Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Nandi, B. K. , Goswami, A. , Das, A. K. , Mondal, B. and Purkait, M. K.(2008) 'Kinetic and Equilibrium Studies on the Adsorption of Crystal Violet Dye using Kaolin as an Adsorbent', Separation Science and Technology, 43: 6, 1382 — 1403

To link to this Article: DOI: 10.1080/01496390701885331

URL: http://dx.doi.org/10.1080/01496390701885331

Separation Science and Technology, 43: 1382–1403, 2008

ISSN 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390701885331

Kinetic and Equilibrium Studies on the Adsorption of Crystal Violet Dye using Kaolin as an Adsorbent

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Abstract: Experimental investigations are carried out to adsorb toxic crystal violet dye from aqueous medium using kaolin as an adsorbent. Characterization of kaolin is done by measuring

i. particle size distribution using particle size analyzer,
ii. BET surface area using BET surface analyzer,
iii. structural analysis using X ray diffractometer, and
iv. microscopic analysis using scanning electron microscope.

The effects of initial dye concentration, contact time, kaolin dose, stirring speed, pH, and temperature are studied for the adsorption of crystal violet in batch mode. Adsorption experiments indicate that the extent of adsorption is strongly dependent on the pH of the solution. Free energy of adsorption (ΔG^o), enthalpy (ΔH^o), and entropy (ΔS^o) changes are calculated to know the nature of adsorption. The calculated values of ΔG^o are -4.11 and -4.48 kJ/mol at 295 K and 323 K, respectively, for 20 mg/L of dye concentration, which indicates that the adsorption process is spontaneous. The estimated values of ΔH^o and ΔS^o show the negative and positive sign, respectively, which indicate that the

Received 16 April 2007, Accepted 9 December 2007

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adsorption process is exothermic and the dye molecules are organized on the kaolin surface in more random fashion than in solution. The adsorption kinetic has been described by pseudo first order, pseudo second order and intra-particle diffusion models. It is observed that the rate of dye adsorption follows pseudo second order model for the dye concentration range studied in the present case. Standard adsorption isotherms are used to fit the experimental equilibrium data. It is found that the adsorption of crystal violet on kaolin follows the Langmuir adsorption isotherm.

Keywords: Crystal violet, kaolin, adsorption isotherm, zero point charge, SEM

INTRODUCTION

Dye containing waste stream is one of the major toxic industrial waste. Various types of dyes are used in the process industries like textile, paints, pulp and paper, carpet and printing etc. The effluents containing dyes are highly colored and cause water pollution. Dyes are broadly classified as anionic, cationic, non-ionic, and zwitterionic depending on the ionic charge on the dye molecules. Cationic dyes are more toxic than anionic dyes (1). Crystal violet (CV) is one of the commonly known cationic dye used for various purposes e.g. biological stain, dermatological agent, veterinary medicine, an additive to poultry feed to inhibit propagation of mold, intestinal parasites, and fungus etc. It is also extensively used in textile dying and paper printing. In the present work, treatment of crystal violet dye containing aqueous stream by adsorption technique is addressed.

Research is being carried out using different treatment technologies e.g. chemical coagulation-flocculation (2), different type of oxidation processes (3), biological processes (4), membrane based separation processes (5–7), adsorption (8) etc. for the removal of colored dye from wastewater. Each of the above processes have their own benefits and limitations. Adsorption on solid surface is of growing interest in this field because of its lower price. Activated carbon is one of the common adsorbents due to its high surface area and high adsorption capacity. But its high cost makes the process uneconomical for industrial applications.

Therefore, the process of dye removal by adsorption is being diverted to the use of lower cost adsorbents so that the process becomes economically feasible. For this reason, researches are focused on to use of low-cost, reusable, locally available, biodegradable adsorbents made from natural sources like wheat bran (9), rice husk (10), waste apricot (11), bagasse fly ash (12), powdered peanut hull (13) etc. Natural and modified clays like sepiolite (14), zeolite (15), perlite (16), and bentonite (17) are being considered as alternative low-cost adsorbents.

Adsorption of organic molecules to an adsorbent depends on various factors like; temperature, pH of the solution, the structure and concentration of the adsorbing molecule, the ionic strength of the suspension, and the structure of the adsorbent. However, adsorption over a surface with highly ionic character is mostly effective and very fast for a dye with opposite ionic character. Kaolin is one of the very common low costs natural clay adsorbent with ionic crystalline structure. Kaolinite is a 1:1 aluminosilicate consisting chemical composition SiO_2: 46.5 wt%, Al_2O_3: 39.5 wt% and H_2O: 14 wt% (18). Its crystalline structure consists of stacked pairs of tetrahedral silica sheets and octahedral alumina sheets. Each pair of sheets is bound together through common oxygen atoms, and successive pairs are held together by hydrogen bonding between silica-oxygen and aluminaum-hydroxyl groups. Hence, the resulting crystal contains a silica face of SiO_2 tetrahedra, an alumina face carrying AlOH groups, and edges which carry both SiOH and AlOH sites. The surfaces of kaolinite are believed to carry a constant structural negative charge due to the isomorphous substitution of Si^{4+} by Al^{3+} in silica layer, whereas the charge on the alumina face and on the edges due to the protonation/deprotonation of exposed hydroxyl groups and depend on the pH of the solution (19).

Although several works have been done on adsorption of basic dyes on kaolin, the present work gives detailed information about the adsorption of crystal violet dye on kaolin. Very few works on the adsorption on crystal violet dye are reported. Adsorption experiments using kaolin as an adsorbent have been carried out on different other basic dyes such as methylene blue, malachite green etc (20, 21). They observed the usability of kaolin as an adsorbent for the removal of basic dyes only. Systematic experimentations that include characterization of adsorbent, stirring effect, role of pH, temperature, and the dose of the adsorbent as well as the adsorbate are yet to be done. Again, determination of various thermodynamic parameters, kinetic and equilibrium model parameter will also be the further scope of research.

In the present study, experiments are carried out to remove crystal violet dye by adsorption technique using kaolin as an adsorbent. Characterization of kaolin is done by measuring the particle size distribution, the BET surface area, and the SEM analysis. Influences of temperature, pH of dye solution, effect of adsorbent dose, and initial dye concentration are studied under stirred condition. Thermodynamic parameters are calculated to know the nature of adsorption. Three different kinetic models for the adsorption of dye are presented. The equilibrium data are tested with Langmuir and Freundlich isotherm models. This fundamental study will be helpful for further application in designing a batch adsorber for the treatment of dye containing effluent coming out from dying industries.

EXPERIMENTAL

Materials and Methods

Crystal violet dye (C.I.: 42555, FW: 408, λ_{max}: 584 nm, Dye content: 92%), supplied by Qualigens, Fine Chemicals, Mumbai, India is used as an adsorbate. Structure of the crystal violet molecule is shown in Fig. 1. Crystal violet molecule exists as cation in acidic medium, which reacts with

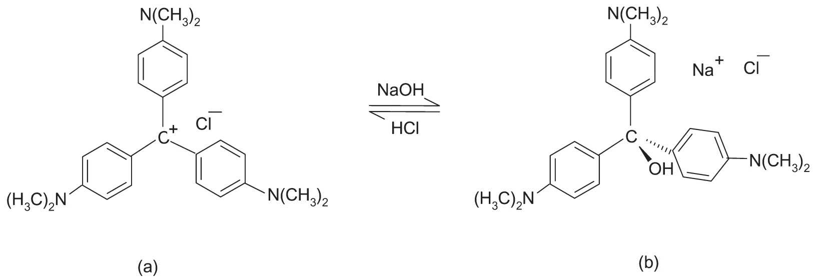

Figure 1. Structure of crystal violet molecule (a) in acidic pH (<7), (b) in basic pH (>7).

NaOH to produce a colorless neutral molecule. The violet color starts disappear from pH 9.5 and above. This is due to the formation of CVOH. Thus, the color of crystal violet solution in aqueous medium is very sensitive to OH^- ion concentration. pH of the solution is maintained by using 0.1 N HCl and 0.1 N NaOH solution. NaOH and 0.1 N HCl solutions are obtained from Merck, India. Kaolin, natural clay is procured from Central Drug House (P) Ltd. New Delhi, India and used without any further purification. The characteristics of kaolin are presented in Table 1. The zero point charge (ZPC) of kaolin used for the adsorption experiment is determined by using solid to liquid ratio of 1:1000. For this, 0.1 mg of kaolin is added to 100 ml of water with varying pH from 2 to 12 and stirred for 24 hours. Final pH of the solution is plotted against initial pH of the solution and shown in Fig. 2. pHZPC for kaolin is determined as pH 7.0.

Batch experiments are carried out using a 2 L capacity glass beaker at ambient temperature (22 ± 2°C). Stock solution of crystal violet of concentration 1000 mg/L is prepared by dissolving an accurately weighed quantity (1.0 g) of solid dye in 1 L of deionized water (pH is 6.9). Experimental

Table 1. Characteristics of kaolin

Property	Kaolin
Average particle size	2.37 μm
Moisture (at 105°C for 2 hr)	0.13%
Acid soluble(as sulphate)	0.5%
Water soluble	Nil
Specific surface area (m^2/g)	13.69
Free settling velocity ($u_t{}^a$, m/s) (in aqueous medium)	
Laminar zone	5.09×10^{-6}
Turbulent zone	3.38×10^{-4}

[a] $u_t = D^2(\rho_S - \rho)g/18\mu$ for $N_{\mathrm{Re}} < 0.1$ and $u_t = \left[4D(\rho_s - \rho)g/3C_p\right]^{0.5}$ for $N_{\mathrm{Re}} \geq 0.1$ and where, D is the diameter of particle, ρ_s is the particle density, ρ the fluid density, m is the fluid viscosity, C_p (=0.44) is the drag coefficient.

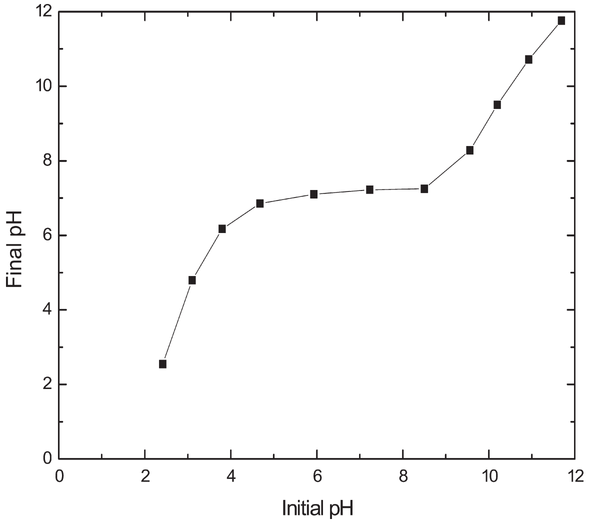

Figure 2. Zero point of charge (ZPC) of commercial kaolin used for the adsorption experiments.

solutions of desired concentrations are obtained by successive dilution of the stock solution. Standard technique is used to determine the dye concentration using UV-Vis spectrophotometer (22). Initial dye concentrations are varied from 10 to 100 mg/L. The pH of the solution decreases gradually with increasing concentration of dye and is shown in Fig. 3 for the initial dye concentration of 10–100 mg/L. For studying the effect of solution pH on dye adsorption, experiments in different pH (varying from 3 to 9.5) have been conducted for initial dye concentration of 20 mg/L. To observe the effect of adsorbent dose on dye adsorption, different amounts of adsorbent (varying from 0.25–4.0 g/L) are used with three different initial dye concentrations e.g. 20, 30, and 40 mg/L. To observe the effect of temperature on dye adsorption, experiments are carried on three different concentrations (20, 30, 40 mg/L) at three different temperatures (22°C, 40°C, and 50°C), where all other variables remain unchanged. A common adsorbent dose of 1 g/L, stirring speed of 2500 rpm and pH 7 is used for all the above experiments. Magnetic stirrer (Icon instruments, India, length of stirrer: 2.0 cm) is used for stirring purpose Three different agitation speeds of 500 ($N_{\mathrm{Re}} = 0.34 \times 10^4$) 1500 ($N_{\mathrm{Re}} = 1.04 \times 10^4$) and 2500 ($N_{\mathrm{Re}} = 1.7 \times 10^4$) rpm are used for observing the effect of turbulence on the dye adsorption. Where, N_{Re} is the Reynolds number. Calculation of N_{Re} is shown in Appendix 1.

In order to study the adsorption isotherm, 0.1 g of kaolin is kept in contact with 100 ml dye solution of different concentrations (10, 20, 30, 40, 60, 80, and 100 mg/L) at pH 7 for 24 hours with constant shaking at ambient temperature of 22 ± 2°C. After 24 hours the solution attains equilibrium and the amount of dye

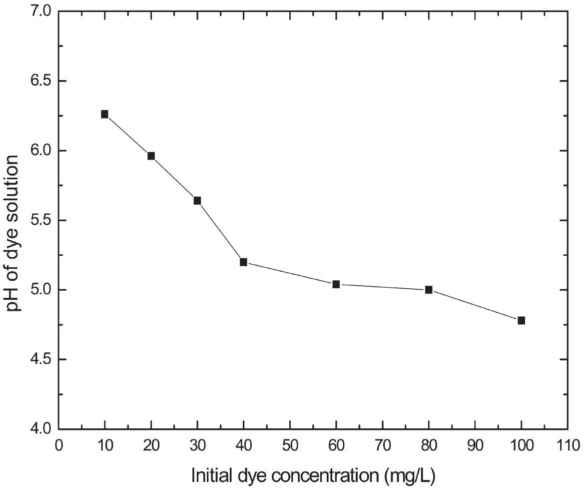

Figure 3. Variation of pH of the dye solution with initial concentration of crystal violet.

adsorbed (mg/g) on the surface of the adsorbent is determined by the difference of the two concentrations. Duplicate experiments are carried out for all the operating variables studied and only the average values are taken in to consideration. The average deviation of duplicate results in the units of concentration is found to vary as ±2%. Blank experiments are carried out with dye solution and without the adsorbent to ensure that no dye is adsorbed onto the walls of the beakers.

Instruments

The particle size distribution of kaolin is evaluated using a laser particle size analyzer (Malvern, Mastersizer 2000). A BET surface analyzer (SA 3100, Beckman Coulter) is used to measure nitrogen adsorption isotherm at 77 K. Before measurement, the sample is degassed using Helium at 553 K for 3 hour. The BET surface area, total pore volume, average pore radius, micropore area are obtained from the adsorption isotherms. Mesopore volume is determined by subtracting the micropore volume from the total pore volume. Structural analysis of the kaolin is done by X ray diffractometer (D8 ADVANCE, Bruker Axs). Microscopic analysis of kaolin and dye-adsorbed kaolin is performed using a Scanning Electron Microscope (Oxford, Leo 1430VP). A digital pH meter (Century Instruments (P) Ltd, Chandigarh, India) is used to measure the pH of the solution. The concentration of dye solution is determined spectrophotometrically using a UV-Vis spectrophotometer (Perkin-Elmer Precisel, Lamda-35) at a wave length of 584 nm.

Dye Uptake

The amount of dye adsorbed per unit weight of kaolin at time t, q_t (mg/g) and percentage dye removal efficiency, $R$are calculated as follows

$$q_t = \frac{(C_0 - C_t)V}{M} \tag{1}$$

$$R = \frac{C_0 - C_t}{C_0} \times 100 \tag{2}$$

Where, C_0 is the initial dye concentration (mg/L), C_t is the concentration of dye at any time t, $V$is the volume of solution (L) and M is the mass of kaolin (g).

RESULTS AND DISCUSSION

Characterization of Adsorbent

The particle size distribution of kaolin, determined by the laser particle size analyzer is shown in Fig. 4(a). It shows that the size of the kaolin particles are in the range of 0.23 μm to 20 μm. More than 90% particles are of below 5 μm. Average particle size of the adsorbent is 2.37 μm. The X-ray diffraction (XRD) patterns of kaolin is shown in Fig. 4(b). It shows that kaolin used for the experiment is ideal kaolinite [$Al_2Si_2O_5(OH)_4$] with anorthic (triclinic) lattice structure and the corresponding lattice parameters are $a = 5.15$, $b = 8.94$, $c = 7.40$ with $a/b = 0.57$, $c/b = 0.83$, $\alpha = 91.69$, $\beta = 104.61$, $\gamma = 89.82$ and $Z = 2$. The specific surface area of the kaolin determined from BET surface area analyzer is 13.72 m^2/g. Figure 4(c) shows the pore size distribution curves of adsorbents based on the nitrogen equilibrium adsorption isotherms at 77 K. It may be found from this figure that these materials exhibit multimodal distribution in both the micropore and mesopore domains. About 51% of total pores are in the range of pore diameter below 40 nm with total pore volume of $0.033\ ml/g \cdot nm$, suggesting that the material contain a very high volume of micropores. The second fraction of pores appears in the field from 40 to 100 nm evidenced by a broad peak in that area. In this range pore volume is $0.025\ ml/g \cdot nm$ with 39% of total pore volume. This indicate the existence of the mesopores in the sample.

SEM Studies

SEM analysis is one of the most widely used method for the surface morphology and physical properties of the adsorbent. SEM photographs for

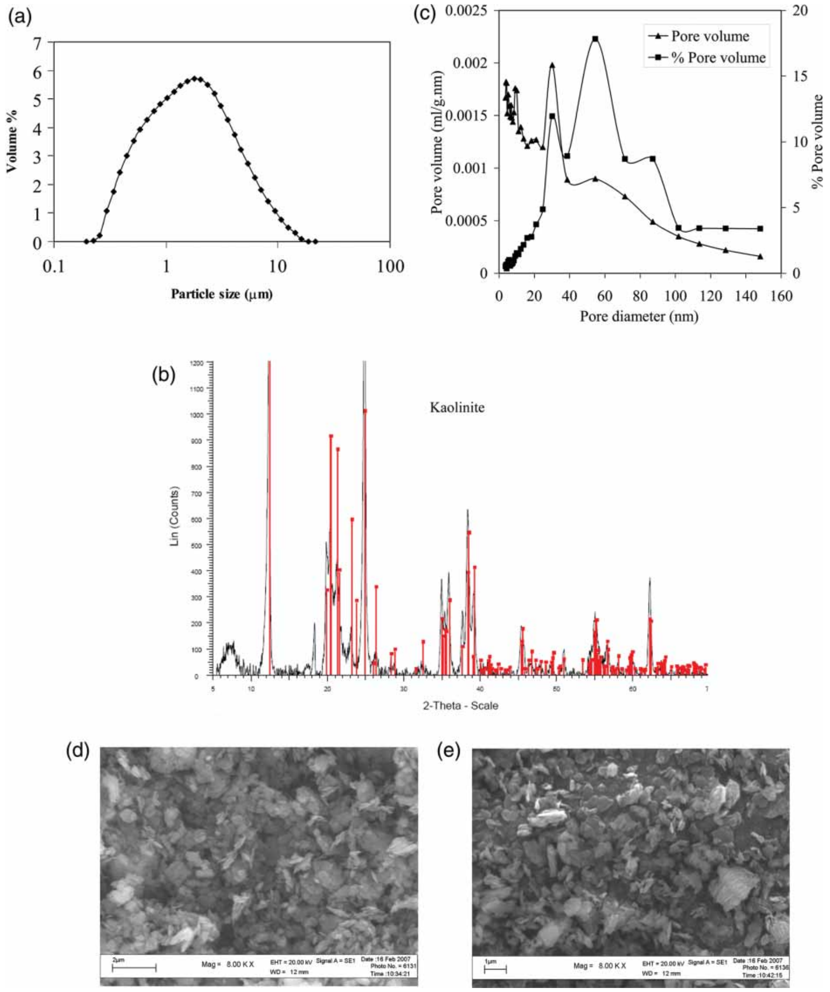

Figure 4. (a) Particle size distribution of kaolin; (b) XRD of kaolin; (c) Pore size distribution of kaolin particles; (d) SEM photograph of kaolin (before adsorption experiment). Magnification = 8.00 KX; (e) SEM photograph of kaolin (after adsorption experiment) using 20 mg/L of crystal violet dye at pH 7. Magnification = 8.00 KX.

kaolin and dye adsorbed kaolin are shown in Figs. 4(d) and 4(e), respectively. From the photographs it is evident that almost all particles of kaolin are of below 2 μm. Microscopic studies suggest that there is no significant change in the surface structure of the kaolin after the dye adsorption. SEM pictures also suggest that kaolin surface still has some open pore after the dye adsorption.

Adsorption Studies

Effect of Contact Time and Initial Dye Concentration

The variation in percentage removal of dye with contact time at different initial concentrations ranging from 10 to 100 mg/L is presented in Fig. 5. It may be observed from the figure that the maximum amount of dye adsorption taking place within the contact time of 5 minutes and attains equilibrium there after. This indicates that the rate of adsorption is very fast. Data has been taken upto 30 minutes of operation which is more than sufficient to attain equilibrium. After that no significant change in the extent of adsorption is observed. For the initial concentration of up-to 40 mg/L, more than 90% adsorption has been observed, whereas for 80 and 100 mg/L, the percent removal of dye is 89 and 87%, respectively. From the above observation, it is evident that for lower initial concentration of dye, the adsorption is very fast. The percent removal of dye decreases with increase in initial concentration and takes longer time to reach equilibrium because of the fact that with increase in dye concentration, there will be increased competition for the active adsorption sites and the adsorption process will increasingly slow down. This explains the more adsorption time for higher concentration.

Effect of Adsorbent Dose

The effect of kaolin dose (varying from 0.25 g/L to 4.0 g/L) on the percentage removal of dye at three different initial dye concentrations, like; 20,

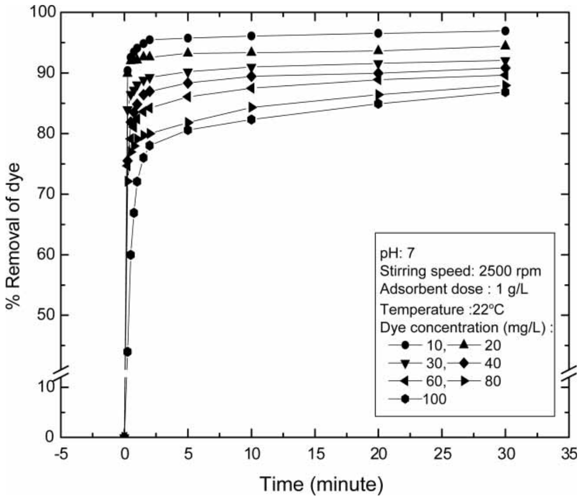

Figure 5. Effect of contact time and initial concentration of crystal violet on the extent of adsorption.

30, and 40 mg/L is shown in Fig. 6. It is observed from the figure that the dye removal increases with increase in kaolin dose up to a certain limit (1 g/L) and then the rate of increase is slowed down. Initially, rapid increase in the adsorption with the increase in the adsorbent dose can be attributed to a greater surface area and availability of more adsorption sites. After this critical dose (1 g/L) the extent of adsorption is increasingly slow down due to the fact that although there is increasing number of active sites but there is shortage of adsorbate in the solution. The decrease in q_e value may also be due to the splitting effect of flux (concentration gradient) between adsorbate and adsorbent. With increasing kaolin concentration causing a decrease in amount of dye adsorbed onto unit weight of kaolin. The increase in percentage color removal is because, at higher kaolin, there is a very fast superficial adsorption onto the kaolin surface that produces a lower solute concentration in the solution than when kaolin dose is lower.

Effect of Agitation Speed

Agitation is an important parameter in adsorption phenomena, influencing the distribution of the solute in the bulk solution and the formation of the external boundary film. Figure 7 shows the percentage removal of crystal violet using kaolin at different agitation speed (500, 1500, and 2500 rpm) within contact time of 30 minutes. From the figure, it is clear that with increasing agitation speed from 500 to 2500 rpm, the percentage removal of dye does not change at equilibrium. Only it takes more time and follows different path to reach the equilibrium. So, the difference in agitation speed can change the kinetics of the adsorption but not the equilibrium adsorption capacity. This

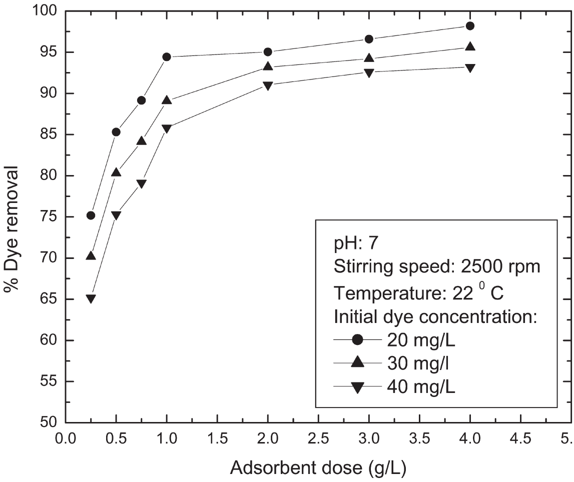

Figure 6. Variation of dye adsorption with adsorbent dose.

can be explained by the fact that increasing agitation speed reduced the film boundary layer surrounding particles, thus increasing the external film transfer coefficient, and hence the adsorption capacity. Similar result is also reported in the literature (23). The degree of agitation reduces the boundary layer resistance and increases the mobility of the system. With agitation, the external mass transfer coefficient increases resulting in quicker adsorption of the dye molecules.

Effect of pH

The initial pH of the dye solution is an important parameter, which controls the adsorption process particularly the adsorption capacity. pH of the solution may change, (1) the surface charge of the adsorbent, (2) the degree of ionization of the adsorbate molecule and (3) extent of dissociation of functional groups on the active sites of the adsorbent. To observe the effect of pH on the extent of dye adsorption, dye solution pH is varied from 3 to 9.5. The percentage of dye removal at different pH is shown in Fig. 8 for the initial dye concentration of 20 mg/L. From this study, it is observed that the maximum adsorption takes place at pH value of 7. Figure 8 also shows that the removal of dye increases with the increase of pH up to 7 and then it gradually deceases. The variation in the dye uptake with respect to the initial solution pH can be explained on the basis of the structure of dye molecule with varying pH and zero point charge (pHZPC) of kaolin (Figs. 1 and 2). For kaolin, the zero point charge is estimated to be as 7.0. Above this pH, the kaolin particle acquires a negative surface charge leading to a lesser the dye uptake since, dye molecule becomes neutral at that pH. At a pH lower than pHZPC the

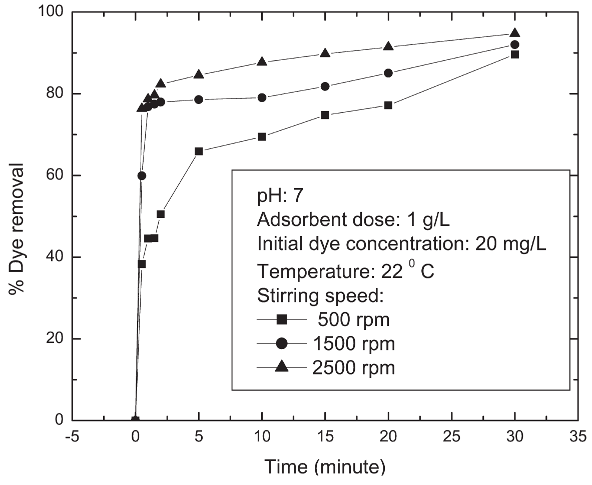

Figure 7. Effect of stirring on the percentage adsorption of crystal violet dye.

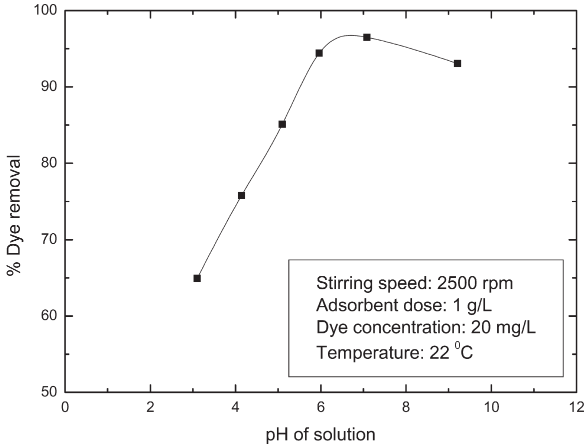

Figure 8. Effect of pH on the percentage adsorption of crystal violet dye.

kaolin surface acquires a positive charge and dye molecules also become positively charged. Due to this there is an electrostatic repulsion between the dye molecules and kaolin that causes a decrease in dye uptake.

Effect of Temperature

To observe the effect of temperature on the adsorption capacity, experiments are carried out for three different dye concentrations (20, 30, and 40 mg/L) and at three different temperatures (22°C, 40°C, and 50°C) using 1 g of kaolin per liter of the solution. It has been observed that with increase in temperature, adsorption capacity decreases as shown in Fig. 9. This implies that for the initial dye concentration of each solution, the adsorption is exothermic in nature.

The thermodynamic parameters, e.g. change in Gibb's free energy (ΔG^0), entropy (ΔS^0) and enthalpy ΔH^0 for the adsorption of crystal violet on kaolin have been determined by using the following Equations (24).

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{3}$$

$$\log\left(\frac{q_e}{C_e}\right) = \frac{\Delta S^0}{2.303R} + \frac{-\Delta H^0}{2.303RT} \tag{4}$$

where, q_e is the amount of dye adsorbed per unit mass of activated charcoal (mg/g). C_e is equilibrium concentration (mg/L) and T is temperature in K. q_e/C_e is called the adsorption affinity. The values of Gibb's free energy (ΔG^0) have been calculated from the enthalpy (ΔH^0) and entropy of adsorption (ΔS^0). The values of ΔH^0 and ΔS^0 are obtained from the plot of $\log(q_e/C_e)$

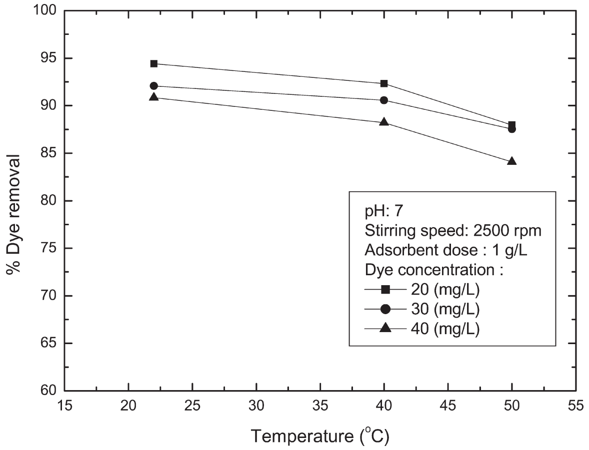

Figure 9. Effect of temperature on the extent of adsorption at different initial dye concentration.

versus 1/T, from Eq. (4). Once these two parameters are obtained, ΔG^0 is determined from Eq. (3).

The values of ΔH^0, ΔS^0, and ΔG^0 for the initial dye concentrations of 20, 30, and 40 mg/L are shown in Table 2. Negative ΔH^0 indicates that the adsorption is exothermic in nature. The exothermic nature is also indicated by the decrease in the amount of adsorption with temperature (Fig. 9). The adsorption is associated with an increase in entropy of 13.14, 14.28, and 11.14 J mol^{-1} K^{-1}, respectively, which indicates that the adsorbed dye molecules on the kaolin surface are organized in a more random fashion compared to those in the aqueous phase. Similar observations have been reported in the literature (25). The lower heat of adsorption obtained in this work indicates that physical adsorption rather than the chemical adsorption is prevalent in this case. It is reported (26) that the value of ΔH^0 about 40 kJ/mole signifies chemisorption rather than physical adsorption.

Adsorption Kinetics

In order to investigate the adsorption of crystal violet on the surface of kaolin, different kinetic models are used to examine the controlling mechanism of adsorption process. The proposed kinetic models are based on literature for sorption processes. In this study, a pseudo-first-order kinetic model, a pseudo-second-order kinetic model, and an intra-particle diffusion model are investigated to find the best fitted model for the experimental data.

Table 2. Thermodynamic parameters for the adsorption of crystal violet in kaolin at different temperatures

Dye concentration (mg/L)	$-\Delta H^0$ (J mol^{-1})	ΔS^0 (J mol^{-1} K^{-1})	ΔG^0 (kJ mol^{-1}) at temperature 295 K	313 K	323 K
20	235.34	13.14	4.11	4.35	4.48
30	139.25	14.28	4.35	4.61	4.75
40	179.40	11.14	3.46	3.66	3.78

Pseudo-First-Order Kinetic Model

This model assumes that the rate of change of the solute uptake with time is directly proportional to the difference in saturation concentration and the amount of solid uptake with time. The rate constant of adsorption is expressed as a first-order rate expression given as (24).

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{5}$$

where q_t and q_e are the amount of dye adsorbed (mg/g) at contact time t (min) and at equilibrium, k_1 is the pseudo-first-order rate constant (min^{-1}). After integrating with the boundary conditions at $t = 0$, $q_t = 0$ and at $t = t$, $q_t = q_t$ and rearranging Equation (5), the rate law for a pseudo-first-order reaction becomes

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \tag{6}$$

Figure 10 shows the plot of $\log(q_e - q_t)$ versus t which gives a straight line with slope of $-(k_1/2.303)$ and intercept $\log q_e$. Adsorption rate constant k_1 is calculated from the slope and shown in Table 3. In most cases the adsorption reaction preceded by diffusion through a boundary, the kinetics follows the pseudo-first order rate equation. But from Fig. 10 and the regression coefficient in Table 3 it may be concluded that the kinetics of the crystal violet adsorption on kaolin is not probably diffusion controlled.

Pseudo-Second-Order Kinetic Model

The sorption kinetics may be represented by pseudo-second-order model (24) as

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{7}$$

where k_2 is the equilibrium rate constant for pseudo-second-order sorption (g/mg min). Integrating Eq. (7) using the boundary conditions at $t = 0$, $q_t = 0$ and at $t = t$, $q_t = q_t$ and rearranging we get the rate law for a pseudo-

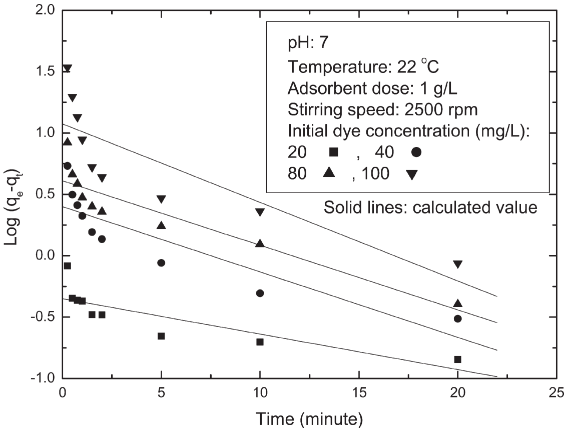

Figure 10. Pseudo-first-order kinetic model for the adsorption of crystal violet dye on kaolin.

Table 3. Different kinetic model parameters at 22°C

Feed concentration (C_o) (mg/L)	$q_{e,\mathrm{expt}}$ (mg/g)	$q_{e,cal}$ (mg/g)	k_1 (1/min)	Regression constant R^2
Pseudo first order				
20	17.26	0.45	0.067	0.70
40	31.94	2.51	0.123	0.79
80	63.81	4.08	0.121	0.85
100	74.03	11.08	0.147	0.72
	$q_{e,cal}$ (mg/g)	$1/k_2q_e^2$ (mg/g min)	k_2 (g/min)	Regression constant R^2
Pseudo second order				
20	17.21	526.32	1.78	1
40	31.95	416.67	0.41	1
80	63.69	1000.00	0.25	1
100	74.07	454.55	0.083	1

	Initial			Final		
	$k_{i,1}$ (mg/g . min$^{1/2}$)	I_1 (mg/g)	Regression constant R^2	$k_{i,2}$ (mg/g . min$^{1/2}$)	I_2 (mg/g)	Regression constant R^2
Intra particle diffusion						
20	0.78	16.119	0.74	0.07	16.83	0.95
40	4.04	25.399	0.85	0.25	30.55	0.97
80	10.47	50.83	0.91	0.59	60.69	0.99
100	39.49	23.76	0.92	1.04	68.46	0.99

second -order reaction as

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{8}$$

Figure 11 shows that the plot of t/q_t versus t gives a straight line with slope of $1/q_e$ and intercept $1/k_2 q_e^2$. Using the value of q_e calculated from the slope, the value of k_2 is determined from the intercept. The calculated value of k_2, q_e and their corresponding regression coefficient (R^2) values are presented in Table 3. The value of the regression coefficient is unity for all the three concentration of crystal violet confirms that, the sorption kinetics of crystal violet follows a pseudo second order process. It may also be found from Table 3 that the calculated q_e values are very close to that of the experimentally obtained q_e. Thus it may be concluded that the adsorption of crystal violet on kaolin can be better explained by the pseudo-second-order kinetic model than that of the first-order kinetic model.

Intra-Particle-Diffusion Model

In this model, it is assumed that the mechanism for dye removal by adsorption on a sorbent material is taking place through four steps:

a. migration of dye molecules from the bulk solution to the surface of the adsorbent through bulk diffusion,
b. diffusion of dye molecules through the boundary layer to the surface of the adsorbent via film diffusion;

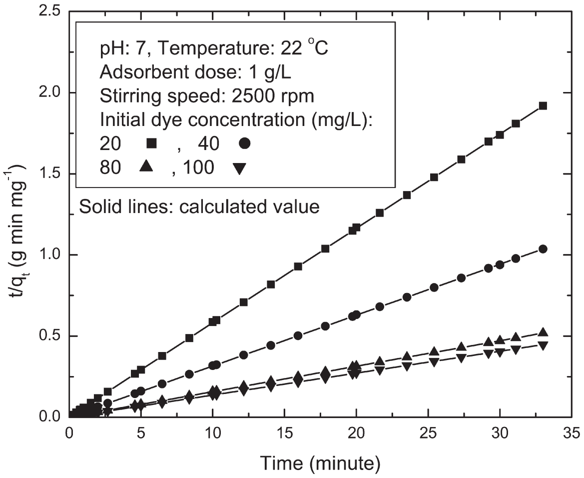

Figure 11. Pseudo second-order kinetic model for the adsorption of crystal violet on kaolin.

c. the transport of the dye molecules from the surface to the interior pores of the particle occur through intra-particle diffusion or pore diffusion mechanism and
d. the adsorption of dye at an active site on the surface of material by chemical reaction via ion-exchange, complexation and/or chelation.

In general, the dye sorption is governed by either the liquid phase mass transport rate or through the intra-particle mass transport rate. Thus, the adsorption process is a diffusive mass transfer process where the rate can be expressed in terms of the square root of time (t). The intra-particle diffusion model is expressed as follows (27)

$$q_t = k_i t^{0.5} + I \tag{9}$$

Where, q_t is the fraction dye uptake (mg/g) at time t, k_i is the intra-particle diffusion rate constant (mg/g min$^{0.5}$) and I is the intercept (mg/g). The plot of q_t versus $t^{0.5}$ will give k_i as slope and I as intercept. The intercept C represents the effect of boundary layer thickness. Minimum is the intercept length, adsorption is less boundary layer controlled.

Figure 12 represents the q_t versus $t^{0.5}$ plot for the initial dye concentration of 20, 40, 80 and 100 mg/L. It may be found that for all the four concentrations plots are double linear with different in slope (k_i) and intercept (I). The values of k_i and I are summarized in Table 3 along with the regression constant (R^2) for different initial dye concentrations. In the first straight line, the sudden increase (within a short time period) in slope signifies that the dye molecules are transported to the external surface of the kaolin particle through film diffusion and its rate is very fast. After that, the dye molecules are entered into the kaolin particle by intra-particle diffusion through pore, which is represented in second straight line. Both the lines do not pass through the origin that concludes that both film diffusion and intra-particle-diffusion are simultaneously occurring during the adsorption of crystal violet onto kaolin. A similar result is found in the literature (28) for the adsorption of cationic dye using silkworm pupa as adsorbent.

Adsorption Equilibrium

Adsorption properties and equilibrium parameters, commonly known as adsorption isotherms, describe how the adsorbate interacts with adsorbents, and comprehensive understanding of the nature of interaction. Isotherms helps to provide an information about the optimum use of adsorbents. So, in order to optimize the design of an adsorption system to remove dye from solutions, it is essential to establish the most appropriate correlation for the equilibrium curve. There are several isotherm equations available for analyzing experimental sorption equilibrium parameters. However, the most

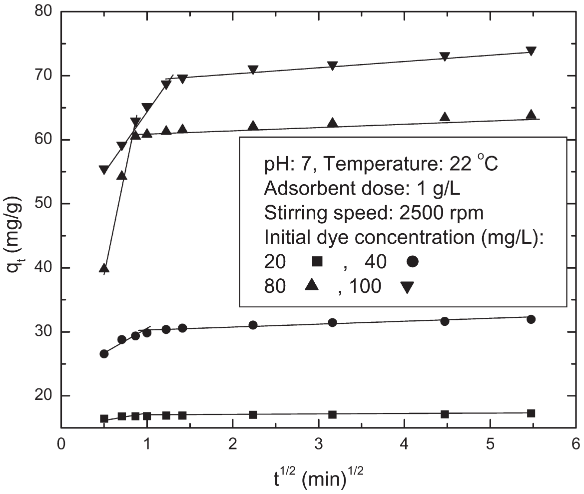

Figure 12. Intra-particle-diffusion model for adsorption of crystal violet onto kaolin.

common types of isotherms are the Langmuir, Freundlich, and Redlich–Peterson Models. The Langmuir isotherm is based on the assumption that there is a finite number of binding sites which are homogeneously distributed over the adsorbent surface. These binding sites have the same affinity for adsorption of a single molecular layer and there is no interaction between the adsorbed molecules. The equation of Langmuir isotherm (24) is

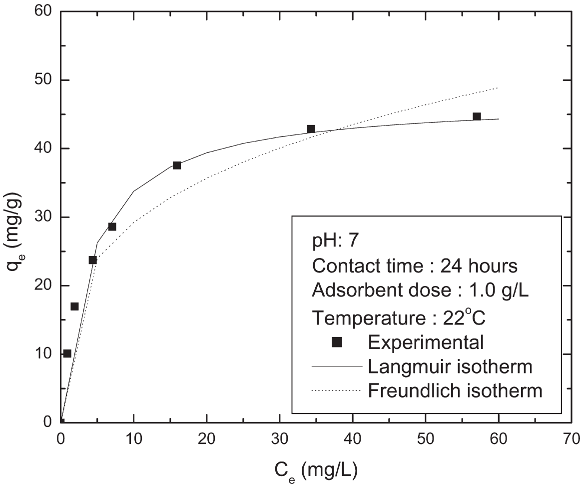

Figure 13. Langmuir and Freundlich adsorption isotherms for crystal violet using kaolin.

represented as below

$$q_e = \frac{Q_0 b C_e}{1 + b C_e} \tag{10}$$

Where C_e (mg/L) and q_e (mg/g) are the liquid phase concentration and solid phase concentration of adsorbate at equilibrium, respectively, and Q_0 (mg/g) and b (L/mg) are the Langmuir isotherm constants.

The Freundlich isotherm model is an exponential equation which applies to adsorption on heterogeneous surfaces with interaction between adsorbed molecules and is not restricted to the formation of a monolayer. This model assumes that as the adsorbate concentration increases, the concentration of the adsorbate on the adsorbent surface also increases and correspondingly that sorption energy exponentially decreases on completion of the sorption centers of an adsorbent. The well-known expression for the Freundlich model is given as (24).

$$q_e = K_F C_e^n \tag{11}$$

Where, K_F is the Freundlich constant [$\text{mg} \cdot \text{g}^{-1}(\text{L/g})^{\text{n}}$] related to the bonding energy, and n is the heterogeneity factor. n is a measure of the deviation from linearity of the adsorption. It indicates the degree of non-linearity between the solution concentration and the adsorption.

Both the isotherms for crystal violet – kaolin system at 30°C and neutral pH are shown in Fig. 13. This figure provides some information on the amount of kaolin required to adsorb a particular mass of crystal violet under the specified system conditions. Correlation coefficients for Langmuir and Freundlich adsorption isotherm are calculated by fitting the experimental adsorption equilibrium data and are shown in Table 4. It is found from the correlation coefficients (R^2) that the adsorption isotherm for the present system is explained better by Langmuir isotherm model.

Table 4. Langmuir and Freundlich isotherm constants for the adsorption of crystal violet on kaolin at 22°C

Langmuir isotherm constant			Freundlich isotherm constant		
Q_o (mg/L)	b (L/mg)	Regression constant R^2	K_F [$\text{mg} . \text{g}^{-1}(\text{L/mg})^{\text{n}}$]	n	Regression constant R^2
47.27	0.25	0.996	15.12	0.29	0.971

CONCLUSION

Kaolin has proved to be an effective adsorbent for the removal of crystal violet dye from the aqueous medium. It has crystal violet adsorption capacity of about 45 mg/g. The adsorption is highly dependent on various operating parameters, like the adsorbent dose, the contact time, the pH, the initial dye concentration, the stirring speed and the temperature. It has been observed that the percentage adsorption increases with an increase in the agitation time and attains equilibrium almost within 5 minutes. As for example, about 97% adsorption is observed within 5 minutes and thereafter the extent of the adsorption remains almost constant for the initial dye concentrations of 10 mg/L. The percentage adsorption is maximum at the pH value of 7 and decreases with acidic and or basic strength of the dye solution. The percentage adsorption decreases from about 95% to 65% for the initial dye concentrations of 20 mg/L at the end of the experiment when the pH is gradually decreased from 7 to 3. Adsorption kinetic follows pseudo-second-order kinetic. Adsorption capacity decreases with temperature. The temperature effect is used to calculate the activation enthalpy (ΔH^o), free energy of adsorption (ΔG^o) and entropy (ΔS^o). The analysis of these thermodynamic parameters suggests that adsorption is

a. spontaneous and ΔG^o is negative,
b. mainly physical because of the low ΔH^o values.

Positive value of ΔS^o dictates that adsorbed dye molecules remains on the kaolin surface in more random fashion. The equilibrium data are analyzed against Langmuir and Freundlich isotherm equation. The result shows that the experimental data are best correlated by the Langmuir isotherm. The constants of both the isotherms are determined that are most useful to design a single-stage batch adsorber for the removal of crystal violet using kaolin. Further study is under investigation to develop a suitable regeneration method to reuse kaolin for multi-operational cycles.

APPENDIX 1

The kinectics of adsorption of dye on adsorbent is mainly depends on the extent of turbulence of the system. The extent of turbulence in the system is represented by the Reynolds number (N_{Re}) and is calculated as. $N_{\mathrm{Re}} = nD^2\rho/\mu$. Where, n is the rotational speed of the stirrer, D is the length of the agitating blade, ρ is the density of the liquid solution and μ is the viscosity of the liquid solution. From the expression, it is clear that N_{Re} mainly depends on the length of agitator blade and the agitation speed. at constant density and viscosity of solution. For three different agitation speeds 500, 1500, and 2500 rpm, N_{Re} is calculated as 0.34×10^4,

1.04×10^4, and 1.7×10^4, respectively. Where, $D = 2$ cm, $\rho = 1.001$ g/cm^3 and $\mu(22^\circ\mathrm{C}) = 0.963$ cp.

ACKNOWLEDGMENTS

This works is partially supported by a grant from the Defense Research Laboratory, Tezpur, India under the scheme no. DRLT-P1-2006/Task 10. Any opinions, findings and conclusions expressed in this paper are those of the authors and do not necessarily reflect the views of Defense Research Laboratory, Tezpur, India.

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