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Adsorption studies on the removal of cationic dye from shrimp shell using chitin

Soheir A. Khedr[1], Mona A. Shouman[1], Amina A. Attia[1]*

ABSTRACT

Recent developments have given positive indications that biomaterials, in their nature or modified states are effective, environmentally friendly adsorbents of pollutants. This study investigates the chitin obtained from shrimp shell as an adsorbent for Crystal violet dye removal. Effect of various physico-chemical parameters such as contact time, initial dye concentration (250- 75 mg/L), pH (2-10) and temperature (293-333K) were investigated. Experimental data were analyzed by using Langmuir, Freundlich, Temkin and Dubinin – Radushkevich adsorption models. Equilibrium data were fitted well with the Langmuir model with maximum monolayer adsorption capacity of 37.02 mg/g. The kinetics of Crystal violet adsorption followed the pseudo-second order rate expression which suggests that intraparticle diffusion plays a significant role in the adsorption mechanism. Thermodynamic parameters, such as changes in Gibbs free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were calculated to appreciate the nature of adsorption process. The surface morphology of chitin obtained from shrimp shell was studied using FTIR, SEM, and TG - DTG. The results of this work indicate that the chitin extracted from natural materials constitutes a promising and efficient low cost adsorbent for the removal of dyes from aqueous effluents.

Keywords: *adsorption, chitin, crystal violet, isotherms, kinetics study.*

1. INTRODUCTION

The release of large quantity of dyes into water bodies by textile industries poses serious environmental problems due to persistent and recalcitrant nature of some of these dyes. The dye loss from the dyeing process to the effluent is estimated 10-50% for reactive dyes and 0-5% for basic dye one [1]. Untreated or partially treated effluents from other industries namely, paper, plastic, leather, cosmetic, food, woolen, and carpet also contributes to pollution load [2]. The discharge of highly colored wastes is not only aesthetically displeasing but it also impedes light penetration, thus upsetting biological processes within a stream. In addition, many dyestuffs are toxic to some organism and may cause direct destruction of aquatic communities and the anaerobic break down of some dyes in the sediments /or their incomplete bacterial degradation often produces toxic amines [3]. Hence, the removal of dyestuffs from such waste water is necessary [4] .Thus the removal of dyes from colored effluents particularly from textile industries is one of the major environmental concern these days [5]. In general, there are five main methods used for treatment of dye- containing effluent: adsorption, oxidation- ozonation, biological treatment, coagulation- flocculation, and membrane processes [6-7]. Most of these conventional treatment techniques are rather expensive [8-9]. But adsorption process has been found to be more effective method and least expensive for treating dye containing effluents [10-11]. Although the activated carbon [12] is most effective for adsorption of dyes, but it is quite expensive and hence there is an increasing need for equally

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[1] Surface Chemistry and Catalysis Laboratory, National Research Center, 12622 Dokki, Cairo, Egypt
*Corresponding author e-mail address: ***mollyattia@hotmail.com***

effective and cheaper sorbents. Recently, considerable attention has been directed towards low cost, naturally occurring adsorbents. These novel adsorbents include a wide range of materials ranging from byproducts derived from agricultural, industrial and fishery wastes (Peanut skins wool, sugar cane bagasse, tea leaves, coffee powder, rice straw, chitin, etc) to microbial biomass [13]. Chitin is a white, hard, inelastic, nitrogenous polysaccharide found in the exoskeleton of all animals with an outer skeleton such as insects and crustaceans [14]. It is also found in microorganisms, e.g. in the cell walls and structural membranes of mycelia of fungi, yeast and green algae [15]. Chitin is composed of β (1→4) linked 2- acetamido-2- deoxy- β-D- glucose (N- acetylglucosamine) [16]. Chitin is an adsorbent which contains an amine group in varying proportions. These groups can lead to the adsorbent having a larger adsorption capacity for acid or anionic dyes.Chitin is structurally identical to cellulose, but it has acetamide groups (-NH $COCH_3$) at the C- 2 positions. It has strong inter – and intra – molecular hydrogen bonds between the polymer chains and is water insoluble due to its rigid crystalline structure. Adsorption can occur by Van der Waals attraction, hydrogen bonding and coulombic attraction [17]. Chitin will display no significant attraction towards basic dyes [18]. Since chitin, also, carries one linear amino group per glucose ring, thus making electron pairs available for coordination. It behaves as a Lewis base [19] (Fig. 1).

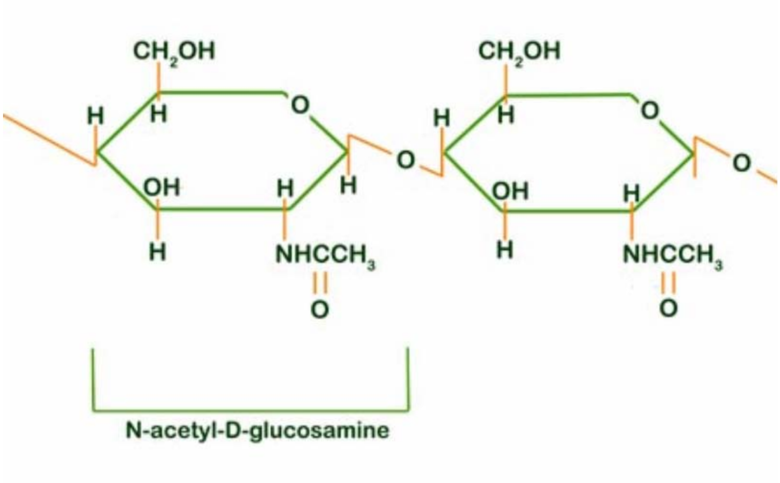

Figure 1: Chemical structure of chitin

The common procedure for isolating chitin from crustacean shells involves demineralisation, deproteinisation and decoloration. Minerals in the shells are dissolved using acid while proteins are hydrolysed by alkali. The residues are decolorised using solvents and/or oxidants. Many authors [20-22] have noted that dye adsorption onto biological adsorbents occurs through various mechanisms. For example, cellulose-containing adsorbents prepare from eucalyptus bark, maize cob or bagasse pith are found to be efficient in binding basic dyes rather than acid dyes as a result of chemical and physical adsorption. Unlike cellulose, natural nitrogen-containing adsorbents such as chitin (and its derivatives) adsorb acid better than basic dyes.

The aim of this study is to investigate the adsorption behavior of chitin obtained from shrimp shell for removal of cationic (Crystal violet) dye from aqueous solution. For that reason, the influence of some physical parameters (contact time, initial dye concentration, solution pH and temperature) were studied. Langmuir, Freundlich, Temkin and DR models were used to fit the equilibrium isotherms. The kinetics of adsorption was determined by using pseudo first order, pseudo – second order reaction and intraparticle diffusion. In addition, the equilibrium thermodynamic parameters were determined for the Crystal violet adsorption on the chitin. The influence of contact time and pH was also studied.

2. EXPERIMENTAL SECTION

2.1. Materials. The raw material exoskeleton of fresh prawn for preparation of chitin was obtained from fish market. The shells and heads of fresh prawn were thoroughly and repeatedly washed in hot water for 1h then dried in an oven at 50°C and left for overnight. Various procedures have been adopted to obtain high quality chitin by removing protein, inorganic material (mainly $CaCO_3$), pigments and lipid. Demineralization is usually carried out by treatment with HCl and deproteinization with NaOH. The shrimp shell was demineralized with 0.65M HCl solution (1:5 w/v) at ambient temperature (25-30°C) for 12 h. The residue was washed and soaked in tap water from 6 -8 h. It was then dewatered and deproteinated with 0.6 M NaOH (1:5 w/v) at ambient temperature for 24h. Then they were crushed into discrete particle size ranges between 147-300μm. Some physicochemical properties of the obtained chitin are given in Table 1.

Table 1. Characteristics of obtained chitin flakes

Molecular formula	$(C_8H_{13}NO_5)n$
Formula weight	~ 400 $gmol^{-1}$
BET surface area	152.3 m^2g^{-1}
Pore volume	0.09
Density	~0.45 gml^{-1}
Pk_a	6.1
Color	Light yellow
Average pore diameter	11.7
Pore volume	0.094 cm^3
Pore width	36.2
Particle radius	18.1

Crystal violet is a mutagen and mitotic poison, and it is used in vast quantities for textile and paper dyeing. Numerous methods have been developed to treat Crystal violet pollution. The three most prominent are chemical bleaching, biodegradation and photodegradation. The dye used in the tests was Crystal violet which has a molecular formula $C_{25}H_{30}$ N_3 Cl, Mw= 407.979k, C.I.no42555]. This cationic dye was purchased from Parloba Company (Fig. 2). An accurately weighted quantity of the dye was dissolved in double – distilled water to prepare stock solution (250 mg/L). The stock solution was used to prepare by dilution, the working solutions with desired concentrations.

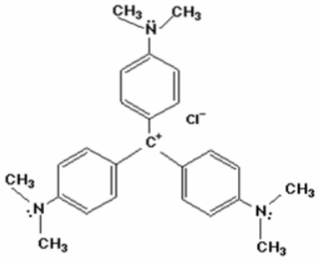

Figure 2: Chemical structure of Crystal violet

2.2 Sorption experiments. Sorption of chitin obtained from shrimp shell onto Crystal violet was carried out in batch experiments carried out at different temperatures (293, 313 and 323K). Various concentrations of the adsorbate ranging from 10 – 60 mg/L were prepared by dilution with distilled water in contact with a known weight of the adsorbent (0.15g). The initial pH was adjusted by using 0.1 M HCl or 0.1 M NaOH. The flasks were homogenized at a shaking rate of 125 rpm using Orbital

Shaker Incubator GFL 3031. After equilibrium (24 hours), the solution was then filtered at different time intervals and the residual dye concentration was measured.

Kinetic experiments were carried out by stirring a known amount of the adsorbent (1g) with 500 ml of the solution containing the dye (100 mg/L) on a magnetic stirrer equipped with temperature controller. At pre-determined time intervals, portions of the mixture were drawn by a syringe and then centrifuged. The dye concentration was then determined. This procedure has been done at three different dye concentrations (75, 150 and 250 mg/L) at constant temperature 25 °C and pH=8.

Dye concentration in solutions was determined spectrophotometrically using Shimadzu UV- visible 240IPC spectrophotometer at λ= 590 nm. The amount of Crystal violet adsorbed on chitin q_{ee} (mg dye/g adsorbent) was determined as follows:

$$q_e = \frac{C_o - C_e}{m} \times V \tag{1}$$

Where C_o and C_e are the initial and equilibrium dye concentrations (mg/L), respectively, V is the volume of solution (L), and m is the chitin weight (g) in dry form.

The zero point charge of the carbon (pH_{PZC}) was measured using the pH drift method [23].The pH of the solution was adjusted by using 0.01 mol/L sodium hydroxide or hydrochloric acid. Nitrogen was bubbled through the solution at 25 °C to remove the dissolved carbon dioxide. 50 mg of the chitin was added to 50 mL of the solution. After stabilization, the final pH was recorded. The graph of final pH versus initial pH was used to determine the zero point charge of the Chitin. (Figure not shown).

2.3. Sorption isotherms. Adsorption isotherms parameters from different models provide important information on the surface properties of the adsorbent and its affinity to the adsorbate. Several isotherms models can be used to describe the equilibrium of adsorption. Four common isotherms equations were applied in the present study: Langmuir [24], Freundlich [25], Temkin [26] and Dubinin – Radushkevich [27]. Langmuir isotherm model is applied to the equilibrium sorption supposing the monolayer of sorbate on the homogeneous surface with a finite number of identical sites; the linear form the Langmuir model is represented as follows:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \tag{2}$$

Where K_L is the Langmuir equilibrium constant of adsorption (L/mg), q_m maximum adsorption capacity (mg/g), q_e the amount adsorbed at equilibrium (mg/g), C_e equilibrium concentration (mg/L).

The Freundlich equation is an empirical relationship established upon sorption onto a heterogeneous surface, involving different sites with several adsorption energies. In the linear form Freundlich isotherm is expressed by the following equation

$$q_e = K_F C_e^{1/n} \tag{3}$$

where K_F and n are the isotherm constants of Freundlich. K_F is a constant (mg/g) related to the bonding energy, $1/n$ (heterogeneity factor, ranging between 0 and 1) is a measure for the adsorption intensity or surface heterogeneity. A plot of $\ln q_e$ versus $\ln C_e$ enables the empirical constants K_F and $1/n$ to be determined from the intercept and slope respectively (not shown).

The Dubinin–Radushkevich isotherm was used to determine the characteristic porosity and the apparent free energy of adsorption. The DR isotherm is expressed in linear form as follows:

$$\ln q_e = ln q_m - k_{DR}\varepsilon^2 \tag{4}$$

where K_{DR} is a constant related to the mean free energy of adsorption (mol^2/J), q_m is the theoretical maximum adsorption capacity (mg/g), ε is the polyani potential (J/mol), which is related to the equilibrium concentration *Ce* (mg/L) as follows:

$$\varepsilon = RT\ln(1+\frac{1}{C_e}) \tag{5}$$

The slope of the plot of ln q_e versus ε^2 (Fig. not shown) gives K_{DR} and the intercept yields the adsorption capacity q_m. The mean free energy of adsorption (E) (KJ/mol) was calculated from the equation.

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

These parameters give 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 [7].

Temkin isotherm model predicts a uniform distribution of binding energies over the population of surface binding adsorption. Linear form of Temkin equation was expressed by:

$$q_e = \beta\ln K_T + \beta\ln C_e \tag{7}$$

$$\beta = \frac{RT}{b}$$

where T is the absolute temperature in Kelvin, *b* is Temkin isotherm constant, R is the universal gas constant (8.314 J/mol), K_T is a constant related to the Temkin isotherm constant (L/mg), and β is the Temkin constant related to the heat of adsorption (J/mol). A plot of q_e versus lnC_e enables one to determine the constants *A & β.* (Fig not shown).

2.4 Sorption kinetic models. The kinetic of dye adsorption on the sorbent were analyzed using pseudo first order equation [28], pseudo second order equation [29] , and intraparticle diffusion models [30] .

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad \text{(pseudo-first order)} \tag{8}$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e}t \quad \text{(pseudo-second order)} \tag{9}$$

$$q_t = k_p t^{0.5} + C \quad \text{(intraparticle diffusion)} \tag{10}$$

where q_e and q_t are the amount of Crystal violet adsorbed (mg/ g) on chitin at equilibrium and at time *t*, respectively, k_1 and k_2 are the rate constant for the pseudo – first order (min^{-1}) and pseudo –second order kinetics (g/mg.min), K_p the intraparticle diffusion rate constant ($mg/gmin^{0.5}$), *C* the intercept for the intraparticle diffusion model (mg/g).

2.5 Thermodynamics of the sorption. The thermodynamic parameters for sorption of the Crystal violet onto chitin obtained from shrimp shell were evaluated using the Langmuir equilibrium constant, K_L, which depends on temperature. The change in free energy (ΔG^o), was evaluated using the following equation [31]

$$\Delta G = -RT\ln K_L \tag{11}$$

where R is the gas constant (J/mol) and T is the temperature (K). The standard enthalpy (ΔH^o) and standard entropy (ΔS^o) changes associated to the sorption process were calculated by eq. (12)

$$lnK_L = \frac{\Delta S^{\circ}}{R} - \frac{\Delta H^{\circ}}{RT} \tag{12}$$

For an exothermic process, ΔH^o is negative [32]. The enthalpy and entropy change of adsorption can be determined from the slope and intercept of the plot of ln K_L versus 1/T.

2.6 Characterization of the chitin sample. The surface morphology of chitin was examined by means of scanning electron microscopy (SEM, Joel JSM 60). The samples were dried and coated with gold before scanning. Specific surface was determined with a Quantachrome Nova Automated Gas Sorption System Report, version 1.12. The measurement is based on the application of the method of Brunauer, Emmet, and Teller (BET). The total pore volume was determined by liquid nitrogen adsorbed at a relative pressure of $P/P_o = 0.98$ [33]. Thermogravimetric (TG) analysis was carried out using Perkin Elmer Diamond TG/ DTG thermogravimetric analyzer instrument. The resolution of this instrument is 0.02µg as a function of temperature. Runs were carried out at linear heating rate 10.00°C/min from 50 to 1000°C under high purity nitrogen. The FTIR of pure chitin was obtained by a Perkin – Elmer FTIR spectrophotometer model spectrum 1000, in the range of 4000-400cm^{-1} using KBr pellets containing the prepared material.

3. RESULTS SECTION

3.1 Effect of pH. The effect of pH on adsorption can be described on the basis of point zero charge (pH_{PZC}), which is the point at which the net charge of the adsorbent is zero. The (pH_{PZC}) of chitin was found to be 6.2. At $pH < pH_{PZC}$, the surface becomes positively charged, concentrations of H+ were high and compete with dye cations for vacant adsorption sites causing a decrease in dye uptake. At $pH > pH_{PZC}$, the adsorbed surface is negatively charged and favors the uptake of cationic dye due to the increase in electrostatic force of attraction [34].

The pH of the solution affects the surface charge of the adsorbents as well as the degree of ionization of different pollutants. The hydrogen ion and hydroxyl ions are adsorbed quite strongly and therefore the adsorption of other ions is affected by the pH of the solution. Change of pH affects the adsorptive process through dissociation of functional groups on the adsorbent surface active sites. This subsequently leads to a shift in reaction kinetics and equilibrium characteristics of adsorption process.

The influence of pH on the Crystal violet adsorption onto chitin is represented in Fig. 3. The results reveal that the adsorption of Crystal violet increase from 15% to 58% with an increase in the pH of the solution from 2.5 to 8. In acid solution, all amino group of the chitin are cationized and protonated as well as Crystal violet (cationic dye)

$$\text{Chitin-NH}_3^+ + H_2O \rightarrow H_3O^+ + \text{Chitin-}\tilde{N}H_2 \qquad pKa= 6.6 \tag{13}$$

Since the p*K*a value of chitin ($\text{Chitin\_ } NH_3^+$) is in the pH range of 6.2–7, the amino groups of chitin are protonated at low pH values. Crystal violet is a cationic basic dye as denoted by the presence of the positive nitrogen ion which enters the aqueous solution ensuring that the dye has an overall positive charge, as a result, this will create a strong columbic repulsion between chitin and Crystal violet [35]. For this reason, the adsorption of Crystal violet onto chitin is low in acidic pH. However, in basic medium, the biopolymer contain functional groups (-OH, NH- C- CH_3 and NH_2), which could be adsorbed by the cationic dye. Also the amino groups of chitin are deprotanated so the adsorption of dye onto chitin at basic pH values is relatively high [36,37].

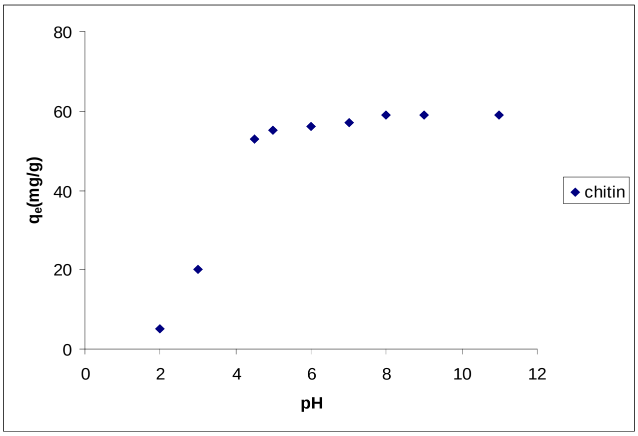

Figure 3: Effect of pH on adsorption of CV onto chitin

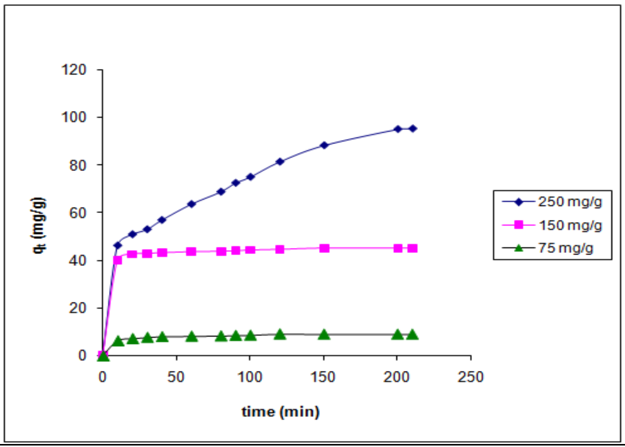

Figure 4: Effect of initial dye concentration and contact time on chitin

3.2 Effect of dye concentration and contact time. The effect of dye concentration on the extent of adsorption as a function of time for the initial dye concentration 250, 150, 75 mg/L at pH=8 is shown in Fig. 4. Available adsorption studies in literature reveal that the uptake of adsorbate species is fast at the initial stages of the contact period, and there after it becomes slower near the equilibrium. In between these two stages of the uptake, the rate of adsorption is found to be nearly constant. This is obvious from the fact that a large number of vacant surface sites are available for adsorption during the initial stage, and after a lapse of time, the remaining vacant surface sites are difficult to be occupied due to repulsive forces between the solute molecules on the solid and bulk phases. According to Fig. 4 the equilibrium adsorption capacity of the sorbent increased with increasing initial dye concentration and the necessary time to reach equilibrium is variable according to the initial concentration of dye; about 2.5h (C_o = 75mg/L), 3h (C_o= 150mg/L) and 4h (Co= 250mg/L) because the initial adsorbate concentration provided an important driving force to overcome all mass transfer resistance. The increase of loading capacity of chitin with increasing initial dye concentration may also be due to higher interaction between dye and chitin. As chitin offered a finite number of surface binding sites, dye adsorption showed a saturation trend at higher initial concentration or in other words, this can be explained on the basis that chitin has amine groups dispersed on the surface and this group has a great ability to adsorb contaminants due to its Lewis base character [38,39].

3.3 Sorption isotherms. The equilibrium data obtained from sorption experiments of Crystal violet from solutions at different temperatures (293,313 and 323 K) onto chitin were fitted to linear Langmuir equation (eq. 11). The values of Langmuir parameters (q_m and K_L) determined by plotting Ce/q versus Ce (Fig. 5) are presented in Table 2. The values of Freundlich parameters (K_F and n) determined from plots of $log\ q_e$ versus $log\ Ce$ together with the corresponding correlation coefficients (R^2) are given in Table 2. The Temkin adsorption data were analyzed according to the linear form of Temkin isotherm (Eq. 13). The R^2 values obtained from Temkin model were comparable to those obtained for Langmuir and Freundlich equations. To determine the nature of sorption process (physical or chemical), a plot of $ln\ qe$ versus ε^2 enabled the determination of the values of D-R isotherms parameters (Table 2). The values of the mean free energy of sorption E calculated with eq.(6) indicates that the process follows a chemical sorption. The values of correlation coefficients higher than 0.99 show that the experimental data were more suitable to the

Table 2: Adsorption Isotherm constants for CV onto Chitin

Adsorption Parameters	**293 K**	**313 K**	**323 K**
Langmuir isotherm constant			
q_m (mg/ g)	37.03	20	18.86
K_L (L/ mg)	0.385	0.038	0.165
R^2	0.988	0.99	0.99
Freundlich isotherm constant			
K_F (mg/ g)	11.22	1.318	3.16
n_F	2.61	1.515	1.85
R^2	0.90	0.89	0.90
Temkin constants			
K_T (L/ mg)	2.9	1.5	2.9
β	304	1083	720
R^2	0.92	0.93	0.93
D-R constants			
q_m (mg /g)	71	20	45
K_{DR} (mol^2/J)	0.068	0.085	0.089
E (KJ/ mol)	14.7	11.8	11.2
R^2_{DR}	0.96	0.97	0.96

Langmuir model of monolayer coverage of chitin with the dye. This may be due to homogeneous distribution of active sites on the material, since the Langmuir model assumes that the surface is homogenous. This model is also based on monolayer, form and finite adsorption site assumptions. It is also noted in Table 2 that the monolayer adsorption capacity q_m (37.03mg/g) is significantly important: this adsorbent exhibit high sorption capacities toward cationic dye at lower temperature [40, 41].

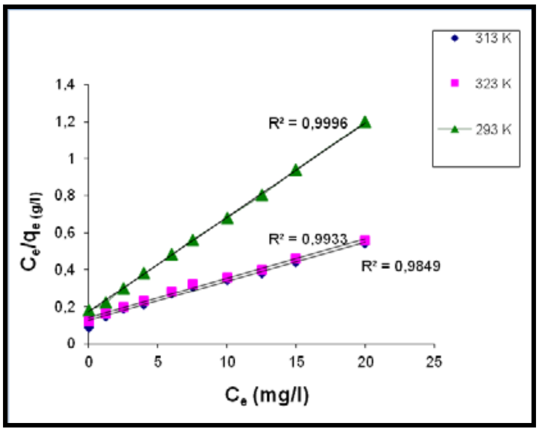

Figure 5: Langmuir isotherm for adsorption of CV onto chitin

Values of the monolayer adsorption capacity obtained in this work was compared with other results reported in literature and are given in Table 3.

Table 3: Adsorption capacities of chitin for different cationic dyes

Adsorbent	***Adsorbate***	***Adsorption Capacity***	***Reference***
Chitin Hydrogels	Malachite green	35.7(mg/g)	[32]
Chitin	Gentian Violet	57.1(mg/g)	[56]
Chitin	Crystal Violet	31.6(mg/g)	[7]
Chitin	Reactive yellow 2	38(mg/g)	[45]
Chitin modified by sodium hydroxide	Synthetic reactive dye waste water	59-124(mg/g)	[55]
Our study	Crystal violet	37.5(mg/g)	

3.4 Adsorption kinetics. The kinetics of adsorption of Crystal violet onto chitin derived from shrimp shell was investigated using three different kinetic models, pseudo-first-order, pseudo-second-order, and intraparticle diffusion models. A series of contact time experiments were conducted out at constant temperature (room temperature) with three different initial dye concentrations (250, 150, 75mg/L). The straight line plots of $1/q_t$ against $1/t$ for the pseudo- first order reaction and t/q_t against t for the pseudo- second order reaction of the adsorption Crystal violet onto chitin have been investigated to obtain the rate parameters. The k_1, k_2, q_e , q^2_e and correlation coefficients R_1^2 and R_2^2 of Crystal violet under different conditions were calculated from these plots and are given in Table 4 [42]. As shown from Table 4, the data shows a good compliance with the pseudo – second order kinetic model suggesting that chemisorption might be the rate limiting step that controlled the adsorption process [43].

Table 4: Kinetic parameters for Crystal violet adsorption onto chitin at different concentrations

	Initial Dye Concentration		
Kinetic Parameters	***250(mg/L)***	***150(mg/L)***	***75(mg/L)***
Pseudo-first order			
k_1(min^{-1})	0.005	0.003	0.005
q_e (mg/ g)	57.5	34.6	16.6
R_1^2	0.90	0.89	0.88
Pseudo-second order			
k_2(g/ mg.min)	4.7×10^{-4}	5.7×10^{-4}	5.8×10^{-3}
q_e (mg/ g)	93.4	56.2	11.9
R_2^2	0.98	0.98	0.99
Intraparticle Diffusion			
K_p (mg min$^{0.5}$/g)	6.0	3.05	0.72
C	30	35	1.8
R^2	0.99	0.98	0.99

According to Fig. 6, a plot of q_t versus $t^{1/2}$ should be a straight line when adsorption mechanism follows the intraparticle diffusion process. Values of K_p, C and R^2 are listed in Table 4, from which it will be seen that the kinetics of the dye sorption on the sorbent follows this model with correlation coefficient higher than 0.988 for all the three experiments carried out with 250, 150, 75mg of sorbent. As shown from Table 4, the values of K_p generally increased with the increase in dye concentration, which shows that the adsorption rate is governed by the diffusion of the dye within the pores of the adsorbent [44]. The intercept of the plot reflects the thickness of the boundary layer.

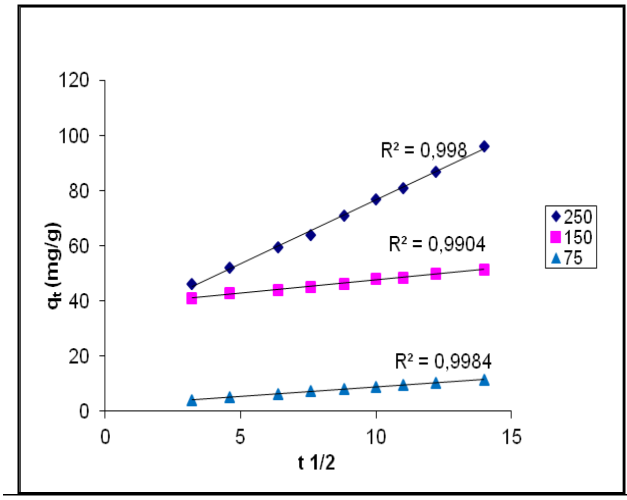

Figure 6: Intraparticle diffusion of CV onto chitin for various initial concentration

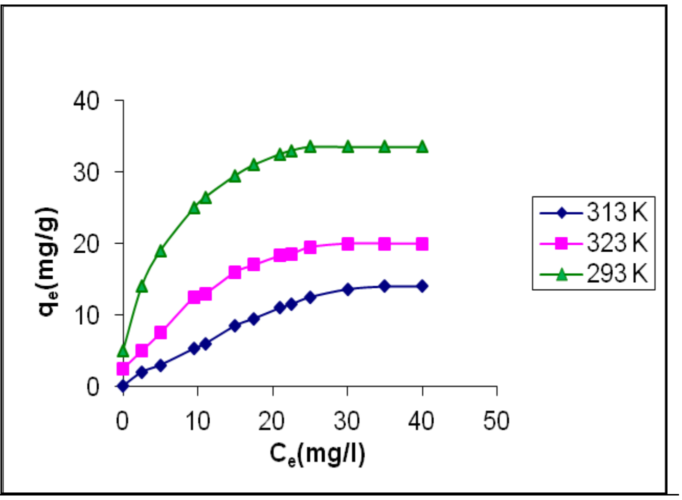

Figure 7: Adsorption isotherms of CV on chitin at different temperatures

If the regression of the plot is linear and passes through the origin, then diffusion is the sole rate – limiting step. However, in this study the linear plots at each concentration did not pass through the origin. The deviation of straight lines from the origin may be due to the difference in rate of mass transfer in the initial and final stages of adsorption. Such a deviation from the origin indicates that the pore diffusion is only the controlling step and not the film diffusion (i.e. the linear portion of the curves do not pass through the origin suggesting that the mechanism of Crystal violet removal on chitin is complex and may involve a chemical reaction process) chemisorptions reaction or an activated process was becoming predominant the rate controlling step [45, 42].

3.5 Determination of thermodynamic parameters. The study of the adsorption process with respect to temperature can give valuable information about the free energy as well as the enthalpy change during adsorption. The effect of temperature on the adsorption capacities was studied by carrying out a series of experiments at 293,303 and 313 K. It was observed that the amount adsorbed of Crystal violet onto chitin decreases with increase in temperature from 293 to 313K (Fig. 7). The observed decrease in the adsorption of Crystal violet on chitin with increase in temperature is indicative of the fact that the adsorption process is exothermic in nature. The increase in temperature of the system affects the solubility and particularly the chemical potential of the adsorbate dye which is known to be a controlling factor in the process of adsorption [46, 47]. It has been reported earlier by several workers [48], that with the increase of temperature, the solubility of the dye also increases, so the interaction forces between the solute and the solvent become stronger than solute and adsorbent, consequently the solutes are more difficult to adsorb.

As depicted from Table 5 the negative values of $\Delta G°$ confirm the feasibility of the process and the spontaneous nature of adsorption. The change in enthalpy, ΔH°, was found to be negative confirming the exothermic nature of the adsorption. The negative value of ΔS^o described the decrease in randomness at the adsorbent solution interface during the adsorption of dye on chitin [49-51].

Table 5. Thermodynamic parameters for adsorption of CV onto chitin (C_o = 100ppm)

Temperature(K)	*ΔH (kJ/mol)*	*ΔS (J/mol K)*	*ΔG (kJ/mol)*
293	-67.97	-129.1	-29.12
313			-25.06
323			-29.82

3.6 Characterization of the adsorbent

3.6.1 FTIR Analysis. As shown in Fig. 8, the common, large and intense bands located at 3500-3000 cm^{-1} can be attributed to axial OH and NH group deformation. On the other hand, the adsorption band at nearly $3430cm^{-1}$ can be assigned to the hydrogen between OH on carbon 5 of the biopolymer structure with the carbonylacetamide, attributed to amide in the $1700cm^{-1}$ region [52].

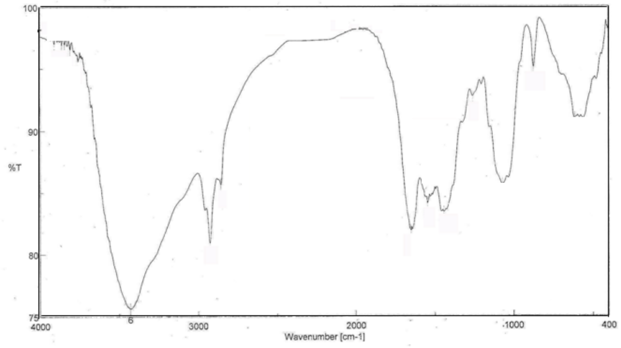

Figure 8: FTIR spectra of chitin

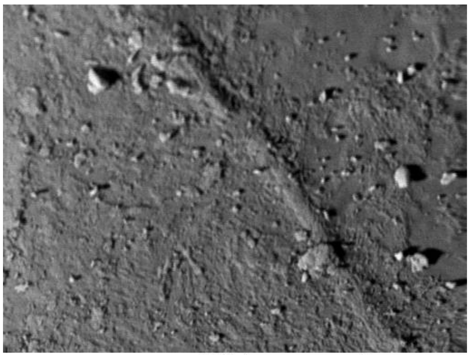

Figure 9:SEM images of chitin

The other adsorption at 3000- 2800 cm^{-1} is associated to the axial carbon – hydrogen bond. The symmetrical and asymmetrical carbon – oxygen carbon ring gives rise to the bands located at 1050 and 1200 cm^{-1} respectively. The band observed at 1650 and 1450 cm^{-1} correspond to N- H bending vibrations. Finally, it is important to mention the absorptions at 1440 and 1600 cm^{-1} that are assigned as CH_2- CH bending bands [52].

3.7 SEM, TG and BET analysis. Fig. 9 represents the scanning electron microscope (SEM) of chitin. The SEM shows that chitin is made of several very thin sheets of material loosely bound together with porous and heterogeneous surface structure [53]. Fig. 10 illustrates the TG- DTG curve of chitin which represents the stages of thermal decomposition behavior of chitin. The first thermal event represents a peak at 183.3^{o}C coupled with weight – loss 13.27%.This thermal event was related to the evaporation of water present in the sample. The second main thermal event for chitin was a peak coupled with weight – loss 28.94%, when heated around 326.67^{o}C. This is expected to be due to the depolymerisation of chitin. In the temperature range of 326.67 to 885^{o}C a weight loss (18.14%) was observed which was related to the formation of volatile low molecular products and the formation of char [54].

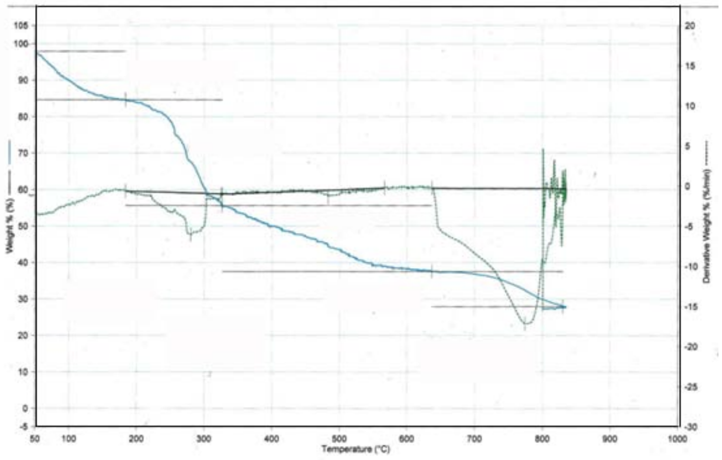

Figure 10: TG curves of Chitin

The BET surface area, average pore volume and pore width of chitin are shown in Table 1. From the pore size distribution data, results revealed that chitin exhibited a small amount of microporous character in the range 5-13Å, while a huge rise of its mesopore character was observed in the range 36.5Å, which plays a significant role in the adsorption of Crystal violet (bulky molecule).

4. CONCLUSIONS

The present investigation showed that chitin extracted from the shrimp shell has appreciable adsorption capacity for the removal of Crystal violet from aqueous solution. The adsorption process of Crystal violet dye onto chitin was found to be dependent on the system temperature, dye solution pH and initial dye concentration. Based on value of correlation coefficient (R^2), the adsorption experimental data was fitted for Langmuir model (monolayer adsorption capacity of 37 mg/ g at 293 K) than Freundlich, Temkin isotherm models. The value of mean free energy E, evaluated by Dubinin – Radushkevitch suggest that the process follows a chemical sorption. isotherm models. The negative values ofΔ $G°$ andΔ $H°$ suggested the studied adsorption process was spontaneous and exothermic in nature. The adsorption kinetics was well described by the pseudo – second order kinetic model and intraparticle diffusion mechanism.

5. REFERENCES

[1] Vandevirere P.C., Bianchi R., Verstraete W., Treatment and reuse of waste water from the textile wet processing industry: review of emerging technologies, *J. Chem. Technol. Biotechnol.*, 72, 289-302, **1998.**

[2] Zollinger H., *Color chemistry* – Synthesis, properties and applications of organic dyes and pigments, Third ed. Wiley- VCH, Weinheim – Fedral Republic of Germany, **2001**.

[3] Weber E., Wolfe N.L., Kinetic studies of reduction of aromatic azo compounds in anerobic sediment / water systems, *Environ. Toxicol. Chem.*, 6, 911-920, **1987**.

[4] Dabrowski A., Adsorption- from theory to practice, *Adv. Col. Interf. Sci.*, 93, 135-224, **2001**

[5] Perkkuz H., Uzun I., Guzel F., Kinetics and thermodynamics of the adsorption of some dyestuffs from aqueous solution by polar sawdust, *Biores. Technol.*, 99, 2009-2017, **2008**.

[6] Bekci Z., Özveri C., Seki Y., Yurdakoc K., Sorption of malachite green on chitosan bead, *J. Hazard. Mat.*, 154, 254-261, **2008.**

[7] Ling S.L.Y., Yee C.Y., Eng H.S., Removal of a cationic dye using deacetylated chitin (chitosan), *J. Appl. Sci.*, 11, 1445 -1448, **2011**.

[8] Robinson T., McMullan G., Marchant R., Nigam P., Remediation of dyes in textile effluent; a critical review on current treatment technologies with a proposed alternative, *Biores. Technol.*, 77, 247-255, **2001**.

[9] Saha T.K., Bhoumik N.C., Karmaker S., Ahmed M.G., Ichi H.K., Fukumori Y., Adsorption of Methyl orange onto Chitosan from aqueous solution, *J. Wat. Res. Protect.*, 2, 898-906, **2010.**

[10] Girgis B.S., Attia A.A., Fathy N.A., Potential of nano- carbon xerogels in the remediation of dye-contaminated water discharges, *Desalination*, 265, 169 – 176, **2011**.

[11] Attia A.A., Girgis B.S., Fathy N.A., Removal of methylene blue by carbons derived from peach stones by H_3PO_4 activation: Batch & column studies, *Dyes & Pigments*, 76, 282-289,**2008**.

[12] Attia A.A., Girgis B.S., Khedr S.A., Capacity of activated carbon derived from pistachio shells by H_3PO_4 in the removal of dyes and phenolics, *J. Chem. Technol. Biotechnol.*, 78, 611-619,**2003.**

[13] Dursun A.Y., The effect of pH on the equilibrium of heavy metal bisorption by *Aspergillus miger*, *Fresenius Environ. Bull.*, 12(11), 1315-1322, **2003**.

[14] Kim S.K., Rajapakse N., Enzymatic production and biological activities of chitosan oligosaccharides (COS): A review. *Carboh. Pol.*, 62 (4), 357-368, **2005**.

[15] Marthur N.K., Narang C.K., Chitin and Chitosan, versatile polysaccharides from marine animals, *J. Chem. Ed.*, 67 (11), 938 -942. **1990**.

[16] Dutta P.K., Ravikumar M.N.V., Dutta J., Chitin and chitosan for versatile applications, *J. Macromol. Sci., Pol. Rev.*, C42, 307-354, **2002**.

[17] Majeti N.V., Kumar R ., A review of chitin and chitosan applications. *React. Funct. Pol., 46*, 1-27, **2000**.

[18] Blackburn R., Natural polysaccharides & their interactions with dye molecules: applications in effluent treatment, *Environmen. Sci. Technol.*, 38, 4905-4909, **2004**.

[19] Sugimoto M., Morimoto M., Sashiwa H., Saimoto H., Shigemasa Y., Preparation and characterization of water- soluble chitin and chitosan derivatives, *Carboh. Pol.*, 36, 49-59, **1998**.

[20] McKay G., Bino M.J., Adsorption of pollutants from wastewater onto activated carbon based on external mass transfer and pore diffusion. *Water Res.*, 22**,** 279, **1988**.

[21] Mckay G, El-Geundi M, Nassar M.M. Equilibrium studies during the removal of dyestuffs from aqueous sol utions using bagasse pith. *Water Res.*, 21**,** 1513, **1987**.

[22] Morais L.C., Freitas O.M., Gonclves E.P., Vasconcelos L.T., Gonzhlez Beca C.G., Reactive dyes removal from wastewaters by adsorption on eucalyptus bark: variables that define the process. *Water Res.* 33**,** 979, **1999**.

[23] *Jia Y. F.*, Xiao B., *Thomas K. K.*, Adsorption of metal ion on nitrogen surface functional groups in activated carbon. *Langmuir.*, *18*, *470* – 478, ***2002***.

[24] Langmuir I., The adsorption of gases on plane surfaces of glass, mica and platinum. *Journal of American Chemical Society*. 40**,** 1361-1403, **1918**.

[25] Freundlich H.M.F., Über die adsorption in lösungen, *Zeitsdchrift für Physikalische Chemie*, 57, 385-470, **1906**.

[26] Temkin M.J., Pyzhev, V., Kinetics of ammonia synthesis on promoted iron catalyst, *Acta Physicochimie URSS*,12, 217-222,**1940**.

[27] Dubinin M.M, and Radushkevitch L.V., Equation of the characteristic curve of activated charcoal, *Chem. Zentr*. 1, 875-890, **1947.**

[28] Langergren S., Svenska B.K., Zur theorie der sogenannten adsorptiongeloester stoffe, *Veternskapsakad Handlingar*, 24 (4), 1–39, **1898.**

[29] Ho Y.S., Mckay G., Pseudo – Second order model for sorption processes, *Process Biochem.*, 34, 451-465, **1999**.

[30] Weber W.J., Morris J.C., Kinetics of adsorption on carbon solution, *J. San. Eng., Diverse Am. Soc. Civ. Eng.*, 89, 31-59, **1963**.

[31] Barka N., Abdennouri M., EL Makhfouk M., Removal of Methylene Blue and Eriochrome Black T from aqueous solutions by biosorption on *Scolymus hispanicus* L.: Kinetics, equilibrium and thermodynamics, *J. Taiwan Inst. Chem. Eng.* ,42**,** 320-326, **2011.**

[32] Tang H., Zhou W., Zhang L., Adsorption isotherms and kinetic studies of malachite green on chitin hydrogels, *J. Haz. Mat.*, Article in Press, **2012**.

[33] Brunauer S., Emmett P.H., Teller E., Adsorption of gases in multimolecular layers, *J. Am. Chem. Soc.,* 60, 309-319, **1938**.

[34] Mall I. D., Srivastava V. C., Kumar G. V. A., Mishra I. M., Characterization and utilization of mesoporous fertilizer plant waste carbon for adsorptive removal of dyes from aqueous solution. *Col. Surf. A: Physicochem. Eng. Aspect.*, 323, 47-53, **2006.**

[35] Kyzas G.Z ., Lazaridis N.K., Reactive and basic dye removal by sorption onto chitosan derivatives, *J. Col. Interf. Sci.*, 331, 32-39,**2009**.

[36] Samiey B., Toosi A., Kinetic of malachite green fading in alchol –water binery mixtures , *Int. J. Chem. Kinetic.*,42,508-518,**2010**.

[37] Sakkayawong N., Thiravetyan P., Nakbanpote W., Adsorption mechanism of synthetic dye waste water by chitosan, *J. Col. Interf. Sci.*, 286, 36-42, **2005.**

[38] Knorr D., Dye binding Properties of Chitin and Chitosan, *Journal of Food Science,* 48(1), 36-37,**1938.**

[39] Benguella B., Benaissa H., Cadmuim removal from aqueous solutions by chitin: Kinetic & equilibrium studies, *Water Res.*, 36, 2463-2474, **2002.**

[40] Grini G., Non conventional low – cost adsorbents for dye removal: a review, *Bioresource Technol.*, 97, 1061-1085, **2006.**

[41] Grini G., Recent developments in polysaccharide – based materials used as adsorbents in waste water treatment, *Progressive. Pol. Sci.*, 30, 38-70, **2005.**

[42] Ho Y.S., Mckay G., Kinetic models for the sorption of dye from aqueous solution by wood, *Trans. I. Chem. E.*, 73, 183-191, **1998.**

[43] Dogan M., Özolemir Y., Alkan M., Adsorption kinetics and mechanism of cationic methyl violet and methylene blue dyes onto sepiolite, *Dyes & Pigment*, 75, 701-713, **2007.**

[44] Kadirvelu K., Karthika C., Venilamani N., Pattabhi S., Activated carbon prepared from industrial solid waste as an adsorbent for the removal of Rhodamine B from aqueous solution. Kinetic and equilibrium studies. *Chemosphere*, 60, 1009-1017, **2005**.

[45] Akkaya G., Uzun I., Guzel F., Kinetic of the adsorption of reactive dyes by chitin, *Dyes & Pigments* ,73, 168-177,**2007**.

[46] Elizalde- Gonzalez M.P., Pelaez- Cid A.A., Removal of textile dyes from aqueous solution by adsorption on biodegradable waste, *Environ. Technol.*, 24, 821-829, **2003**.

[47] Annadurai G., Krishnan M.R.V., Adsorption of basic dye using chitin. *I. J. Environ. Prot.*, 16, 444-449, **1996.**

[48] Saha T.K., Karmaker S., Ichikawa H., Fukumori Y., Mechanisms & Kinetics of trisoduim 2- hydroxyl -1, 1 azo naphthalene -3, 6, 6- trisulfonate adsorption onto chitosan, *J. Col. Interf. Sci.*, 286, 433-439,**2005**.

[49] Chiou M.S., Li H.Y., Adsorption behavior of reactive dye in aqueous solution on chemical cross- linked chitosan beads, *Chemosphere*, 50, 1095 -1105, **2003.**

[50] Akkaya G., Uzun I., Guzel F., Adsorption of some highly toxic dyestuffs from aqueous solution by chitin and its synthesized derivatives, *Desalination*, 249, 1115-1123,**2009**.

[51] Khan T.A., Singh V.V., Kumar D, Removal of some basic dye from artificial textile waste water by adsorption on Akash Kinari coal, *J. Sci. Ind. Res.*, 63, 355-364, **2004.**

[52] Lima I.S, Airoldi C.A., Thermodynamic investigation on chitosan – divalent cation interactions, *Thermochimica Acta.*, 421 (1, 2), 133-139, **2004**.

[53] Maruca R, Jo Sunder B., Wightman J.P., Interaction of heavy metals with chitin & chitosan. III. Chromium, *J. Appl. Pol. Sci.*, 27, 4827-4837, **1982**.

[54] Wanjun T., Cuxin W., Donghua C., Kinetic studies on the pyrolysis of chitin and Chitosan, *Pol. Deg. Stab.*, 87, 389-394, **2005**.

[55] Dolphen R., Sakkayawong N, Thiravetyan P, Nakbanpote W., Adsorption of Reactive Red 141 from wastewater onto modified chitin, *J. Haz. Mat.*,145,250-255, **2007**.

[56] Shirsath D.S, Shrivastava , V.S., Removal of Hazardous dye Ponceau-S by using chitin, An organic bioadsorbent, *Afr. J. Environ. Sci. Technol.*, 6(2), 115-124, **2012**.