The various plots in the two parts of the figure have the following meanings: (a) —, after adsorption at 35°C; ---, after adsorption at 45°C; ···, after adsorption at 65°C; -.-, after adsorption at 80°C. (b) —, before adsorption at 35°C; ···, before adsorption at 80°C.

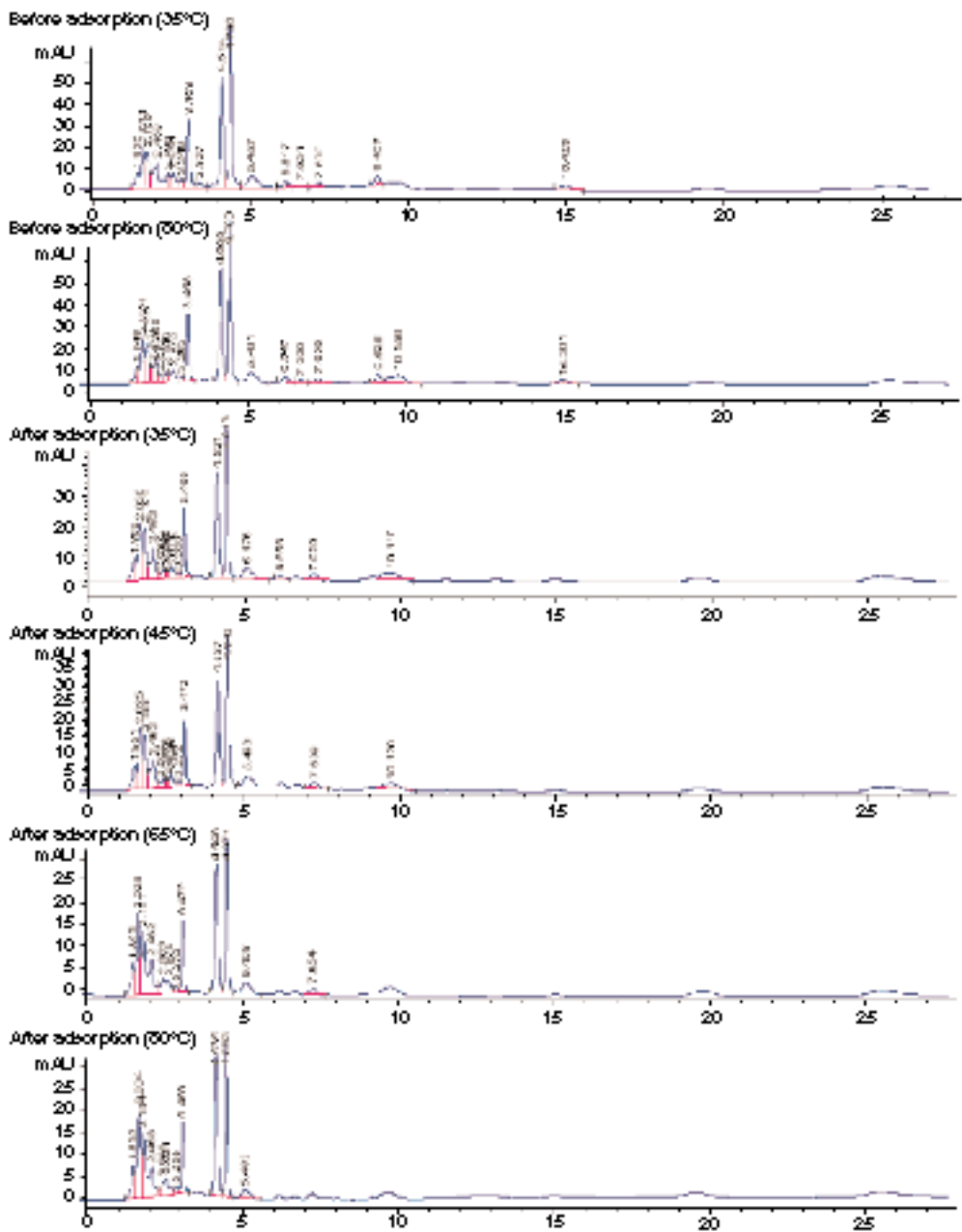


Figure 2. HPLC chromatograms for caprolactam solutions before and after adsorption at different temperatures by activated carbon.

Figure 1(b) shows that merely increasing the temperature in the absence of activated carbon had no effect upon the ultraviolet absorbance observed. This fact is further confirmed by the HPLC chromatograms depicted in Figure 2. Thus, the HPLC chromatograms of caprolactam solution

treated under different conditions exhibited virtually the same kind of spectral peaks at a wavelength of 290.16 nm. This means that, irrespective of the conditions under which the caprolactam solution was treated (including heating the solution up to 80°C), the same components were retained on the HPLC column. It will be noted from Figure 2 that the absorbance (mAU) of the caprolactam solution, which represents the total concentration of coloured impurities present, decreased with temperature. Thus, when the temperature was increased from 35°C to 80°C, the absorbance decreased from 42 mAU to 28 mAU. Similarly, Figure 2 shows that changing the temperature from 35°C to 80°C in the absence of activated carbon led to virtually identical HPLC chromatograms. This illustrates that, over the temperature range studied, the coloured impurities present in the caprolactam solution could not be decomposed thermally.

## Characterization of the diffusion process

### *Effective diffusion coefficient for adsorption in the liquid phase*

To fully understand the mechanism for the adsorption of the coloured impurities in caprolactam solution and to interpret the resulting adsorption process, it is important to identify the step governing the overall removal rate in the process. Many mathematical treatments relating to adsorption and diffusion have been reported, e.g. those of Boyd *et al.* (1947), Reichenberg (1953) and Helfferich (1962). These treatments provide a means of establishing the sorption/ion exchange kinetics involved by distinguishing the various steps controlled by film, particle diffusion and mass-action-controlled exchange mechanisms.

The present studies involved poor mixing conditions with a high affinity between the adsorbate and the adsorbent. Furthermore, the mass transmission resistance could not be neglected. For these various reasons, we have employed the following equations (DiGiano and Weber 1972) to obtain  $D_i$ , i.e. the effective diffusion coefficient of the coloured impurities in the aqueous phase:

$$\frac{f(\lambda)}{g(\lambda)} = -\frac{D_i}{K_f R} - \frac{3W}{\rho_s R^2} \cdot \frac{D_i}{g(\lambda)} \cdot t \quad (3)$$

$$f(\lambda) = \int_1^\lambda \frac{1}{\lambda} \left\{ \frac{1}{\left[ (\lambda - \lambda_e)/(1 - \lambda_e) \right]^{1/3}} - 1 \right\} d\lambda \quad (4)$$

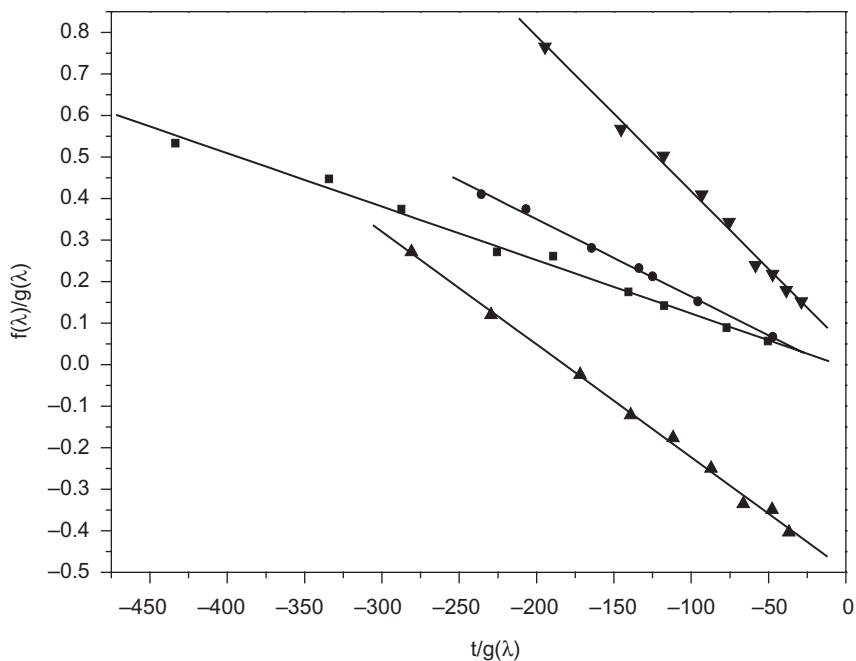
$$g(\lambda) = \ln \lambda \quad (5)$$

where  $\lambda = C_t/C_0$ ;  $\lambda_e = C_\infty/C_0$ ;  $K_f$  is the mass transmission coefficient;  $\rho_s$  is the apparent density of the activated carbon;  $W$  is the dosage of activated carbon employed;  $R$  is the radius of the activated carbon particles;  $t$  is the contact time;  $C_0$  is the initial concentration of the coloured impurities in the solution at time  $t = 0$ ;  $C_\infty$  is the (equilibrium) concentration of coloured impurities in the solution at time  $t = \infty$ ; and  $C_t$  is the concentration of coloured impurities in the solution at time  $t$ .

Equation (3) was deduced employing the following diffusion equation under various predetermined conditions:

$$D_i \left( \frac{\partial^2 C}{\partial r^2} + \frac{2}{r} \cdot \frac{\partial C}{\partial r} \right) = \frac{\partial C}{\partial t} \quad (6)$$

while values of  $D_i$  were calculated from the plots of  $f(\lambda)/g(\lambda)$  versus  $t/g(\lambda)$  (see Figure 3). The corresponding results are listed in Table 1. The data recorded in the table indicate that the values of  $D_i$  increased with increasing temperature. This result accords with the higher removal efficiency towards coloured impurities exhibited at higher temperatures. The reason of this improvement in colour removal efficiency may be attributed to the decrease in viscosity of the solution and the increase in the apparent rate of molecular motion at higher temperatures. The data in Table 1 and Figure 3 also show that at temperatures above 80°C the value of the intercept would become negative, thereby indicating that the mass transmission resistance in the intra-membrane was not negligible.



**Figure 3.** Plots of  $f(\lambda)/g(\lambda)$  versus  $t/g(\lambda)$  at (■) 35°C, (●) 45°C, (▲) 65°C and (▼) 80°C, respectively.

**TABLE 1.** Effective Diffusion Coefficient for Adsorption from the Liquid Phase at Different Temperatures

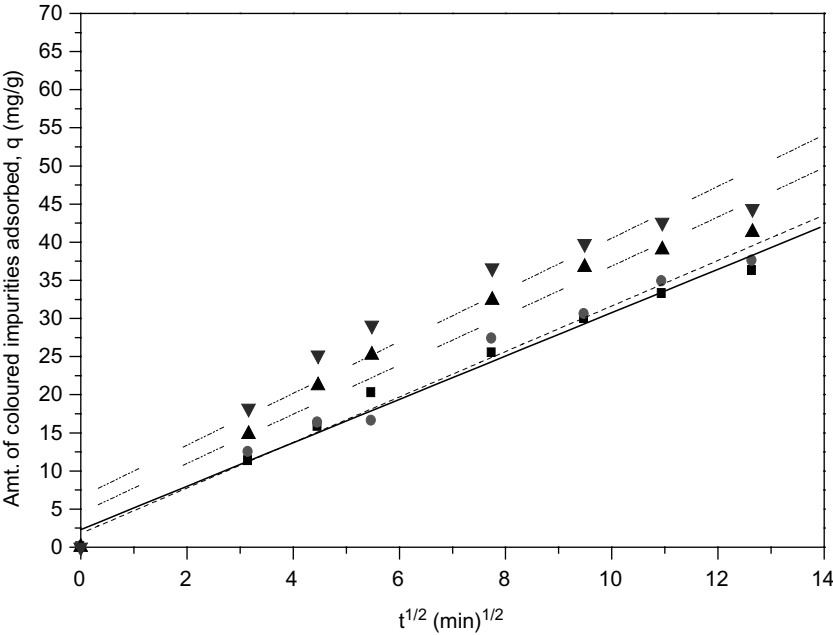
Quantity	Temperature (°C)			
	35	45	65	80
$D_i$ (cm <sup>2</sup> /s)	$1.35 \times 10^{-8}$	$1.93 \times 10^{-8}$	$2.82 \times 10^{-8}$	$3.89 \times 10^{-8}$
$-D_i/K_fR$	-0.0095	-0.0234	-0.4979	0.0410
$K_f$	$5.92 \times 10^{-5}$	$3.44 \times 10^{-5}$	$2.36 \times 10^{-6}$	< 0

Intra-particle diffusion model

The intra-particle diffusion may be evaluated from the rate constant ( $k_{id}$ ) deduced via the Weber and Morris equation which may be expressed as follows (Acemioğlu 2004):

$$q = k_{id}t^{1/2} + c \tag{7}$$

where  $q$  is the amount adsorbed (mg/g) at time  $t$  (min),  $k_{id}$  is the intra-particle diffusion rate constant [mg/(g min<sup>1/2</sup>)] and  $c$  is obtained when  $q$  is plotted versus  $t^{1/2}$  (see Figure 4). The value of  $c$  provides information regarding the boundary layer thickness, with the boundary layer effect being greater the greater the value of  $c$  (Dogan and Alkan 2003). The rate constant for intra-particle diffusion ( $k_{id}$ ) and the  $c$  value were calculated from the slope and intercept of the linear portions of the above plot as obtained at various temperatures. The results obtained in the present work are listed in Table 2.



**Figure 4.** Intra-particle diffusion plots for the removal of coloured impurities by activated carbon. The data points refer to the following experimental temperatures: ■, 35°C; ●, 45°C; ▲, 65°C; ▼, 80°C.

**TABLE 2.** Intra-particle Diffusion Model

Quantity	Temperature (°C)			
	35	45	65	80
$k_{id}$	2.84565	2.98481	3.23463	3.39295
$c$	2.30963	1.78367	4.51147	6.60629

It will be seen from this table that the value of  $k_{id}$  increased with the temperature, thereby indicating a higher rate of diffusion at higher temperatures. The initially curved portion of the plot reflects film or boundary layer diffusion while the subsequent linear portion arises from intra-particle diffusion. Although linear over a wide range of contact times, the plots do not pass through the origin. This indicates that the adsorption mechanism was fairly complex and included both film and intra-particle diffusion. The variation in  $c$  with temperature indicates that the boundary effect was greater at higher temperatures, thereby implying that surface adsorption is more likely to be the rate-limiting step at higher temperatures.

### Energy and entropy of activation

In a previous study, we have found that the batch adsorption kinetics for coloured impurities onto activated carbon follow the pseudo-second-order rate model. This allows the activation energy for the process to be calculated using the Arrhenius equation (Sarkar *et al.* 2003):

$$\ln k_{ad2} = \ln A - E_a/RT \quad (8)$$

where  $k_{ad2}$  is the rate constant of the pseudo-second-order process at a given temperature,  $T$  (K),  $E_a$  is the activation energy of adsorption and  $A$  is the pre-exponential factor. The magnitude of  $k_{ad2}$  can be calculated via the following equations:

$$\frac{dq}{dt} = k_{ad2}(q_e - q)^2 \quad (9)$$

$$\frac{t}{q} = \frac{1}{k_{ad2}q_e^2} + \frac{1}{q_e}t \quad (10)$$

The plot of  $t/q$  versus  $t$  should be linear with a slope of  $1/q_e$  and an intercept of  $1/k_{ad2}q_e^2$ . Similarly, the activation energy for diffusion and the entropy of activation,  $\Delta S^\#$ , may be obtained from the following equations (Mohan *et al.* 2001):

$$D_i = D_0 \exp\left(-\frac{E^\#}{RT}\right), \quad \ln D_i = \ln D_0 - \frac{E^\#}{RT} \quad (11)$$

$$D_0 = 2.72d^2 \left(\frac{kT}{h}\right) \exp\left(\frac{\Delta S^\#}{R}\right) \quad (12)$$

where  $D_0$  is also a pre-exponential factor analogous to the Arrhenius frequency factor;  $k$  is the Boltzmann constant;  $h$  is the Planck constant;  $R$  is the ideal gas constant; and  $d$  is the distance between two active sites of the adsorbent, which is conventionally taken to be  $5 \text{ \AA}$  in inorganic ion exchangers, minerals and other adsorbents similar to carbon. The values of  $A$ ,  $E_a$ ,  $D_0$ ,  $E^\#$  and  $\Delta S^\#$  for the diffusion and adsorption of coloured impurities onto or into activated carbon are listed in Table 3.

The data in the table show that the activation energy for adsorption was less than that for diffusion, i.e.  $18.81 \text{ kJ/mol}$  and  $20.51 \text{ kJ/mol}$ , respectively. This indicates that the whole adsorption



TABLE 3. Thermodynamic Parameters of Activation

Process	Equation	Parameters	Values
Adsorption	$\ln k_{ad2} = \ln A - E_a/RT$	A (min <sup>-1</sup> )	0.489
		E <sub>a</sub> (kJ/mol)	18.81
Diffusion	$D_i = D_0 \exp(-E^{\#}/RT)$	D <sub>0</sub> (m <sup>2</sup> /s)	4.22 × 10 <sup>-5</sup>
		E <sup>#</sup> (kJ/mol)	20.51
	$D_0 = 2.72d^2kT/h \exp(\Delta S^{\#}/R)$	ΔS <sup>#</sup> [J/(K mol)]	18.86 (35°C); 18.59 (45°C)
			18.09 (65°C); 17.73 (80°C)

process was diffusion-controlled. The positive values of ΔS<sup>#</sup> reflect a possible slight change in the internal structure of the activated carbon during the diffusion process — corresponding to an increase in the degrees of freedom of the adsorbed species. It should be noted that the results reported by other workers (Mohan *et al.* 2001; Rawat and Thind 1976; Rawat and Singh 1978; Varshney *et al.* 1984; Srivastava *et al.* 1996, 1997) were the reverse of those above, i.e. negative values of ΔS<sup>#</sup> were exhibited. This illustrates that positive ΔS<sup>#</sup> values are unusual in adsorption and ion-exchange processes, while negative ΔS<sup>#</sup> values are fairly common. Moreover, the low values of the activation energies for diffusion and adsorption indicate that a physical adsorption process occurred in the present studies.

Thermodynamic studies

Characterization and determination of thermodynamic properties

The adsorption of coloured impurities from the caprolactam solution onto activated carbon can be considered to be a reversible reaction involving an equilibrium between the liquid phase and solid phase:



where k<sub>a</sub> is the adsorption rate constant and k<sub>d</sub> is the desorption rate constant. If a is the initial concentration of coloured impurities and x is the amount transferred from the liquid phase to the solid phase at any time t, the rate may then be expressed as:

$$\frac{dx}{dt} = k_a(a - x) - k_d x$$

(14)

At equilibrium, k<sub>a</sub>(a - X<sub>e</sub>) - k<sub>d</sub>X<sub>e</sub> = 0, where X<sub>e</sub> represents the concentration of coloured impurities adsorbed at equilibrium and:

$$K_c = k_a/k_d = X_e/(a - X_e)$$

(15)

Here, K<sub>c</sub> is called the adsorption affinity. The thermodynamic parameters for the adsorption process, viz. the Gibbs energy (ΔG<sup>0</sup>), the adsorption enthalpy (ΔH<sup>0</sup>) and the adsorption entropy

**TABLE 4.** Thermodynamic Parameters at Different Temperatures and Different  $m_{AC}/m_{\text{caprolactam solution}}$  Ratios

Ratio of g AC/g caprolactam solution	Temp. (K)	$\Delta G^0$ (J/mol)	$\Delta H^0$ (J/mol)	$\Delta S^0$ [J/(K mol)]
0.01	308.15	$-3.05 \times 10^3$	$3.22 \times 10^3$	20.34
	318.15	$-3.26 \times 10^3$		
	338.15	$-3.66 \times 10^3$		
	353.15	$-3.96 \times 10^3$		
0.014	308.15	$-3.41 \times 10^3$	$3.61 \times 10^3$	22.78
	318.15	$-3.64 \times 10^3$		
	338.15	$-4.09 \times 10^3$		
	353.15	$-4.44 \times 10^3$		
0.025	308.15	$-4.23 \times 10^3$	$2.88 \times 10^3$	23.07
	318.15	$-4.46 \times 10^3$		
	338.15	$-4.92 \times 10^3$		
	353.15	$-5.26 \times 10^3$		

( $\Delta S^0$ ) may be determined from adsorption experiments conducted at different temperatures through the use of the following equations (Ferreira *et al.* 2004; Singh and Pant 2004):

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{16}$$

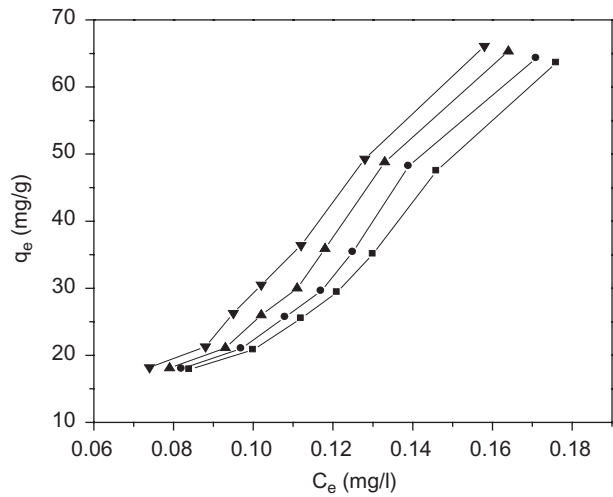
$$\ln K_c = \frac{-\Delta H^0}{RT} + \frac{\Delta S^0}{R} \tag{17}$$

The values of  $\Delta S^0$  and  $\Delta H^0$  were determined from the intercept and the slope of the linear plot of  $\ln K_c$  versus  $1/T$ , and these values were then used to calculate  $\Delta G^0$ . The results obtained are presented in Table 4. As is shown in the table, the negative value of  $\Delta G^0$  confirms the feasibility of the process and the spontaneous nature of adsorption. The fact that the values of  $\Delta G^0$  diminish with increasing temperature also explains why the adsorption is endothermic. At various dosages of activated carbon, the values of  $\Delta H^0$  were 3.22 kJ/mol, 3.61 kJ/mol and 2.88 kJ/mol, respectively, indicating that the adsorption process was physical in nature. In addition, the positive value of  $\Delta H^0$  demonstrated the endothermic nature of the process, while the positive value of  $\Delta S^0$  confirms the increase in the number of degrees of freedom of the adsorbed species.

**Isosteric heat of adsorption**

Using the Clausius–Clapeyron equation in conjunction with the adsorption isotherms depicted in Figure 5, it is possible to obtain the isosteric heat of adsorption, i.e.:

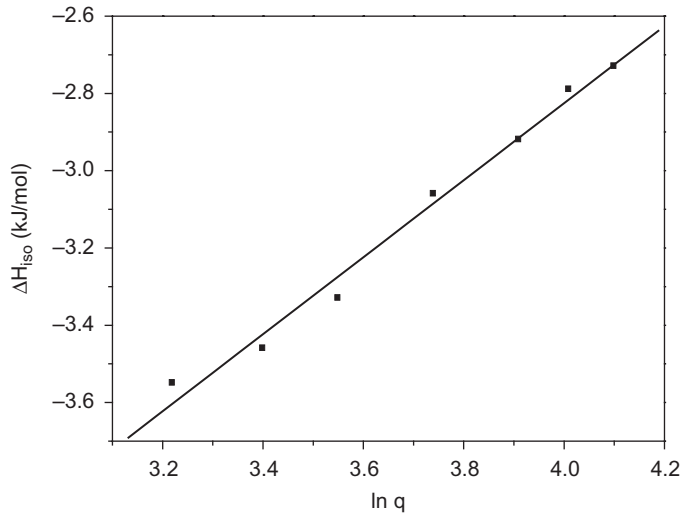
$$\Delta H_{\text{iso}} = RT^2 \left( \frac{\partial \ln C}{\partial T} \right)_q = -R \left( \frac{\partial \ln C}{\partial (1/T)} \right)_q \tag{18}$$



**Figure 5.** Adsorption isotherms for coloured impurities in caprolactam solution onto activated carbon at (■) 35°C, (●) 45°C, (▲) 65°C and (▼) 80°C, respectively.

**TABLE 5.** Isosteric Heats,  $\Delta H_{\text{iso}}$ , at Different Adsorption Capacities,  $q$

$q$	25.10	30.05	34.97	41.83	50.11	55.02	60.14
$\Delta H_{\text{iso}}$ (kJ/mol)	-3.55	-3.46	-3.33	-3.06	-2.92	-2.79	-2.73



**Figure 6.** Plot of isosteric heat of adsorption of the coloured impurities in caprolactam onto activated carbon versus the corresponding adsorption capacity.

The corresponding results are listed in Table 5 and show that  $\Delta H_{\text{iso}}$  increased with increasing adsorption. Furthermore, from the plot depicted in Figure 6, it is seen that the value of  $\Delta H_{\text{iso}}$  changed in a linear fashion when plotted against  $\ln q$ .

Suzuki has pointed out that when the surface of the adsorbent is inhomogeneous it is not possible to neglect the interaction between the adsorbent molecules, with the consequent change in the heat of adsorption with the surface coverage of the carbon. The results obtained in the present study indicate that the surface energy of the activated carbon studied was quite inhomogeneous. This is reflected in the fact that increasing amounts of adsorption, i.e. incremental coverage of the carbon surface, led to a corresponding decrease in the isosteric heat of adsorption.

## CONCLUSIONS

A detailed experimental and theoretical analysis of the mass transfer and thermodynamics of the sorption of coloured impurities onto activated carbons has been undertaken in the present work. On the basis of this study, it is possible to arrive at the following conclusions:

1. The calculated values of  $D_i$  were found to lie in the range  $1.35 \times 10^{-8}$  to  $3.89 \times 10^{-8}$   $\text{cm}^2/\text{s}$  over the temperature range 35–80°C. This tendency illustrates the importance of temperature in the removal of coloured impurities from caprolactam solutions with a higher efficiency being exhibited at higher temperatures.

The larger values of  $k_{\text{id}}$  observed at higher temperatures reflected the higher rate of diffusion. The initial curvature of the plot of  $q$  versus  $t^{1/2}$  and its subsequent linearity reflected the effects of film or boundary layer diffusion and intra-particle diffusion, respectively. The fact that the plots did not pass through the origin demonstrated that the adsorption mechanism was fairly complex. The intercept of the plot increased with increasing temperature and implied that surface adsorption was more likely to be the rate-limiting step at higher temperatures.

The relative values of 18.81 kJ/mol and 20.51 kJ/mol for the adsorption and diffusion activation energies indicate that the overall adsorption process was diffusion-controlled. The positive values of  $\Delta S^\ddagger$  reflect the slight change which occurs in the internal structure of the activated carbon during the diffusion process; this accords with the increase in the number of degrees of freedom of the adsorbed species. The low values of both types of activation energy indicate that the adsorption process was physical in nature.

2. Various thermodynamic parameters such as  $\Delta G^0$ ,  $\Delta H^0$  and  $\Delta S^0$  were also evaluated. The negative value for  $\Delta G^0$  confirmed the feasibility of the process and the spontaneous nature of adsorption. The positive value for  $\Delta H^0$  demonstrated the endothermic nature of the process while the positive value for  $\Delta S^0$  accorded with an increase in the number of degrees of freedom of the adsorbed species.
3. The value of  $\Delta H_{\text{iso}}$  increased as the extent of adsorption increased and demonstrated a linear change when plotted versus  $\ln q$ . The results obtained show that the surface energy of the activated carbon studied was quite inhomogeneous. As the amounts adsorbed on the surface increased, i.e. as the extent of surface coverage increased, the isosteric heat of adsorption exhibited a tendency to decrease.

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