ADSORPTION KINETICS AND THERMODYNAMICS OF MALACHITE GREEN ONTO CHITOSAN/SODIUM CITRATE BEADS

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ABSTRACT

The adsorption of malachite green unto chitosan/sodium citrate beads has been studied. Langmuir and Freundlich isotherm models were applied to the adsorption equilibrium data and isotherms constants were estimated. The adsorption equilibrium data fitted reasonably well with the Langmuir but do not agree with Freundlich model. The adsorption mechanism was also tested using pseudo-first-order and pseudo-second-order kinetic models and the process followed the pseudo-second-order model. Chemically cross-linking reagent, sodium citrate was used to stabilise the chitosan and it enhanced the adsorption capacity of the Chitosan. The maximum adsorption capacity for the cross-linked beads ranges from 52-800 g/kg. The effects of varying initial concentrations, temperature, pH and contact time on the adsorption process were also investigated and the results show that the adsorption capacity is highly dependent on the initial concentration of the dye. It was observed that the amount of dye adsorbed increased largely with increase in temperature. The adsorption was maximal at acidic pH and decreased with increase in pH. The thermodynamic parameters of the adsorption process, the Gibb's free energy change ($\Delta G°$), enthalpy change ($\Delta H°$) and entropy change ($\Delta S°$) were also estimated.

Keywords: Adsorption, Malachite green, Chitosan bead, Equilibrium and Diffusion.

INTRODUCTION

Organic dyes are an integral part of many industrial effluents and appropriate methods are needed for their disposal (Ilhan Uzun 2006). Most commercial dyes are chemically stable and are difficult to remove from water (Nassar and Magdy 1997, Santhi et al. 2009). The release of coloured wastewater from these industries may present an eco-toxic hazard and introduce the potential danger of bioaccumulation, which may eventually affect man through the food chain. Many methods have been adopted for treating dye wastewater. Among them are physical or chemical treatment processes which include chemical coagulation/ flocculation, precipitation, adsorption, irradiation, ion-exchange and photo degradation (Gong et al. 2005). Some of these techniques have shown to be effective, although they have limitations. Among these limitations are excess amount of chemical usage, or accumulation of concentrated sludge with disposal problems; expensive plant requirements and operational cost; lack of effective colour reduction; and sensitivity to variable wastewater input (Robinson et al. 2001).

As a potential alternative to the conventional treatment methods, biomaterials have been used for the treatment of wastewater. Biomaterials hold promise for biosorption processes because of their high selectivity, cost effectiveness and good removal performance. Numerous low cost biomaterials have been tried for biosorption of dyes (Walker et al. 2003); yeasts (Zeumriye and Deonmez (2003); wheat bran (Papinulti et al. 2006); composite of chitosan and activated clay (Min-Yun Chang and Ruey-Shin Juang 2004); Fungi biomass (Cabuk et al. 2005); Rice husk and sawdust (Malik (2003)) and plant oil (Mahmoud et al. 2007).

Malachite green is 4-[(4-dimethylaminophenyl)- phenyl-methyl]-N,N-dimethyl-aniline. It is a basic organic, which is most widely used for colouring purpose, amongst all other dyes of its category. Malachite green has properties that make it difficult to be removed from aqueous solutions. A discharge of this dye to a receiving stream can affect aquatic life and cause detrimental effects

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in liver, gill, kidney, intestine and gonads. In humans, it may cause irritation to gastrointestinal tract upon ingestion and redness and pain while contact with eyes will lead to permanent injury of human eyes. (Srivastava et al. 2004)

Chitosan is the deacetylated form of chitin, which is a linear polymer of acetylamino-D-glucose and contains high content of amino and hydroxyl functional groups. Chitosan has been reported for the high potential of adsorption of metal ion (Shengling and Wang (2006)) and dyes (Kamari et al. 2009, Wu et al. 2000, Min-Yun and Ruey-Shin 2004, Chiou et al. 2002, Antonio et al. 2004). Other properties of chitosan includes its abundance, non-toxicity, hydro-philicity, biocompatibility, biodegradable, and anti-bacterial property (Kumar and Kumar 2000). The adsorption of reactive dyes in neutral solution using chitosan shows large adsorption capacity of 1000-1100g/kg (Krishna and Bhattacharyya 2002). In acid aqueous solution, the amino groups of chitosan are much easier to be cationized and they adsorb the dye strongly by electrostatic attraction.

It has been reported that chitosan formed gels below pH 5.5 and could not be evaluated. Therefore some cross-linking reagents are used to stabilise chitosan in acidic solutions (Ngar et al. 2002). Chiou and Li (2002, 2003) cross-linked chitosan with epichlorohydrin (ECH), glutaraldehyde as well as ethylene glycol diglycidyl ether and obtained a high adsorption capacity of reactive dye (RR 189) on the cross-linked chitosan beads in acid aqueous solutions at pH 3.0. The author concluded that it was feasible to remove reactive dyes from acid aqueous solutions by cross-linked chitosan. Therefore the aim of this present work is to explore the possibility of utilizing sodium citrate cross-linked chitosan beads for the removal of malachite green from aqueous solution and to also investigate the effect of factors such as pH, temperature, initial dye concentration and contact time on the adsorption process.

MATERIALS AND METHOD

Chitosan produced from lobster shell wastes was offered as flakes from Aldrich Chemical Co. with 85% degree of deacetylation, and used without further purification. The particle size is of 0.25-0.42 with average diameter of 0.335 mm. The commercial-grade reactive malachite green was purchased from Bektoh (Germany) and used as received. The aqueous solutions were prepared by dissolving the solutes in distilled water without pH adjustment. All other chemicals used for this experiment were obtained from Aldrich chemical Co. and used without further purification.

Preparation of Chitosan/Sodium Citrate Beads

The chitosan/sodium citrate beads were prepared using the method of Wan-Ngah et al., 2004. 8.0 g of chitosan flakes was dissolved in 100 ml of 5% (v/v) acetic acid solution. The chitosan solution was left for 24 h at room temperature. Sodium citrate in an amount of 6.0 g was dissolved in 100 ml of distilled water in a beaker and agitated on a magnetic stirrer at about 500 rpm at 70° C for 1 h. The two solutions were then blended together with stirring on the magnetic stirrer at about 500 rpm at 70°C for 1h and followed by another 2 h under room temperature to obtain a homogeneous gel blend. The gel blend was sprayed into a precipitation bath containing 500 ml of 0.5 M NaOH, which neutralized the acetic acid within the chitosan gel and thereby coagulated the chitosan gel to spherical uniform chitosan gel beads. The aqueous NaOH solution was agitated at about 300 rpm. Freshly prepared wet chitosan/sodium citrate gel beads were filtered and intensively washed and finally air-dried. The newly formed blended beads (hereafter called chitosan/sodium citrate beads) were then ground by using a laboratory jar mill and sieved to a constant size (<250 m) before use. The chitosan/sodium citrate beads (as shown in Fig. 1) obtained was confirmed by an FTIR Nicolet5 by Thermo Scientific model at center for Energy Research, Obafemi Awolowo University, Ile-Ife, Nigeria
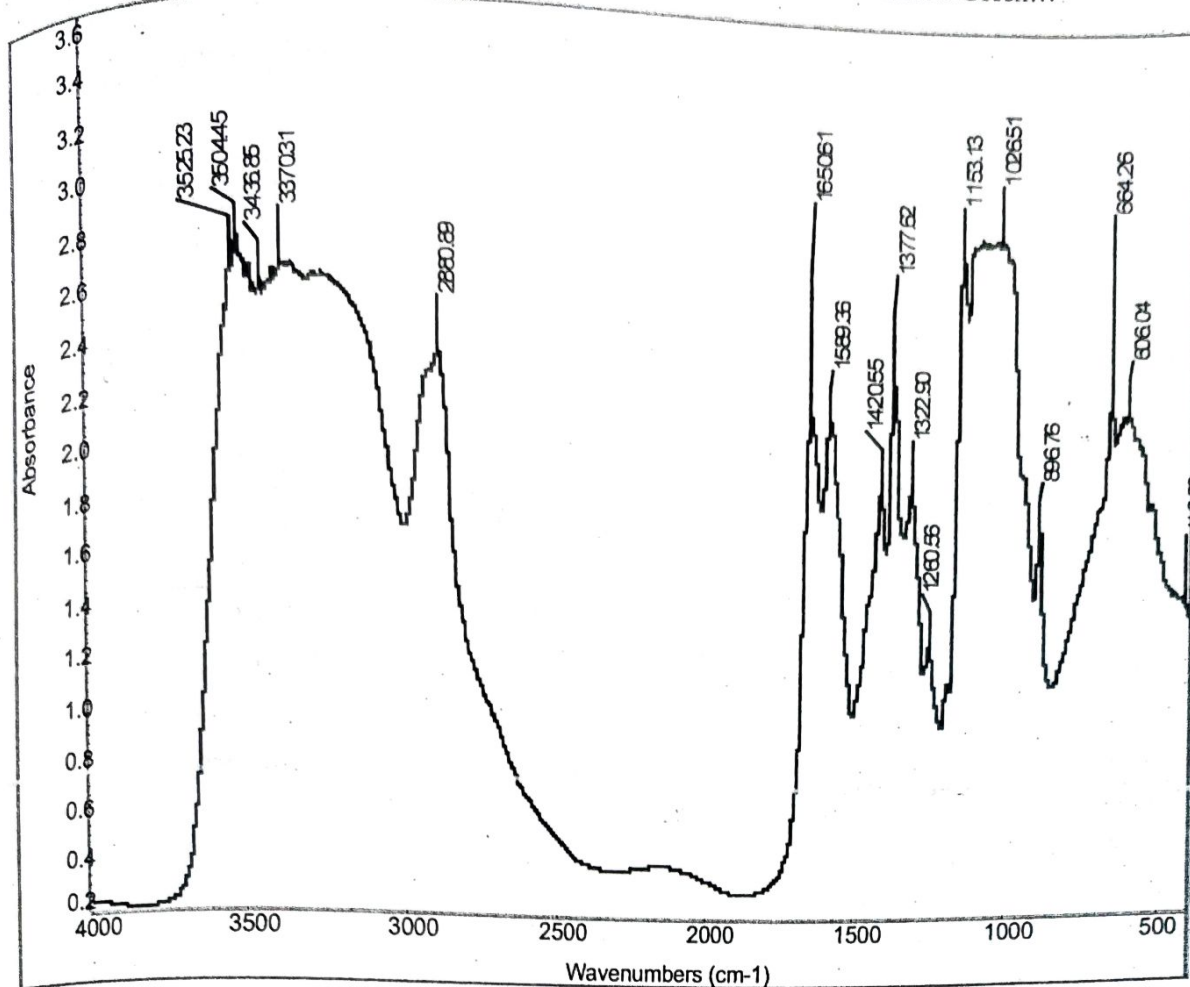
Figure 1: FTIR Spectrum of Chitosan.

Batch Kinetics Studies

Batch experiment was conducted using 250ml flask to which 50 ml aqueous dye solution and 0.2 g of chitosan/sodium citrate beads were added. The flasks were agitated in a thermostarted water bath with shaker (Haake model K-F3) at a constant speed of 150 rpm to study the effect of important parameters like pH, initial dye concentration, contact-time, and temperature. Samples were withdrawn at appropriate time intervals of 10, 20, 30, 40, 50, and 60 minutes and filtered. The filtrate was used for analysis of residual dye concentration using double beam UV-spectrophotometer (Thermo Helios Zeta UV/visible Spectrophotometer - Thermo Scientific) at a wavelength corresponding to the maximum absorbance of the dye (619 nm). The effect of pH on the dye removal was studied over the pH range of 3-10. The pH was adjusted by the addition of dilute aqueous solution of 0.2 M HCl or 0.2 M NaOH. The kinetics of adsorption was determined by analysing adsorptive uptake of the dye from the aqueous solution at different time intervals. The adsorption isotherm was found by agitating malachite green solution at different concentrations of 50, 100, 150, 200, 250, and 300 mg/L with known amount of chitosan (0.2 g) till equilibrium was achieved. The effect of temperature on the sorption characteristics was studied at 20°C, 25°C, 30°C, and 40°C.

The amount of sorption at time t, q_t (mg/g) was calculated using the equation:

$$q_t = \frac{(C_o - C_t)V}{W} \quad (1)$$

Where C_t (mg/L) is the liquid phase concentration of dye at any time t, V (ml) is the initial volume of dye, W (g) is the weight of dry adsorbent used and C_o (mg/L) is the initial concentration of dye. The amount of equilibrium adsorption q_e (mg/g) was calculated from equation:

$$q_e = \frac{(C_o - C_e)V}{W} \quad (2)$$

Where C_e (mg/L) is the liquid phase concentration of dye at equilibrium.
The percentage dye removed is calculated from equation:

$$\%DyeRemoval = \frac{(C_o - C_e) \times 100}{W} \quad (3)$$

RESULTS AND DISCUSSION

The kinetics of the biosorption of malachite green onto chitosan/sodium citrate beads was investigated and the results analysed by fitting to kinetic models. Experimental equilibrium data were fitted to Langmuir and Freundlich isotherm equations. Thermodynamic parameter Gibb's free energy ($\Delta G°$), enthalpy change ($\Delta H°$) and entropy change ($\Delta S°$) were also estimated. The spectral band for chitosan appears at 3501 cm⁻¹ (axial OH group), 3371 cm⁻¹ (N-H stretch of secondary amine) and 1153-1026 cm⁻¹ (ether linkage, C-O-C band stretching). However, the peak is more pronounced at 3000 cm⁻¹ which indicates that the (C-H) peak is more intense in this compound. There are also bands at 1653 cm⁻¹ (C=O stretch of amide), 1523 cm⁻¹ (NH angular deformation in CONH plane) and 2360 cm-1 (CN asymmetric band stretching). The bending vibrations between 1500 and 1000 cm⁻¹ intensity indicate some interactions of the amino group (Fig 1) (Bamgbose et al., 2012).

Chitosan beads obtained after a blend with 5% w/v sodium citrate solution show two peaks which signify asymmetric and symmetric stretching at 1379 cm⁻¹ and 1451 cm⁻¹ respectively. There is also a peak at 1556 cm⁻¹ of ammonium ion (Fig. 2A). However, comparable peaks were obtained in chitosan beads obtained after blending with 3% w/v sodium citrate solutions at pH 3 (Fig. 2B). It is observed that the two terminal $-COO^-$ groups of sodium citrate molecules are assumed to be linked with two $-NH_3^+$ and $-(CH_3COO^-)$ groups of two chitosan monomers, one on each side.

The effect of contact-time and Initial Concentration

Effect of the initial concentration of malachite green dye solution on the adsorption onto chitosan was investigated at various concentrations from 50 (mg/L) to 300 (mg/L) and different temperature ranging from 20°C to 40°C as shown in Table 1.
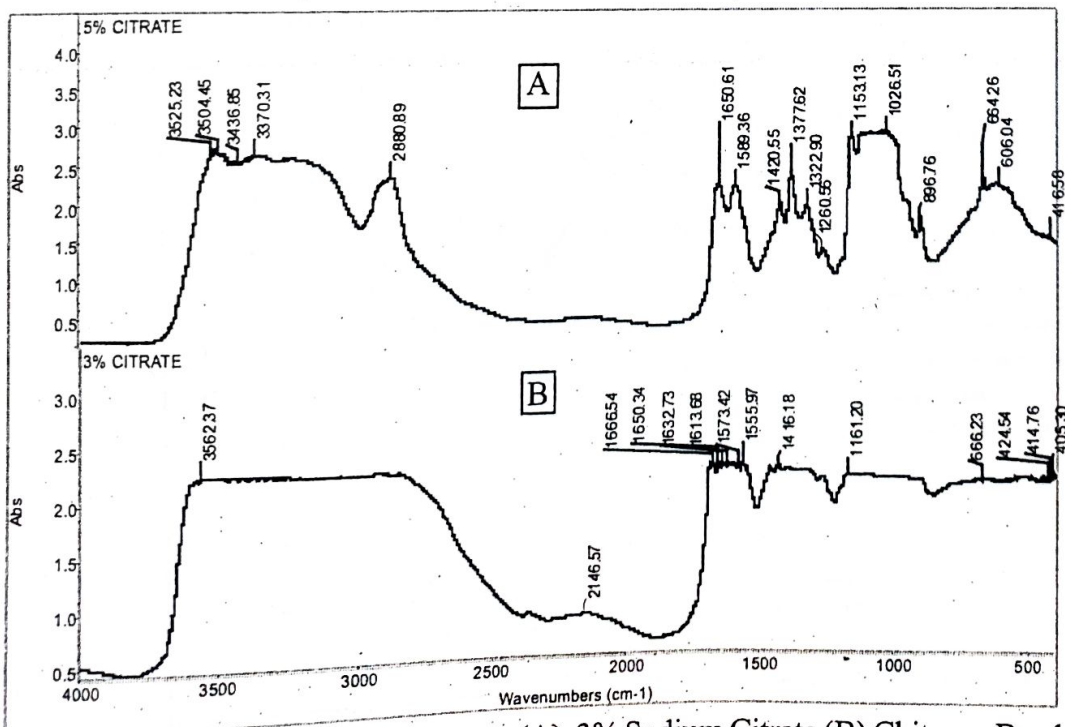

Figure 2: FTIR Spectra of 5% Sodium Citrate (A), 3% Sodium Citrate (B) Chitosan Beads

Table 1: Effect of initial Concentration at Different Temperatures

C_0(mg/L)	C_e(mg/L)					q_e(mg/g)					%Dye Removed				
	20°C	25°C	30°C	35°C	40°C	20°C	25°C	30°C	35°C	40°C	20°C	25°C	30°C	35°C	40°C
50	14.8	9.95	7.90	5.80	4.90	8.80	10.0	10.5	11.1	11.3	70.4	80.1	84.2	88.4	90.2
100	31.9	21.8	18.0	15.9	13.6	17.0	19.6	20.5	21.0	21.6	68.1	78.2	82.0	84.1	86.4
150	53.6	35.4	32.6	31.2	29.7	24.1	28.7	29.4	29.7	30.1	64.3	76.4	78.3	79.2	80.2
200	79.2	54.8	51.2	49.0	47.4	30.2	36.3	37.2	37.8	38.2	60.4	72.6	74.4	75.5	76.3
250	103.5	93.0	92.5	89.5	89.0	36.7	39.3	39.4	40.1	40.3	58.6	62.8	63.0	64.2	64.4
300	137.4	133.2	128.7	126	124.8	40.7	41.7	42.8	43.5	43.8	54.2	55.6	57.1	58.0	58.4

Table 2: Equilibrium Constant and Thermodynamic Parameter for Adsorption of Malachite Green

C_0(mg/L)	K_c					$\Delta G°$(KJ/mol)					$\Delta H°$(KJ/mol)	$\Delta S°$(J/mol)
	Temperature					Temperature						
	20°C	25°C	30°C	35°C	40°C	20°C	25°C	30°C	35°C	40°C		
50	2.38	4.03	5.33	7.62	9.20	-2.11	-3.45	-4.22	-5.20	-5.78	51.55	168.7
100	2.14	3.59	4.56	5.29	6.35	-1.85	-3.17	-3.82	-4.27	-4.81	41.47	135.2
150	1.80	3.24	3.60	3.81	4.05	-1.43	-2.91	-3.22	-3.43	-3.64	30.92	100.2
200	1.53	2.65	2.91	3.08	3.22	-1.04	-2.42	-2.69	-2.88	-3.04	28.37	93.3
250	1.41	1.69	1.70	1.79	1.81	-0.84	-1.30	-1.34	-1.49	-1.54	9.52	29.6
300	1.18	1.25	1.33	1.38	1.40	-0.40	-0.55	-0.72	-0.82	-0.88	6.52	20.9

This table reveals that percentage adsorption decreased with increase in initial dye concentration, but the actual amount of dye adsorbed per unit mass of chitosan bead increased with increase in dye concentration. This means that the adsorption is highly dependent on initial concentration of dye. At lower concentration, the ratio of the initial number of dye molecules to the available surface area is low. Subsequently, the fractional adsorption become independent of initial concentration. However, at high concentration, the available sites of adsorption become fewer and hence the percentage removal of dye is dependent upon initial concentration (Namasivayam et al., 1996, Namasivayam and Yamuna, 1995, Senthilkumar et al., 2005).

The removal of malachite green from aqueous solution by adsorption onto chitosan beads increases with time, till equilibrium is attained in 40 minutes for all concentrations as shown in Figure 3.
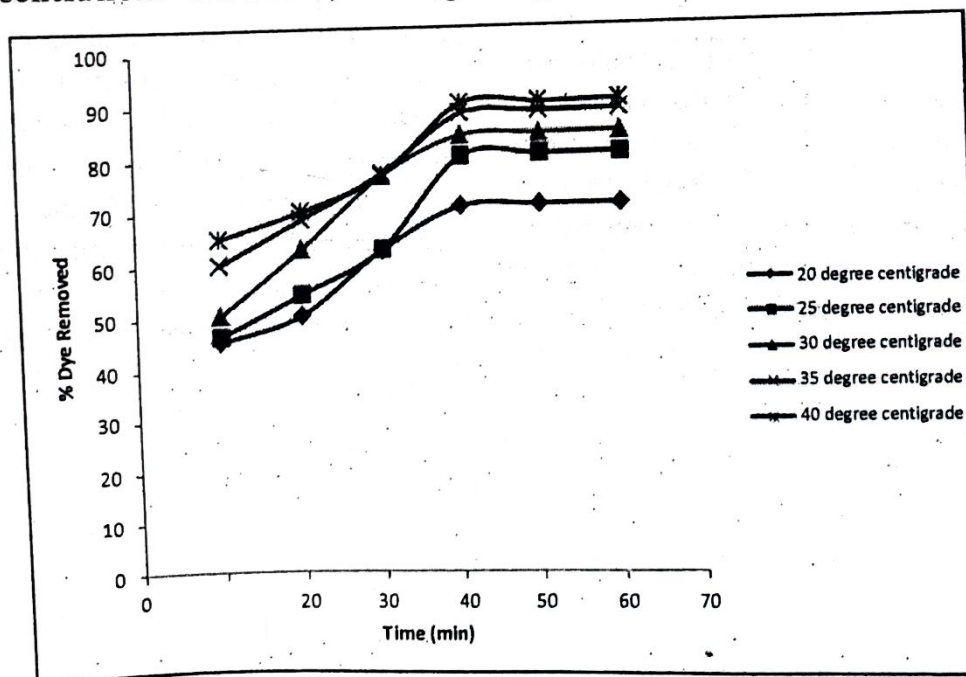
Figure 3: Effect of Contact-time at Different Temperatures

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Effect of Temperature

The effect of temperature on the adsorption of malachite green onto chitosan/sodium citrate beads was studied at different temperatures, (20°C to 40°C) and the results shown in Table 1 and 2. These indicate that when the temperature is increased from 20°C to 40°C, the adsorption capacity of malachite green onto chitosan bead increased. Therefore, the higher temperature facilitates the adsorption of malachite green onto chitosan beads. This may be due to the fact that increasing the temperature may produce swelling effect within the internal structure of chitosan beads, the enlargement of pore size and activation of the adsorbent surface (Arivoli et al., 2007, Kalpana et al., 2007, Gong et al., 2005, Bhattacharyya and Sharma 2003).

Effect of Cross-linking

The large number and array of different chemical groups on chitosan chains (e.g. $-NH_2$, $-OH$) imply that there are many types of chitosan-solute interactions (Wu et al., 2001). Chitosan/sodium citrate complexes were formed only by the ionic interaction between the positively charged amino group of the chitosan and the negatively charged counter ion $-COO^-$ moieties of the sodium citrate (Mi et al., 1999).

At pH 3 – 6, these interactions between chitosan and sodium citrate are higher due to the high contents of the positively charged amino groups which confer stability on the chitosan for effective removal of the dye in acidic solutions (Ngah et al., 2002, Chiou and Li 2002, 2003). At pH 8 – 10, the $-NH_3^+$ groups were deprotonated and the ionic interactions between chitosan and the citrate disappear thereby reducing the stability of the chitosan for the adsorption process.

Thermodynamics of the Adsorption

Thermodynamic parameters such as change in free energy (ΔG°) (kJ/mol), enthalpy (ΔH°) (kJ/mol) and entropy (ΔS°) (J/K/mol) for the adsorption process were determined using the following equations, (Vadivelan and Vasanthakumar 2005, Venkata Mohan et al., 2000).

$$\Delta H^o = \frac{R[T_2 T_1]}{[T_2 - T_1]} \ln\left(\frac{K_2}{K_1}\right) \tag{4}$$

$$\Delta G^o = -RT \ln K_o \tag{5}$$

$$\Delta G^o = \Delta H^O - T\Delta S^o \tag{6}$$

$$K_o = \frac{C_{solid}}{C_{liquid}} \tag{7}$$

$$\log K_o = \frac{\Delta S^o}{2.303R} - \frac{\Delta H^o}{2.303RT} \tag{8}$$

The values of, ΔG° ΔH°, & ΔS° for the initial concentration of 50 mg/L to 300 mg/L are presented in Table 2. The increase in the magnitude of ΔG° values will increased temperature revealed that the extent of spontaneity increased with temperature. The negative value of ΔG° indicated the feasibility and spontaneous nature of malachite green sorption onto chitosan/sodium citrate beads. The ΔH° values in the range of 1 - 93kJ/mol indicate that the reaction is physisorption. The low value of ΔH° gives clear evidence that the interaction between malachite green and chitosan beads may be weak hence physisorption is much more favourable for the adsorption of malachite green. The positive value of ΔH° shows the endothermic nature of the adsorption which governs the possibility of physical adsorption (Arivoli and M. Hema 2007, Kalpana et al., 2007). The positive value of ΔS° show the increased disorder and randomness at the solid-solution interface of malachite green with chitosan bead adsorbent.

Adsorption Isotherm

In this study, the adsorption data correlated with Freundlich (Ozacar, and Sengil, 2003) and Langmuir (Lagergren et al., 1898) models. The following linearized Freundlich adsorption isotherm is employed.

$$\ln q_e = \ln K_f + \left(\frac{1}{n}\right)\ln C_e \qquad (9)$$

Where q_e is the amount adsorbed at equilibrium (mg/g), K_f the Freundlich constant, (1/n) is the heterogeneity factor which is related to the capacity and intensity of the adsorption respectively and C_e is the equilibrium concentration (mg/L). The value of K_f and $\left(\frac{1}{n}\right)$ can be obtained from the slope and intercept of the plots of $\ln q_e$ against $\ln C_e$.

Langmuir isotherm is based on the assumption that point of valence exists on the surface of the adsorbent and that each of these sites is capable of adsorbing one molecule. The adsorbed layer will be one molecule thick. Furthermore, it is assumed that all the adsorption sites have equal affinities for molecules of the adsorbate and that the presence of adsorbed molecule at one site will not affect the adsorption of molecules at an adjacent site. A well-known linear form of Langmuir equation can be expressed as:

$$\frac{C_e}{q_e} = \frac{1}{(q_m \times b)} + \frac{C_e}{q_m} \qquad (10)$$

Where, C_e and q_e has usual meaning and q_m and b are the Langmuir constant related to the capacity and energy of adsorption, respectively. According to the equation (10) a plot of $\frac{C_e}{q_m}$ versus C_e should be a straight line with a slope $\frac{1}{q_m}$ and intercept $\frac{1}{(q_m \times b)}$ when the adsorption obeys the Langmuir equation as presented in Figure 4.
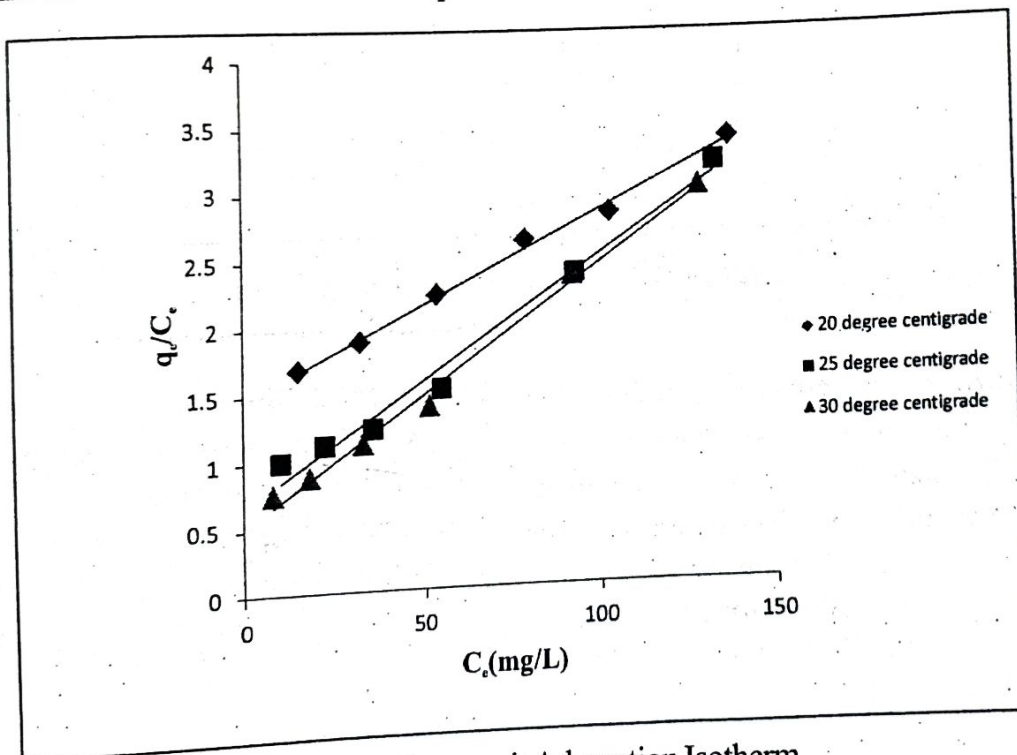

Figure 4: Langmuir Adsorption Isotherm

The important characteristic of the Langmuir isotherm can be expressed in terms of a dimensionless factor, R_L (Arivoli et al., 2006) which is defined as:

$$R_L = \frac{1}{1 + bC_o} \qquad (11)$$

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The R_L values indicate the type of the isomerism to be either unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$).

From the result shown in Table 3, it is clear that the value of adsorption efficiency q_m and adsorption energy b, of the chitosan decreases on increasing the temperature which suggests that the maximum adsorption corresponds to a saturated monolayer of adsorbate molecules on adsorbent surface and the endothermic nature of the adsorption (Lagergren et al., 1898, Arivoli et al., 2006). Favourability of the adsorption process was calculated from dimensionless separation factor (R_L), which was found between 0 and 1 which confirms the on-going adsorption of malachite green (Lagergren et al., 1898).

Linear plots of $ln q_e$ versus $ln C_e$ show that the adsorption of malachite green dye obeys the Freundlich adsorption isotherm (Figure 5).
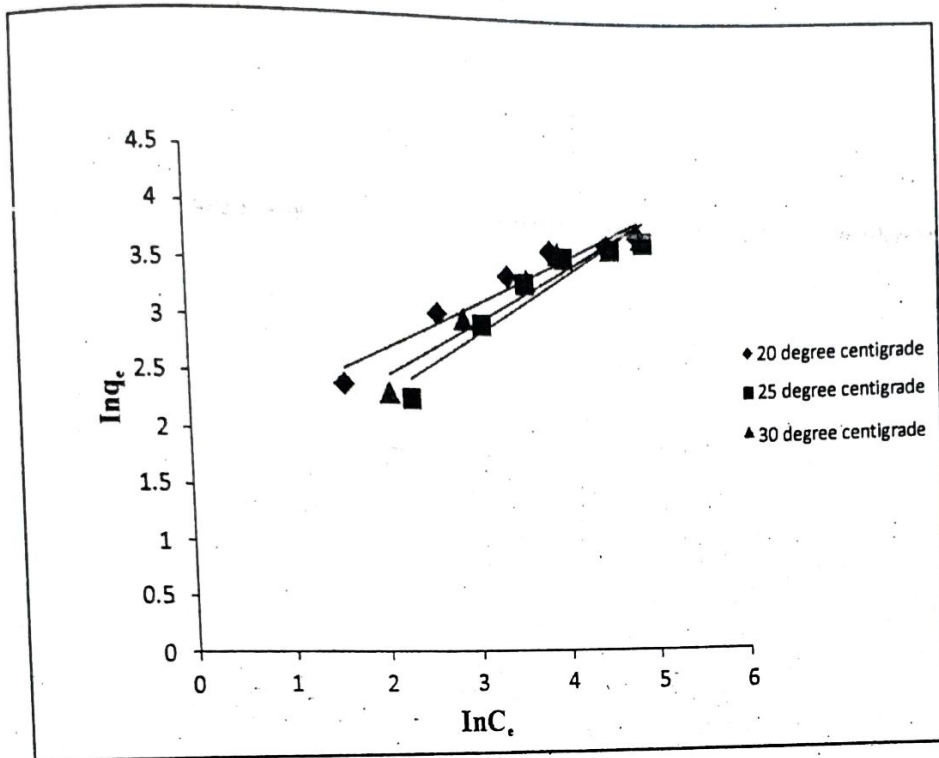

Figure 5: Freundlich Adsorption Isotherm

The values of K_f and n were calculated from the plots and are shown in Table 4. This show that the increase of negative charge on the adsorbent surface that enhances the electrostatics forces between the chitosan/sodium citrate beads, surface and the dye ion, in turn increases the adsorption of the dyes. The values clearly show the dominance of adsorption capacity. The intensity of adsorption is an indication of the bond energies between dye and the adsorbent and the possibility of a slight chemisorption rather than physisorption. The possibility of multilayer adsorption of dyes through the percolation process cannot be ruled out. However, the values of n are less than one, indicating the physisorption is much more favourable (Lagergren et al., 1898).

Kinetic Modelling:

In this study, pseudo-first-order, pseudo-second-order and intra-particle diffusion kinetic models were applied. Lagergren's first-order rate equation is the earliest known one describing the adsorption rate based on the adsorption capacity. The linear form of the Lagergren's first order rate equation is as follows (Mckay and Ho 1999):

$$ln(q_e - q_t) = ln q_e - k_1 t \qquad (12)$$

when q_e is amount of dye absorbed on absorbent at equilibrium (mg/g), q_t is amount of dye absorbed on absorbent at any time t(mg/g) and

The calculated values of k_1, k_2, q_e and their corresponding regression coefficient (R^2) values were obtained from the plot. The correlation coefficient for pseudo-second-order kinetic is higher than that for the pseudo-first-order kinetic ($R^2 = 0.997$ for pseudo-second-order kinetic and $R^2 = 0.861$ for pseudo-first-order kinetic). This suggests that the present system can be represented better by the pseudo-second-order model. The calculated values of pseudo-second-order were found to be close to the experimentally determined value which is equal to 0.124, also suggesting the applicability of pseudo-second-order model. The correlation coefficient for the intra-particle diffusion is lower than pseudo-second-order kinetics, which indicates the present system may be followed by intra-particle diffusion.

pH Effect.

Figure 10 shows the effect of pH on the adsorption capacity of malachite green ion onto chitosan/sodium citrate beads at 25°C. The figure shows that the pH of the solution strongly affects the adsorption capacity of the cross-linked chitosan beads. The result shows that the adsorption of the dye decreases as the pH increases over the entire pH range of 3-10, suggesting that a change in pH of the solution results in the formation of different ionic species and a different surface charge on the chitosan beads.
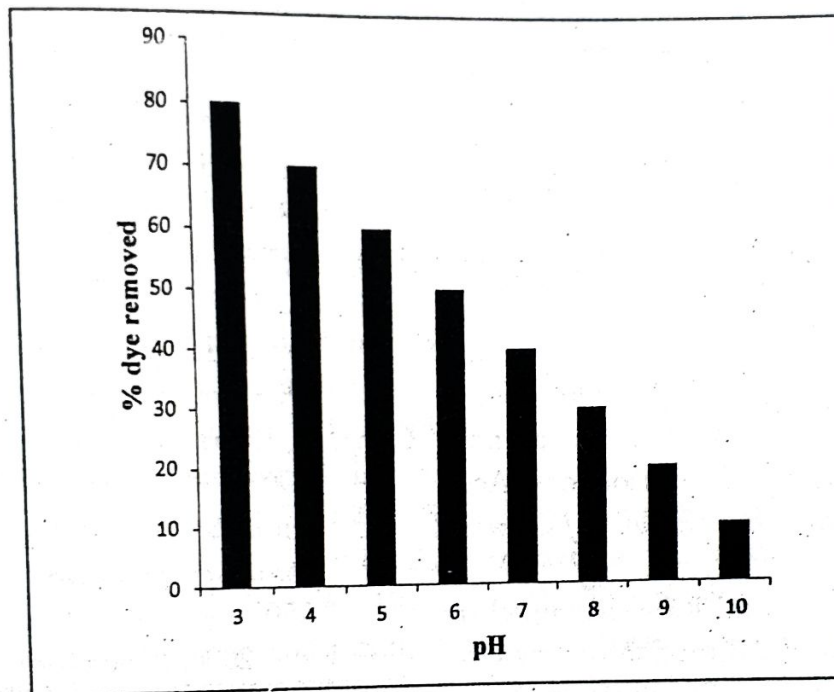

Figure 10: Effect of pH at 25°C.

At pH 3-6 there is observed increase in dye adsorption because the amino groups of chitosan molecule will be protonated thereby promoting electrostatic attractions between the dye molecules and adsorption sites. Above pH 6, the adsorption capacity of the chitosan beads decreases up to pH of 10. At these higher pH values, the zwitter ions form of malachite green in aqueous solution may raise the aggregation of malachite green to form a bigger molecular form (dimer) making it difficult for the dye to diffuse through the pore structure of the chitosan beads. This observation is in agreement with the findings of Arivoli et al., 2009 and Kumar (2000).

CONCLUSION

The removal of malachite green by chitosan beads was investigated under different conditions. Adsorption equilibrium correlated reasonably well with Langmuir but do not agree with Freundlich isotherm. The adsorption of malachite green onto chitosan beads is spontaneous and physical in nature. The amount of dye adsorbed increased with increase in temperature. The pseudo-second order kinetic model agrees better with dynamic behaviour for the adsorption of malachite green onto chitosan beads under different temperatures. The values of $\Delta G°$, $\Delta H°$ and $\Delta S°$ show that the chitosan/sodium citrate beads have a considerable

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potential as an adsorbent for the removal of malachite green.

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