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Effect of temperature, particle size and percentage deacetylation on the adsorption of acid dyes on chitosan

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Abstract The adsorption of five acidic dyes on chitosan—a by-product from waste crustacean shell—has been studied. The equilibrium data have been studied using Langmuir, Freundlich and Redlich-Peterson equations. The best correlations are obtained using the Langmuir isotherm suggesting the mechanism involves one process step of dyes complexing with the free amino group. The effect of chitosan particle size was investigated and showed an increase in adsorption capacity with decreasing particle size indicating that the available external surface was an important factor. Increasing solution temperature resulted in an increase in adsorption capacity indicating an exothermic process with a negative ΔH. Finally, the effect of varying the percentage degree of deacetylation showed that from 52% to 97% resulted in decrease in the dye adsorption capacity suggesting that more amorphisation may cause changes in the internal structure of chitosan and reduce the capacity.

Keywords Acid dyes · Chitosan · Equilibrium · Temperature · Particle size · Deacetylation

1 Introduction

In the textile sector, an estimated 10–20% of dyes (active substance) used is lost in residual liquors through exhaustion and washing operations. For pigments, the rate of loss is about 1–2%, and 10% for paper and leather dyes. All of these, make up to a total of about 30% out of 1.0 billion kg dye consumption as reported in 1994 (Marc 1996). However, available effluent treatment processes for dye containing effluents are currently capable of removing about half the dyes lost in residual liquors. Therefore, about 400 tonnes daily, finds its way into the environment, primarily dissolved or suspended in water.

A range of conventional treatment technologies for dye removal has been investigated extensively (Chu and Tsui 1999; Ganesh et al. 1994; Lin and Lin 1993; Vandevivere et al. 1998; Walker and Weatherley 1997) such as the trickling filter, activated sludge, chemical coagulation, carbon adsorption and photodegradation processes. Adsorption can handle fairly large flowrates, producing a high quality effluent and does not result in the formation of harmful substances, such as ozone and free radicals during the photodegradation process using UV. Therefore, the aim of this research is to study the removal of colour from effluents using adsorption techniques. In recent years, there has been significant research using cheap or waste materials as adsorbents for effluent treatment (McKay 1995). Chitosan, a waste by-product from crab shells had been used in the present research.

Sorption of various dyestuffs onto the chitin and chitosan reported previously demonstrated that the sorption capacities are effected by system parameters such as pH, particle size of sorbent and sorbates, temperature, and initial concentration of sorbate.

Previous investigations showed that the system pH was one of the prime factors influencing the adsorption of textile dyestuffs on chitin and chitosan. Yoshida et al. (1991) demonstrated a feasible technology for the recovery of acid (Acid Orange II) and direct (Brilliant Yellow) dye by using Chitosan Fiber (ChF) and the treatment performance

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was excellent at pH 6.9. Stefancich et al. (1994) reported that no interaction was observed between cationic dyes (Neocuproin hydrochloride, Ethidium bromide, Ruthenium Red, 1-(2-pyridilazo)-2-napthhol) and chitosan in the pH range of 5–6. Smith et al. (1993) and Shimizu et al. (1995) showed that sorption of anionic dyes onto chitosan were related to the protonation of the chitosan's free amino groups at low pH. According to Knorr (1983) and Ravi Kumar et al. (1998), the dye binding capacity of chitin was stable within a pH range of 2.0–7.0.

McKay et al. (1982) and Annadurai et al. (1997) observed the amount of dyestuffs adsorbed by chitin and chitosan was strongly affected by the particle size of the absorbent. The amount of dye adsorbed increased with decreasing particle size due to the inability of the large dye molecule to penetrate into the internal pore structure of chitin and chitosan. This phenomenon was further proved by Smith et al. (1993). Annadurai et al. (1997) concluded that specific dye uptake of reactive dye (Verofix Red) and basic dye (Methylene Blue) at equilibrium increased by about 10–40% with different particle size ranges.

Dye concentration has been shown to significantly affect the dye-binding capacity of chitin and chitosan performed by Knorr (1983) and Ravi Kumar et al. (1998). The treatment performance showed that the dye-binding capacity of chitosan was 25–30% greater than chitin at the same initial dye concentration level. Besides, they also found that increase dosage of chitin or chitosan, i.e. four times, to the system would decrease in the dye-binding capacity about 50%. The dye-binding capacity of chitin and chitosan was being enhanced about 25 and 9 times, respectively, if the initial dye concentration increases from 0.2 mg/g of chitin to 1.6 mg/g of chitin. According to McKay et al. (1982), the film mass transfer coefficients appeared to be independent of initial dye concentration for the adsorption of Mordant Yellow 5 on chitin because there was no apparent difference in the initial gradients. However, the rate of adsorption at the lower initial dye concentration was about 20–50% higher than the rate at the high initial dye concentration. The adsorption of Chitosan Fiber on Acid Orange II and Brilliant Yellow using a column study showed that the amount of the dye adsorbed increased with increase in initial dye concentration due to the increase of the intrafiber effective diffusivity with concentration was reported by Yoshida et al. (1991, 1993, 1997). Safarik (1995) showed that the adsorption of organic polycyclic molecules (Acridine Orange, Congo Red, Safranin O, Neutral Red and Crystal Violet) was a chemical, equilibrated and saturatable mechanism, and therefore adsorption increased with the initial dye concentration, as long as binding sites were not saturated. (Venkatrao et al. 1986) pointed out that the time required to reach equilibrium increased considerably as the initial dye concentration increased for the adsorption of Direct Red 31; no such trend was evident in the adsorption of Reactive Red 73.

In this research, the ability of chitosan to remove acid dyes namely, Acid Green 25 (AG25), Acid Orange 10 (AO10), Acid Orange 12 (AO12), Acid Red 18 (AR18) and Acid Red 73 (AR73) by adsorption, has been studied. The sorption capacities of dyes on chitosan have been investigated using the adsorption isotherm technique. The effects of dye temperature, chitosan particle size and the percentage deacetylation have been studied.

2 Materials and methods

2.1 Materials

2.1.1 Adsorbent

The adsorbent used in this research is a powdered form of chitin purchased from Sigma Chemical Company. This chitin is described by the supplier as a practical graded material extracted from crab shells. All raw chitin was dried at 75 °C in an oven for 6 hours and then was sieved into discrete particle size range from 355–500 µm.

2.1.2 Adsorbate

Five different commercial available textile dyestuffs were used in the study including four azo dyes (AO10, AO12, AR18 and AR73) and one anthraquinone dye (AG25). Those selected dyestuffs are commonly used in dye house nowadays and regarded as dye contaminants in the discharged effluent. All dyestuffs were purchased from Aldrich Chemical Co. and used without any further purification process. The characteristics and chemical structures of the selected dyestuffs are listed in Table 1 and Fig. 1, respectively.

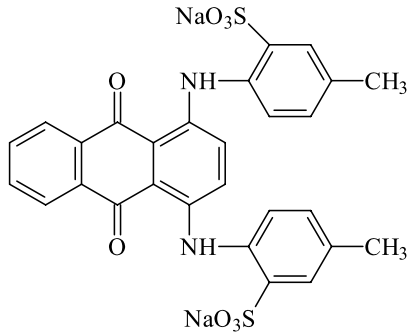
2.2 Methods

2.2.1 Preparation of chitosan

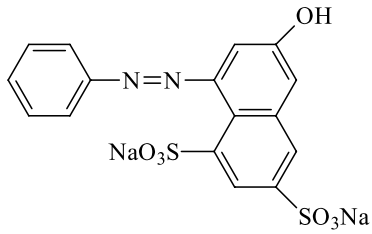
The sieved chitin was deacetylated to chitosan with different degree of deacetylation (DD) by using 48% sodium hydroxide solution (w/w) at 100 °C under nitrogen atmosphere for 1-hour periods. Then, the products were washed with deionized water completely, dried at 70 °C in an oven overnight and sieved again into several particle size ranges from 125–250, 250–355 and 355–500 µm. The fractions were further dried in vacuum oven for one day and stored in a desiccator. The degree of deacetylation of different chitosans characterized by ^{1}H-NMR method is summarized in Table 2.

Table 1 The physical and chemical characteristics of selected dyestuffs

Generic Name	Abbrev.	Commercial name	Purity (%)	Chromophore	F.W.	λ_{max} (nm)
C.I. Acid Green 25	AG25	Acid Green 25	75	Anthraquinone	622.6	642
C.I. Acid Orange 10	AG10	Orange G	80	Monoazo	452.4	475
C.I. Acid Orange 12	AO12	Crocein Orange G	70	Monoazo	350.3	482
C.I.AcidRed l8	AR18	New Coccine	75	Monoazo	604.5	506
C.I. Acid Red 73	AR73	Brilliant Crocein MOO	70	Diazo	566.5	510



C. I. Acid Green 25 (AG25)



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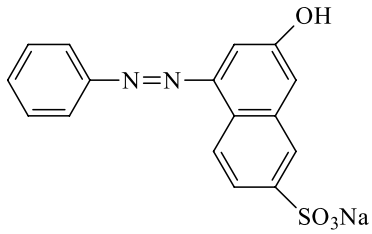

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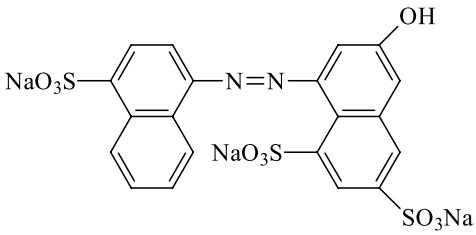
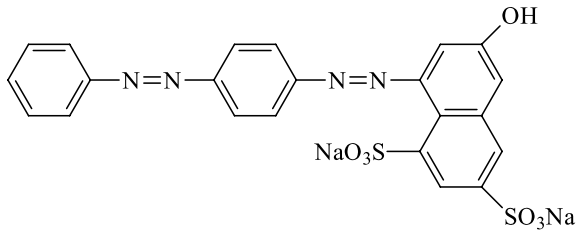


C. I. Acid Red 18 (AR18)



C. I. Acid Red 73 (AR73)

Fig. 1 The molecular structures of the five selected dyestuffs

Table 2 Preparation of chitosan with different degree of deacetylation (DD)

Treatment time, hour	Degree of deacetylation (%)
1	53
2	72
3	87
4	95

2.2.2 Concentration measurement and calibration

In order to calculate the concentration of the sample from each experiment, a calibration curve of each dye was first prepared. For each dye, five different concentrations were prepared and the absorbance was measured using a Perkin-Elmer UV/VIS Spectrophotometer Lambda 18 over a range from 400–700 nm. The calibration checks were carried out in duplicate. Then, the maximum absorbance of each dye was plotted with concentrations. From these results, the concentrations of the dye samples can be calculated with the following equations and constants for calculations which are

Table 3 Constants for calculations of dye concentrations of selected dyes

Name of dye	Constant, k
Acid Green 25 (AG25)	16.650
Acid Orange 10 (AO10)	22.019
Acid Orange 12 (AO12)	23.098
Acid Red 18 (AR18)	25.928
Acid Red 73 (AR73)	40.907

summarized in Table 3.

AG25: Dye Concentration (mmol/L) $= \text{Maximum Absorbance}/k_{AG25}$, (1)

AO10: Dye Concentration (mmol/L) $= \text{Maximum Absorbance}/k_{AO10}$, (2)

AO12: Dye Concentration (mmol/L) $= \text{Maximum Absorbance}/k_{AO12}$, (3)

AR18: Dye Concentration (mmol/L) $= \text{Maximum Absorbance}/k_{AR18}$, (4)

AR73: Dye Concentration (mmol/L) $= \text{Maximum Absorbance}/k_{AR73}$. (5)

2.2.3 *Equilibrium sorption studies*

A fixed mass of chitosan (0.200 g) was weighed into 120 ml conical flasks and brought into contact with 100 ml of dye solutions with predetermined initial dye concentrations. The initial pH of the solutions was adjusted to 4.00 ± 0.1 by the addition of 20% in volume of citric acid buffer, made up of citric acid and sodium hydroxide. The flasks were sealed and agitated for 24 hours at 200 rpm in the thermostatic shaker bath and maintained at a temperature of 25 ± 1 °C until equilibrium was reached. At time $t = 0$ and equilibrium, the dye concentrations of the solutions were measured by UV-VIS Spectrometer. These data were used to calculate the adsorption capacity, q_e, of the adsorbent. Finally, adsorption capacity, q_e, against equilibrium concentration, C_e, was plotted.

The same procedure was employed for the equilibrium sorption studies of chitosan with different degree of deacetylation (DD=53%, 72% and 95%) and various system temperatures (40 °C, 60 °C and 80 °C).

2.2.4 *Calculation of dye concentration of isotherm studies*

The dye concentration at equilibrium, q_e, was calculated from:

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{6}$$

where q_e = dye concentration in sorbent at equilibrium, C_0 = initial dye concentration in liquid phase, C_e = liquid phase dye concentration at equilibrium, V = total volume of dye solution used, M = mass of sorbent used.

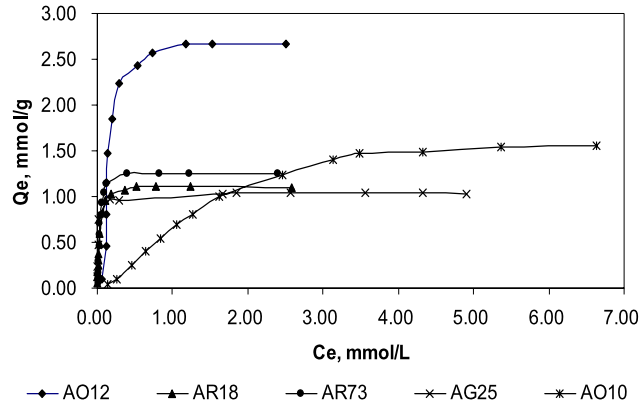


Fig. 2 Sorption of acid dyes onto chitosan at temp. = 25 °C, degree of deacetylation (DD) = 53%, pH = 4.00, dp = 355–500 µm

3 Results and discussion

The correlation of equilibrium data by either theoretical or empirical equations is essential to the practical design and operation of adsorption systems. In order to optimize the design of a sorption system to remove dyes from effluents, it is important to establish the most appropriate correlation for the equilibrium curves. In the present studies, the experimental data of five dye-chitosan equilibrium isotherms, which were the sorption of Acid Green 25 (AG25), Acid Orange 10 AO10), Acid Orange (AO12), Acid Red 18 (AR18) and Acid Red 73 (AR73) as shown in Fig. 2 were compared using three isotherm equations namely, Langmuir, Freundlich and Redlich-Peterson (R-P).

3.1 Langmuir isotherm

Langmuir (1918) proposed a theory to describe the adsorption of gas molecules onto metal surfaces. The Langmuir adsorption isotherm has found successful application to many other real sorption processes of monolayer adsorption. Langmuir's model predicts the existence of monolayer coverage of the adsorbate at the outer surface of the adsorbent. The isotherm equation further assumes that adsorption takes place at specific homogeneous sites within the adsorbent. Moreover, the Langmuir equation is based on the assumption of a structurally homogeneous adsorbent where all sorption sites are identical and energetically equivalent. Theoretically, the sorbent has a finite capacity for the sorbate can be represented by the expression:

$$q_e = \frac{K_L C_e}{1 + a_L C_e} \tag{7}$$

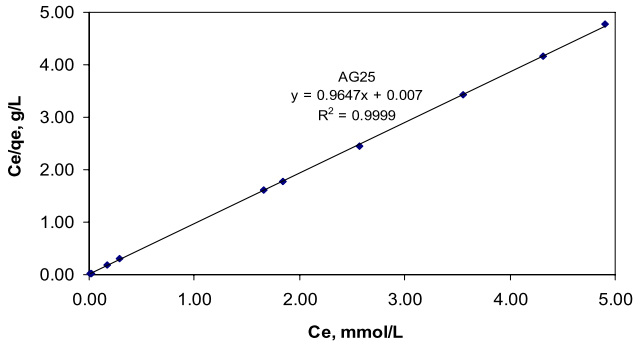


Fig. 3 Langmuir isotherm linear plots for the sorption of Acid Green 25 onto chitosan at temp. = 25 °C, degree of deacetylation (DD) = 53%, pH = 4.00, dp = 355–500 µm

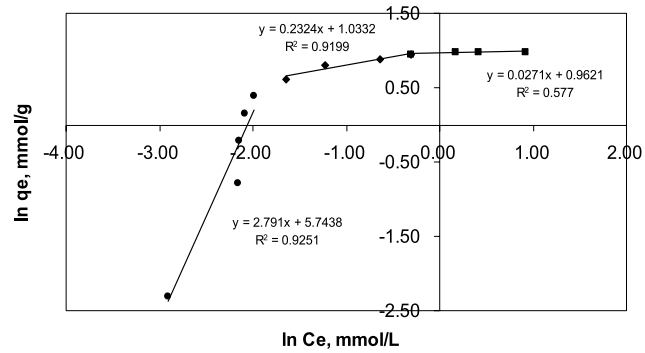


Fig. 4 Freundlich isotherm linear plots for the sorption of Acid Orange 12 onto chitosan at temperature = 25 °C, degree of deacetylation (DD) = 53%, pH = 4.00, dp = 355–500 µm

Table 4 Langmuir sorption isotherm constants for AG25, AO10, AO12, AR 18 and AR73

Dye	K_L (dm^3/g)	a_L (dm^3/mmol)	Q_0(mg dye/g)	R^2
AG25	175.4	169.3	645.1	0.9999
AO10	1.183	0.580	922.9	0.9812
AO12	33.90	12.20	973.3	0.9999
AR18	39.84	34.75	693.2	0.9997
AR73	53.48	41.60	728.2	0.9996

where q_e is solid phase sorbate concentration at equilibrium (mg/g), C_e is aqueous phase sorbate concentration at equilibrium (mg/dm^3), K_L is Langmuir isotherm constant (dm^3/g), a_L is Langmuir isotherm constant (dm^3/mg). Rearranging (7) gives a linear expression:

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a_L}{K_L} C_e. \tag{8}$$

Therefore, a plot of C_e/q_e versus C_e gives a straight line of slope a_L/K_L and intercept $1/K_L$, where K_L/a_L gives the theoretical monolayer saturation capacity, Q_0.

The sorption data were analyzed according to the linear form (8) of the Langmuir isotherm. The plots of specific sorption C_e/q_e against the equilibrium concentration, C_e for Acid Green 25 (AG25) is shown in Fig. 3. The isotherms of AO10, AO12, AG25, AR18 and AR73 were found to be linear over the whole concentration range studies and the correlation coefficients were extremely high as shown in Table 4. These values of the correlation coefficients strongly support the fact that the dyes-chitosan sorption data closely follow the Langmuir model of sorption. The isotherm constants, a_L, K_L and equilibrium monolayer capacities, Q_0 are presented in Table 4. The Langmuir monolayer capacity, Q_0, represents the saturation capacity of acid dyes of AO10, AO12, AG25, AR18 and AR73 and these values are 929.9, 973.3, 645.1, 693.2 and 728.2 mg/g respectively. Table 4 and the plot in Fig. 3 demonstrate that the Langmuir equation provides an accurate description of the experimental data, which is further confirmed by the extremely high values of the correlation coefficient.

3.2 Freundlich isotherm

The Freundlich (1906) equation is an empirical equation employed to describe heterogeneous systems, in which it is characterized by the heterogeneity factor $1/n$. Hence, the empirical equation can be written:

$$q_e = K_F C_e^{\frac{1}{n}} \tag{9}$$

where q_e is solid phase sorbate concentration in equilibrium (mg/g), C_e is liquid phase sorbate concentration in equilibrium (mg/dm^3), K_F is Freundlich constant (dm^3/g) and $1/n$ is the heterogeneity factor. A linear form of the Freundlich expression can be obtained by taking logarithms of (9).

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e. \tag{10}$$

Therefore, a plot of $\ln q_e$ versus $\ln C_e$ enables the constant K_F and exponent $1/n$ to be determined. It describes reversible adsorption and is not restricted to the formation of the monolayer.

By plotting the linear transformation of the Freundlich equation, Fig. 4 shows the logarithmic plots of the Freundlich expression for the selected acid dye, AO12. The figure exhibits deviation from linearity on the Freundlich linear plot for the whole concentration range. However, if the whole concentration range is divided into regions, i.e. region 1, region 2, and region 3, excellent fits to the experimental data can be observed, especially at the lower concentration regions 1 and 2. Region 3 does not fit the Freundlich equation well. Table 5 shows the Freundlich sorption isotherm constants, b_F and K_F, and the correlation coefficients, R^2 for the different concentration regions.

Table 5 Freundlich sorption isotherm constants for AG25, AO10, AO12, AR18 and AR73 at different concentration ranges

Dye	Region	b_F	K_F (dm^3/mg$^{1-1/n}$/g)	R^2	R^2 for single line
AG25	(1)	2.4818	41606	0.9681	
	(2)	0.0715	1.0299	0.8508	0.7503
	(3)	0.0272	1.0046	0.7352	
AO10	(1)	1.3200	0.6510	0.9960	
	(2)	0.5170	0.7755	0.9995	0.8201
	(3)	0.1105	1.2667	0.9011	
AO12	(1)	0.2791	312.25	0.9251	
	(2)	0.2324	2.8100	0.9199	0.5321
	(3)	0.0270	2.6172	0.5770	
AR18	(1)	1.0870	35.784	0.9957	
	(2)	0.4305	2.5053	0.9920	0.7632
	(3)	0.0455	1.1194	0.7874	
AR73	(1)	2.6293	6125.4	0.9886	
	(2)	0.4333	3.0328	0.9622	0.6821
	(3)	0.0298	1.2471	0.6627	

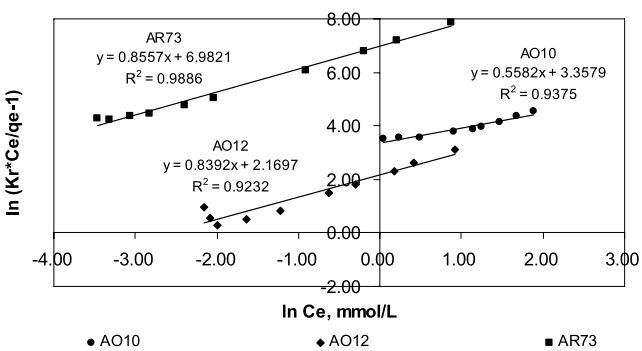


Fig. 5 Redlich-Peterson isotherm linear plots for the sorption of AO10, AO12 and AR73 onto chitosan at temperature = 25 °C, degree of deacetylation (DD) = 53%, pH = 4.00, dp = 355–500 µm

3.3 Redlich-Peterson isotherm

Redlich and Peterson (1959), incorporate three parameters into an empirical isotherm. The Redlich-Peterson isotherm model combines elements from both the Langmuir and Freundlich equation and the mechanism of adsorption is a hybrid one and does not follow ideal monolayer adsorption.

$$q_e = \frac{K_R C_e}{1 + a_R C_e^{\beta}} \tag{11}$$

where q_e is solid phase sorbate concentration in equilibrium (mg/g), C_e is liquid phase sorbate concentration in equilibrium (mg/dm^3), K_R is Redlich-Peterson isotherm constant (dm^3/g), a_R is Redlich-Peterson isotherm constant (dm^3/mg) and β is the exponent which lies between 1 and 0.

Equation (11) can be rearranged as follows:

$$K_R \frac{C_e}{q_e} - 1 = a_R C_e^{\beta}. \tag{12}$$

Table 6 Redlich-Peterson sorption isotherm constants for AG25, AO10, AO12, AR18 and AR73

Dye	β	K_R (dm^3/g)	a_R (dm^3/mg$^{1-1/\beta}$)	R^2
AG25	0.9963	101.8	98.54	0.9992
AO10	0.6081	22.44	26.48	0.9375
AO12	0.9018	25.27	8.220	0.9232
AR18	0.9816	38.03	32.10	0.9944
AR73	0.9074	1378	1119	0.9886

This equation can be converted to a linear form by taking logarithms:

$$\ln\left(K_R \frac{C_e}{q_e} - 1\right) = \ln a_R + \beta \ln C_e. \tag{13}$$

Plotting the left-hand side of (13) against $\ln C_e$ to obtain the isotherm constants is not applicable because of the three unknowns, a_R, K_R and β. Therefore, a minimization procedure is adopted to solve (13) by maximizing the correlation coefficient between the theoretical data for q_e predicted from (13) and experimental data.

The linearized form of the Redlich-Peterson isotherm plots for the sorption of the three dyes, namely, AO10, AO12 and AR73, onto chitosan are presented in Fig. 5. Examination of the data shows that the Redlich-Peterson model describes the sorption of AG25, AR18 and AR73 on chitosan extremely well over the concentration ranges studied and gives moderate fits for AO10 and AO12. The Redlich-Peterson isotherm constants a_R, K_R and β and the correlation coefficients, R^2, for the Redlich-Peterson isotherm are listed in Table 6.

By comparing the results presented in Tables 4 to 6, the Langmuir sorption was found to provide the best prediction

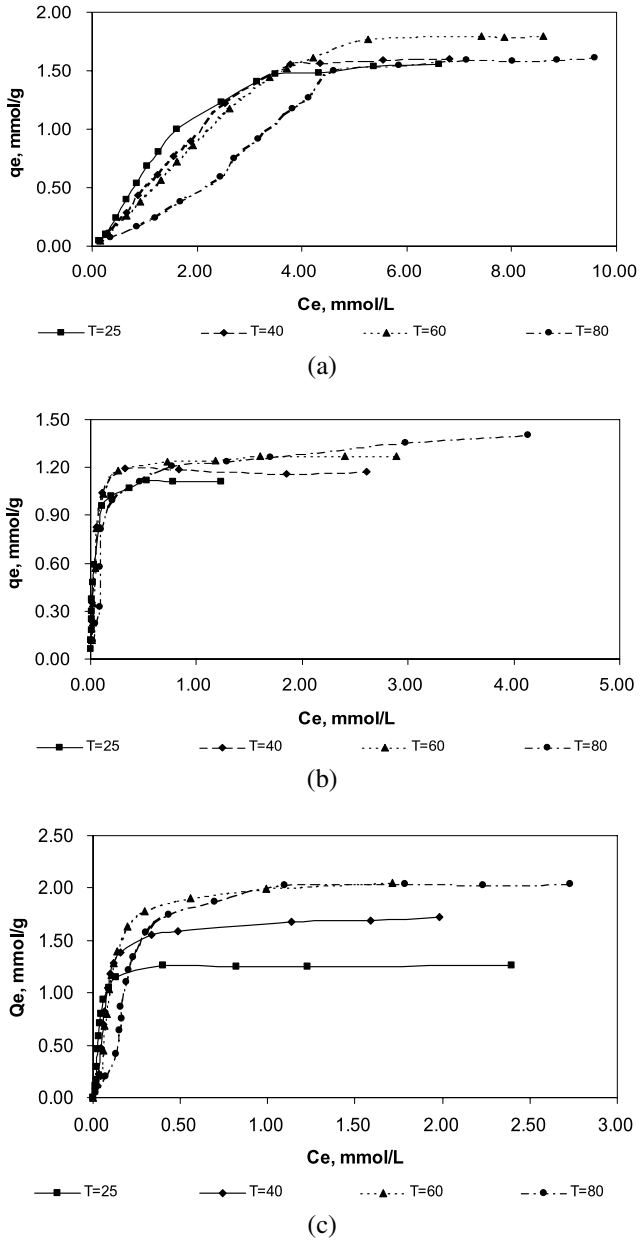


Fig. 6 **a** Sorption of Acid Orange 10 onto chitosan at different temperature, degree of deacetylation (DD) = 53%, pH = 4.00, dp = 355–500 µm. **b** Sorption of Acid Red 18 onto chitosan at different temperature, degree of deacetylation (DD) = 53%, pH = 4.00, dp = 355–500 µm. **c** Sorption of Acid Red 73 onto chitosan at different temperature, degree of deacetylation (DD) = 53%, pH = 4.00, dp = 355–500 µm

for the sorption of all five acid dyes for the entire concentration ranges.

3.4 Effect of temperature

The effect of temperature on the adsorption of Acid Orange 10, Acid Red 18, and Acid Red 73 is shown in Figs. 6a to c, respectively. The results show that the adsorption capacities increase with increasing temperature from 25 °C to 60 °C. This phenomenon is quite common and is due to the fact that increasing temperature not only increases the mobility of the large dye ions, but may also produce a swelling effect within the internal structure of the chitosan. Besides, higher temperature enables the large dye molecules to penetrate further and a similar result was reported previously by McKay et al. (1982), for the adsorption of dyes on chitin. Further increase in the temperature from 60 °C to 80 °C has little or no influence on its ability to adsorb Acid Red 73, but the adsorption capacity of Acid Red 18 increases its maximum at 80 °C. Furthermore, Figs. 6a to c also indicate that the amount of adsorbed dyes on chitosan decreases with an increase in temperature at lower initial concentration levels and is caused by the increase in desorption step when the temperature increases (McKay et al. 1982). A similar finding was reported previously by Yoshida et al. (1991). The results of the Langmuir analysis are presented in Table 7.

Table 7 Langmuir sorption isotherm constants for AO12, AR18 and AR73 at various temperatures with degree of deacetylation (DD) = 53%, pH = 4.0, dp = 355–500 µm

Dye		Temperature			
		25 °C	40 °C	60 °C	80 °C
AO12	K_L (dm^3/g)	33.90	31.23	21.65	12.59
	a_L (dm^3/mmol)	12.20	10.53	5.974	3.418
	Q_0 (mg dye/g)	973.3	1039	1269	1291
	R^2	0.9990	0.9982	0.9923	0.9957
AR18	K_L (dm^3/g)	39.84	48.78	24.04	6.622
	a_L (dm^3/mmol)	34.75	41.22	18.46	5.251
	Q_0 (mg dye/g)	693.2	715.3	787.0	877.5
	R^2	0.9997	0.9997	0.9996	0.9966
AR73	K_L (dm^3/g)	53.48	29.58	25.06	16.86
	a_L (dm^3/mmol)	41.60	16.87	11.60	7.820
	Q_0 (mg dye/g)	728.2	1002	1223	1222
	R^2	0.9998	0.9995	0.9986	0.9987

The change in the enthalpy of adsorption, ΔH_{ads}, can be obtained from the van 't Hoff equation:

$$d \ln K_L = \left(\frac{-\Delta H_{\text{ads}}}{R}\right) d\left(\frac{1}{T}\right) \tag{14}$$

where R is the gas constant and T is temperature in K. From (14), a plot of $\ln K_L$ against $1/T$ has a slope of $-\Delta H_{\text{ads}}/R$ as shown in Fig. 7. Table 8 shows the ΔH_{ads} values for the dyes, AO12, AR18 and AR73. All three dyes have negative values of ΔH_{ads} indicates that the adsorption reaction is an exothermic and adsorption enthalpy-controlled reaction.

3.5 Effect of particle size (dp)

The influence of adsorbent particle size for AG25 and AR73 is shown in Figs. 8a and b indicating that chitosan par-

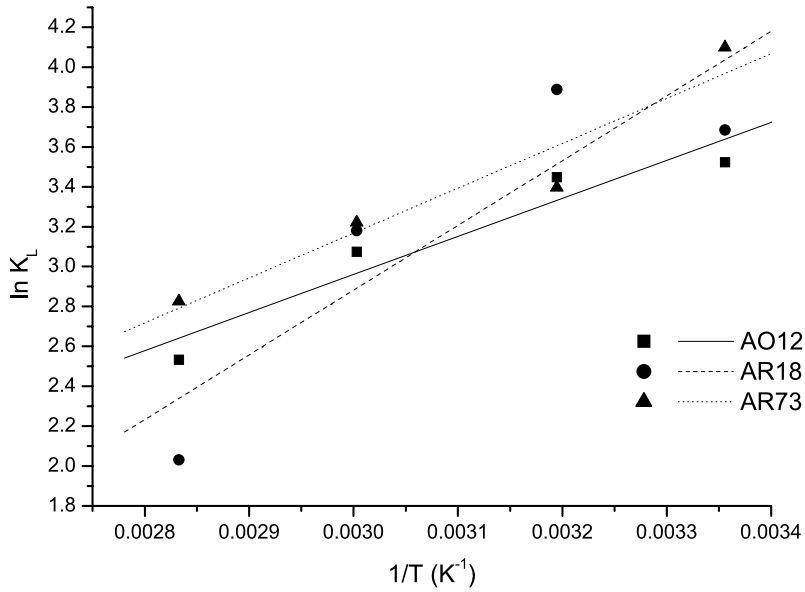


Fig. 7 Plot of van 't Hoff equation ($\ln K_L$ vs $1/T$) for AO12, AR18 and AR73

Table 8 The adsorption enthalpy, ΔH_{ads}, for AO12, AR18 and AR73

Dye	Adsorption enthalpy, ΔH_{ads}
AO12	−15.85
AR18	−26.98
AR73	−18.70

ticle size strongly affected the amount of acid dye being absorbed. The amount of dye adsorbed increased with decreasing particle size due to the inability of the large dye molecules to penetrate into the internal pore structure of chitosan and a similar phenomenon was reported previously Shimizu et al. (1995) and Annadurai et al. (1997). Annadurai and Krishnan (1997) also showed that the specific dye uptake at equilibrium increased owing to the increase in total surface area made available for adsorption that was proved by the increase in the specific BET surface areas in the smaller particle sizes. In another study published by Carlough et al. (1991), their results indicated that decreasing particle size would increase the driving force of a reactive dye from the bulk phase onto and into the solid chitosan, thus increasing the initial adsorption rate and the final equilibrium capacity. If the dye molecules attach themselves to the external surface of the chitosan particles and only some of the larger internal pores, this result would be expected as in the case of present study.

3.6 Effect of degree of deacetylation (DD%)

The effect of degree of deacetylation (DD) on the adsorption of acid dyes, AO12 and AR73 onto chitin and chitosan was presented at Figs. 9a and b. An interesting trend can be observed from Fig. 9. The deacetylated chitin has a higher dye adsorption capacity than chitin. Deacetylation of chitin increases the formation of primary amino groups on the surface. It was found that the amount of amino groups in chitosan (DD = 65%) approximately nine times more than that of chitin (Shimizu et al. 1995). McKay et al. (1982) reported that sorption of dye anions on chitin and chitosan could be attributed to many different interactions between the sorbate and sorbent molecules, namely, ionic bonding ability, hydrophobic interaction due to planarity and other geometric configurations of the dye molecules, chelating ability of the chitin-dye and chitosan-dye system through coordinating bonding in premetallized dyes and hydrogen bonding. The significant increases in sorption capacities of three chitosans were mainly due to an increase in amino groups of the sorbent and low pH of the system, which facilitate ionic bonding between the protonated amino groups of chitosan and dye anions.

However, the adsorption process of dyes onto chitosan decreases with increasing degree of deacetylation. The number and the size of crystalline regions in the chitin structure decrease with the increasing in the degree of deacetylation making it more amorphous (Burkhanova et al. 2000). The degree of crystalline reduces as the degree of acetylation increases resulting an increase in the number of defects in the chitin structure, weakens the intermolecular H-bonds and eliminates the fibrillarity. With the changes in the chitin structure, increasing DD% could also lead to a reduction of amino group. Therefore, explaining that a further increase in the DD% of chitosan leads to a decrease in the specific capacities. Besides, Kim et al. (1997) also suggested that a higher DD% leads to a reduction in the hydrophobicity of the chitosan. This may become substantial, resulting in low capacities. Similar results were published by Coughlin et al. (1990) for the adsorption of nickel ions onto chitosan.

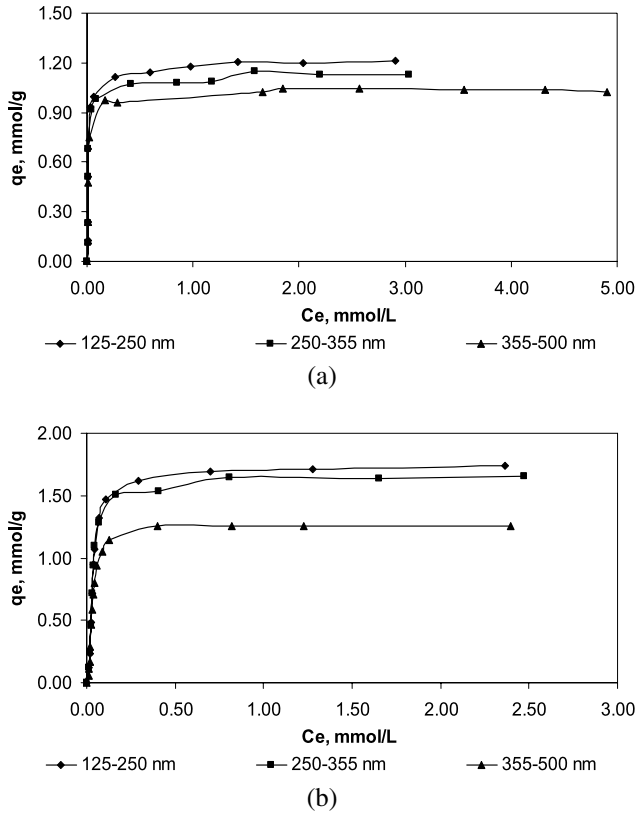


Fig. 8 **a** Sorption of Acid Green 25 onto chitosan with different particle size (dp) at 25 °C, degree of deacetylation (DD) = 53%, pH = 4.00. **b** Sorption of Acid Red 73 onto chitosan with different particle size (dp) at 25 °C, degree of deacetylation (DD) = 53%, pH = 4.00

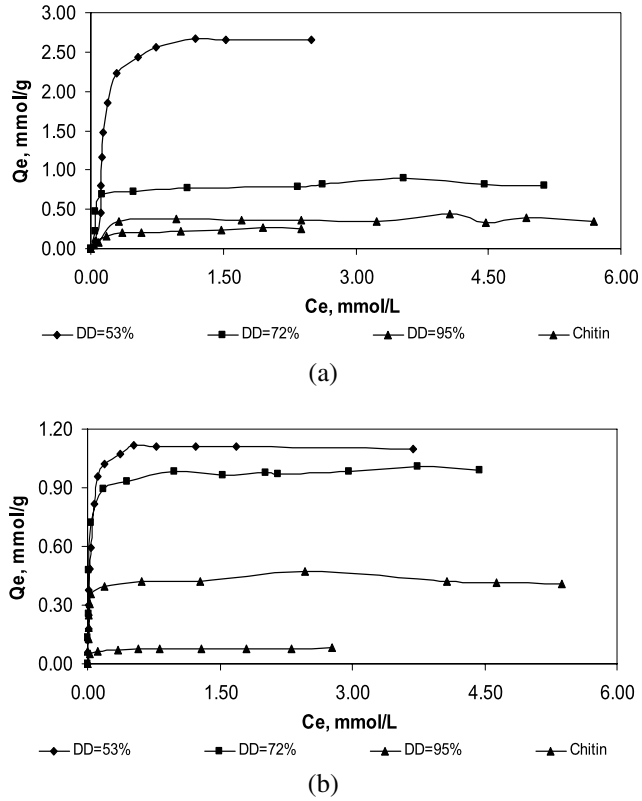


Fig. 9 **a** Sorption of Acid Orange 12 onto chitosan with different degree of deacetylation (DD) at 25 °C, pH = 4.00, dp = 355–500 μm. **b** Sorption of Acid Red 18 onto chitosan with different degree of deacetylation (DD) at 25 °C, pH = 4.00, dp = 355–500 μm

4 Conclusions

The performances of the chitosan as an adsorbent to remove acid dyes, namely, Acid Green 25, Acid Orange 10, Acid Orange 12, Acid Red 18 and Acid Red 73 from the aqueous solution have been investigated.

The experimental isotherm data were analysed using Langmuir, Freundlich, Redlich-Peterson equations for each individual dye. Based on the Langmuir isotherm analysis, the monolayer adsorption capacities were determined to be 645.1, 922.9, 973.3, 693.2 and 728.2 mg per g chitosan for Acid Green 25, Acid Orange 10, Acid Orange 12, Acid Red 18 and Acid Red 73, respectively. The difference in capacities may be due to the difference in the particle size of dye molecules and the number of sulfonate groups of each dye. Results demonstrated that monovalent and smaller dye particle having superior capacities due to increase in dye/chitosan ratio in the system, enabling a deeper penetration of dye molecules to the internal pore structure of chitosan.

The effect of temperature on the equilibrium isotherm was significant. The monolayer adsorption capacities increase with increasing temperature from 25 °C to 60 °C and no further increment at 80 °C. This is possible due to the increase the mobility of the large dye ions and the maximum swelling within the internal structure of the chitosan at 60 °C.

The amount of dye adsorbed increased with decreasing particle sizes due to the inability of the large dye molecules to penetrate into the internal pore structure of chitosan and the increase in active surface areas exposed for adsorption of dyes onto the chitosan.

The effects of degree of deacetylation (DD%) were being evaluated in this study. The reformation of crystalline region within the chitosan due to increase in homogeneity of the internal structure of chitosan with higher DD% resulted in a decrease in overall monolayer equilibrium capacities.

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