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Removal of A Cationic Dye using Deacetylated Chitin (Chitosan)

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Abstract: The removal of a cationic dye which was crystal violet using various degrees of deacetylated chitin (chitosan) has been observed in this study. The degree of deacetylation (DD) studied were 25.54% (w/v), 27.22% (w/v) and 35.02% (w/v). To evaluate the nature of adsorption, Langmuir, Freundlich and D-R isotherm models were used. Good correlation for the three isotherm models with D-R giving the highest correlation was obtained. Chitosan consists of both monolayer and heterogenous adsorption sites. The higher correlation for the Freundlich isotherm as compared to Langmuir concludes that the surface of the 3 types of chitosan contains mostly of small heterogenous adsorption patches. Based on the D-R model, the adsorption of both dyes onto three different types of chitosan was via ion-exchange.

Key words: Chitosan, deacetylation, dyes, isotherms

INTRODUCTION

Chitosan is derived from chitin, a natural aminopolysaccharide found in the exoskeleton of crustaceans, insects and some fungi. It is produced via partial deacetylation of chitin in 40-50% aqueous alkali, sodium hydroxide in most cases at 120-150°C under heterogenous conditions (Kurita, 2006). Chitosan in various forms have shown effectiveness as a pollutant adsorbent. Chitosan beads have shown ability to adsorb Cu(II) ions in aqueous solutions at approximately 100% removal (Ngah and Fatinathan, 2008). Its weak mechanical property requires chemical and physical modifications. Cross-linking using a cross-linking agent such as glutaraldehyde (Cestari *et al.*, 2008; Kyzas and Lazaridis, 2009) is required to reduce the crystallinity of chitosan thus improving its sorption capacities of reactive and basic dyes.

An important feature of chitosan is the degree of deacetylation. Although the hydroxyl groups also attract the dye molecules, it is the amine groups that are the main active groups which influence the polymer's performance. The degree of deacetylation of chitosan depends on the number of available amine groups. Thus an increase in the degree of deacetylation generally gives an increase in sorption capacity for anionic dyes due to the availability of protonated amine groups (Guibal *et al.*, 2003; Saha *et al.*, 2005). The presence of protonated amino groups in chitosan contributes towards better sorption capabilities of chitosan as compared to chitin by allowing ionic bonding between the amino groups and the dye ions (Wong *et al.*, 2008). This study

focuses on the adsorption of a basic dye (crystal violet) using different types of chitosan.

MATERIALS AND METHODS

Chitin from crab shells in powder form and crystal violet as the adsorbate were supplied by Sigma Aldrich Co. (USA). The molecular structure of crystal violet and chitosan is shown in Fig. 1 and 2, respectively. Sodium hydroxide, NaOH for deacetylation was supplied by Merck, Germany.

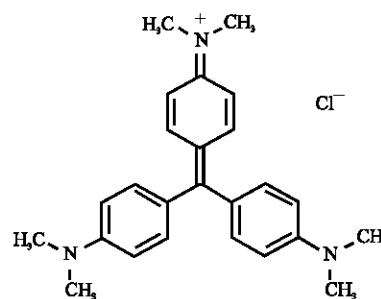


Fig. 1: Molecular structure of crystal violet

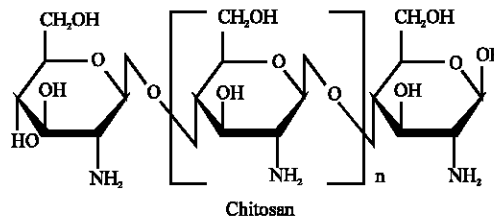


Fig. 2: Molecular structure of chitosan

Table 1: Preparation of chitosan with different degree of deacetylation

NaOH % (w/v)	Temperature (°C)	Time (min)	Degree of deacetylation (%)
5	100	60	25.54
30	100	60	27.22
50	100	60	35.06

Chitin from crab shells were sieved into particles of sizes 1 mm for homogeneity. Chitin was deacetylated to chitosan by using different concentrations of NaOH; 5% (w/v), 30% (w/v) and 50% (w/v) at 100°C for 1 h in a hot water bath. The product was washed with distilled water followed by 50% methanol and 50% acetone. They were then oven dried at 90°C for 24 h. Degree of deacetylation was determined by using an FTIR spectrophotometer by measuring the absorbance at wavenumbers 1655 cm⁻¹ (A₁₆₅₅) attributed to the amide groups and the corresponding value of the hydroxyl band at 3450 cm⁻¹ (A₃₄₅₀) (Cha *et al.*, 1997). The corresponding NaOH concentration and degree of deacetylation are summarized in Table 1. The equation in determining the degree of deacetylation is shown in Eq. 1:

$$\text{Degree of deacetylation} = 1 - \frac{A_{1655}}{A_{3450}} \times \frac{1}{1.33} \times 100 \quad (1)$$

A fixed mass of adsorbent (0.03 g) was weighed into an Erlenmeyer flask with 25 mL of crystal violet solution with predetermined initial concentrations. The temperature remained at room temperature while the solution pH remain constant. The flasks were sealed and shaken on an orbital shaker at 100 rpm for 72 h. The concentration of dye in each sample was determined via UV/Vis at λ_{max} 589 nm. The same procedure was repeated for the different types of deacetylated chitin (25.54, 27.22 and 35.06%). The amount of dye adsorbed per unit mass of chitosan (mg g⁻¹) can be calculated as shown in Eq. 2:

$$q = [(C_0 - C_e)/V]/m \quad (2)$$

where, q is the amount of dye adsorbed per gram adsorbent (mg g⁻¹), C₀ is initial dye concentration (mg L⁻¹), C_e concentration of dye at equilibrium with solid phase (mg L⁻¹), V volume of working solution used (L) and m mass of sorbent used (g).

RESULTS AND DISCUSSION

In order to optimize the design of the adsorption system, the adsorption data were analyzed according to the Langmuir, Freundlich and D-R isotherm models. The most suitable isotherm model for the experimental data for adsorption systems would be evaluated based on the highest correlation coefficient value, R² via linear regression analysis. All equilibrium isotherms were used

to determine the adsorption capacity as well as the nature of adsorption in removing crystal violet.

Langmuir isotherm: Adsorption is assumed to occur via monolayer coverage of the adsorbate at the outer layer of the adsorbent (Wong *et al.*, 2008). Furthermore, adsorption occurs at fixed number of definitive localized sites on the surface which can only adsorb only one molecule known as a monolayer. Furthermore all sites are equivalent and no interaction can be observed between adsorbed moieties and adjacent molecules. Therefore this isotherm considers that the energies and enthalpy resulting from adsorption are the same (Paulino *et al.*, 2007). The linearized equation is represented by Eq. 3:

$$C_e/q_e = C_e/q_{max} + 1/(q_{max} b) \quad (3)$$

where, C_e is the equilibrium dye concentration in solution (mg L⁻¹); q_e is the equilibrium dye concentration on the adsorbent (mg g⁻¹); q_{max} is the monolayer saturation capacity of the adsorbent (mg g⁻¹) while b is the Langmuir constant related to energy (L mg⁻¹). A linear plot as according to Eq. 3 yielding a straight line would prove that the system obeys the Langmuir model. The plots for crystal violet at various DD were strongly linear as shown in Fig. 3a.

The variation in adsorption properties was not proportional to the degree of deacetylation as also reported by Piccin *et al.* (2009). The amine groups of chitosan would be positively charged thus attracting the negative charge of the sulphonate groups found in methyl blue via electrostatic interaction (Chiou *et al.*, 2004; Prado *et al.*, 2004). For basic dye such as crystal violet the adsorption capacity paled in comparison to the acidic dye. This was due to the positive charge of the basic dye that creates strong columbic repulsions between chitosan and the basic dye that explains for the lower adsorption capacity (Kyzas and Lazaridis, 2009). The hydroxyl group (-OH) in chitosan could adsorb the basic dye via covalent and hydrogen bonding as similar to the adsorption mechanism of cellulose polymers with reactive dyes (Sakkayawong *et al.*, 2005). The adsorption of the dyes for the three DDs' were favorable as their R_L values were between 0 and 1. R_L>1 represents unfavourable adsorption, R_L = 1 represents linear adsorption while the adsorption is irreversible if R_L = 0.

Freundlich isotherm: The Freundlich model is used to describe non-ideal sorption onto heterogenous surfaces and multilayer sorption (Rafatullah *et al.*, 2009). The linearized equation is written as:

$$\ln q_e = \ln k_f + (\ln C_e)n^{-1}$$

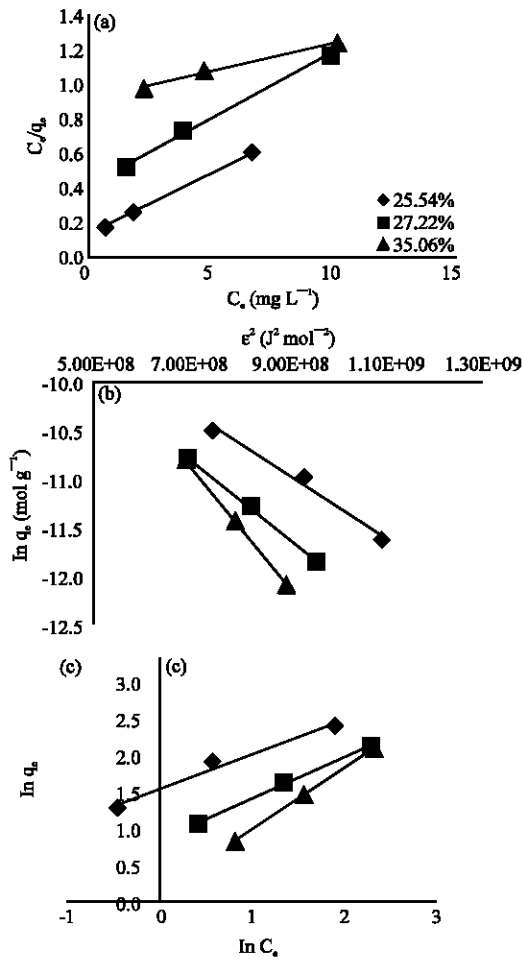


Fig. 3: (a) Langmuir, (b) D-R and (c) Freundlich isotherm plot for the adsorption of crystal violet onto chitosan, degree of deacetylation (DD: 25.54%, 27.22% and 35.06%)

Table 2: Isotherm constants for the adsorption of crystal violet onto chitosan at different degree of deacetylation

Isotherm	Degree of deacetylation (%)		
	25.54	27.22	35.06
Langmuir			
q _{max} (mg g ⁻¹)	14.23	13.09	31.65
b (mg L ⁻¹)	0.526	0.180	0.034
R _L	0.087	0.217	0.595
r _L ²	1	0.9937	0.9934
Freundlich			
K _f (g L ⁻¹)	4.72	2.34	1.16
n	2.37	2.34	1.16
r _F ²	0.9766	0.9981	0.9997
D-R			
q _{max} (mol g ⁻¹)	2.996×10 ⁻⁴	3.312×10 ⁻⁴	1.333×10 ⁻³
β (mol ² /kJ ²)	3×10 ⁻³	4×10 ⁻³	6×10 ⁻³
E (kJmol ⁻¹)	12.91	11.18	9.13
r _{DR} ²	0.9841	0.9996	1.000

where q_e is the solid phase sorbate concentration at equilibrium (mg g⁻¹), C_e is liquid phase sorbate

concentration in equilibrium (mg L⁻¹), K_f is Freundlich constant (L g⁻¹) and 1/n is the heterogeneity factor as shown in Table 2. A plot of ln q_e versus ln C_e yields a straight line with high correlation for crystal violet for all types of chitosan, Fig. 3c. The adsorption capacity for crystal violet decreases with increasing degree of deacetylation as shown by the K_f value. This is due to the increased availability of amine groups that are positively charged that repel against the dye molecules.

The n value denotes the favorability of the adsorption. In this work, the n value for both dyes being studied is above 1 for all DDs thus the adsorption intensity is favorable at higher concentrations (Nghah and Fatinathan, 2008). As the Freundlich isotherm gave a better fit compared to the Langmuir isotherm, it can be concluded that the surface of the deacetylated chitin is made up of small heterogenous adsorption patches.

D-R isotherm: Table 2 shows the conversion to liquid and gaseous products This isotherm is used to determine whether the adsorption is chemical or physical in nature. The linearized form is given in Eq. 4:

$$\ln q_e = \ln q_m - \beta \epsilon^2 \tag{4}$$

where, β is a constant related to the mean free energy of adsorption per mole of the adsorbate (mol²/kJ²); q_m is the theoretical saturation capacity (mol g⁻¹); q_e is the sorption capacity at equilibrium (mol g⁻¹); ε is the polanyi potential (J²/mol²) calculated as in Eq. 5:

$$\epsilon = RT(1+1/C_e) \tag{5}$$

where, R is the gas constant (8.314 J/molK) and T is the absolute temperature (K). Hence by plotting ln q_e versus ε², q_m and β can be obtained (Fig. 3b). The D-R parameters are listed in Table 2. The correlation for this isotherm is much higher compared to the Freundlich isotherm. The constant β gives an idea about the mean free energy E (kJ mol⁻¹) of adsorption per molecule of the adsorbate when it is transferred to the surface of the solid from infinity in the solution and the equation is as shown Eq. 6 (Dubey and Gupta, 2005):

$$E = \frac{1}{\sqrt{2\beta}} \tag{6}$$

This parameter gives information regarding the nature of the adsorption. If E is between 8 and 16 kJ mol⁻¹, the adsorption process is chemisorptions via ion-exchange. If E < 8 kJ mol⁻¹, the process is physical in nature. Based on Table 2, the E value for the three types

of chitosan in adsorbing crystal violet are in the chemisorption process via ion-exchange.

CONCLUSION

In this study, various degrees of deacetylated chitin ranging from 25.54-35.06% DD were able to adsorb both acid and basic dyes. The adsorption systems were evaluated based on three isotherm models which were the Langmuir, Freundlich and D-R models. Increasing the DD improved on the adsorption of methyl blue but not for crystal violet. The adsorption systems showed good correlation for all three isotherm models with D-R giving the highest correlation. This proves that the adsorption systems have both monolayer and heterogenous adsorption sites. Based on the D-R model, the adsorption of both dyes onto three different types of chitosan was via ion-exchange.

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