Adsorption characteristics of brilliant green dye on kaolin

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ABSTRACT

Experimental investigations were carried out to adsorb toxic brilliant green 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, and (iii) structural analysis using X-ray diffractometer. The effects of initial dye concentration, contact time, kaolin dose, stirring speed, pH and temperature were studied for the adsorption of brilliant green in batch mode. Adsorption experiments indicate that the extent of adsorption is strongly dependent on pH of solution. Free energy of adsorption (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) changes are calculated to know the nature of adsorption. The calculated values of ΔG^0 at 299 K and 323 K indicate that the adsorption process is spontaneous. The estimated values of ΔH^0 and ΔS^0 both show the negative sign, which indicate that the adsorption process is exothermic and the dye molecules are organized on the kaolin surface in less randomly fashion than in solution. The adsorption kinetic has been described by first-order, pseudo-second-order and intra-particle-diffusion models. It was 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 were used to fit the experimental equilibrium data. It was found that the adsorption of brilliant green on kaolin follows the Langmuir adsorption isotherm.

1. 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. 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]. Brilliant green (BG) is one of the commonly known cationic dye (structure is shown in Fig. 1(a)) 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. It is also extensively used in textile dying and paper printing. In the present work, treatment of brilliant green dye containing aqueous stream by adsorption technique is reported.

Research is being carried out using different treatment technologies, e.g. chemical coagulation–flocculation [2], different type of oxidation processes [3], biological process [4], membrane-based separation processes [5–7], adsorption [8] for the removal of colored dye from wastewater. Each of the above processes has their own benefits and limitations. Adsorption on solid surface is being growing interest in this field because of its lower price. Activated carbon is one of the common adsorbent due to its high surface area, high adsorption capacity. But its high cost makes the process uneconomical for industrial applications [9].

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 adsorbent made from natural sources like rice husk [9], wheat bran [10], waste apricot [11], bagasse fly ash [12] and powdered peanut hull [13]. 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: 42.14 mol%, Al_2O_3: 15.61 mol% and H_2O: 42.25 mol% [18]. It's crystalline structure (Fig. 1(b)) consists of stacked pairs of tetrahedral silica sheets and octahedral alumina

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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 aluminum-hydroxyl groups. Hence, the resulting crystal contains a silica face of SiO_2 tetrahedral, 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 depend on the pH of the solution [20]. Adsorption experiments using kaolin as an adsorbent have been reported on other basic dyes such as methylene blue and malachite green [21,22]. They observed the usability of kaolin as an adsorbent for the removal of basic dyes only.

In the present study, experiments were carried out to remove brilliant green dye by adsorption technique using kaolin as an adsorbent. Characterization of kaolin is done by measuring particle size distribution, X-ray diffraction (XRD) and BET surface area 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.

2. Experimental

2.1. Materials and methods

Brilliant green dye (C.I.: 42040, FW: 462.65, Dye content: 85%, λ_{max}: 625 nm), supplied by Titan Biotech Limited, Bhiwadi, Rajasthan, India is used as an adsorbate. Brilliant green molecule
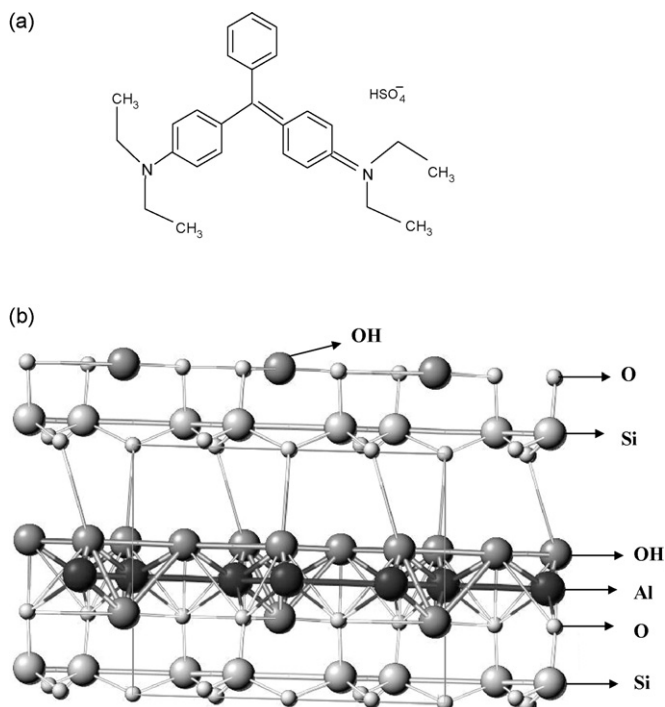

Fig. 1. Structure of (a) brilliant green molecule and (b) kaolinite [19].

Table 1
Characteristics of kaolin

Property	Values
Average particle size (μm)	2.37
Acid soluble (as sulphate) (wt%)[a]	0.5
Water soluble[a]	No
BET specific surface area (m^2/g)	13.69

[a] Data obtained from the supplier.

exists as cation in aqueous medium (Fig. 1(a)). pH of the solution is maintained by using 0.1N HCl and 0.1N NaOH solutions. NaOH and HCl solutions are obtained from Merck, India. Kaolin (99.5% pure), 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 point of zero charge (pHZPC) 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 h. 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 ($26 \pm 2\,^\circ$C). Stock solution of brilliant green 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 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 [23]. Initial dye concentrations are varied from 10 to 40 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 10–40 mg/L. For studying the effect of solution pH on dye adsorption, experiments in different pH (varying from 2.85 to 10.32) 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 1.0 to 4.0 g/L) are used with three different initial dye concentrations, e.g. 10, 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 (26, 40 and 50 °C), where all other variables remain unchanged. A common adsorbent dose of 1 g/L, stirring speed of 800 rpm and pH 7 is used for all the
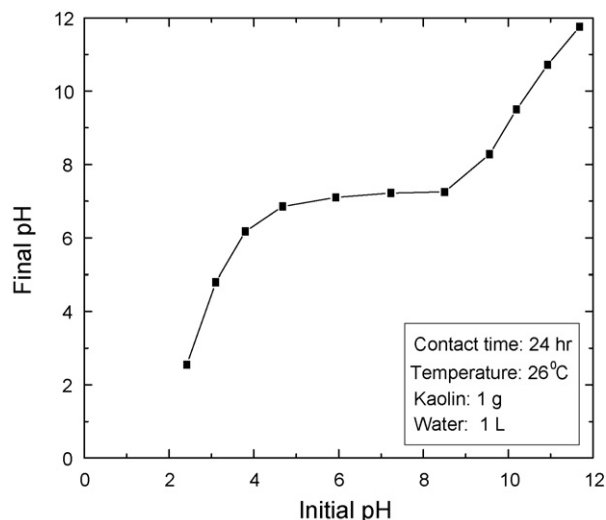

Fig. 2. Point of zero charge (pHZPC) of commercial kaolin used for the adsorption experiments.
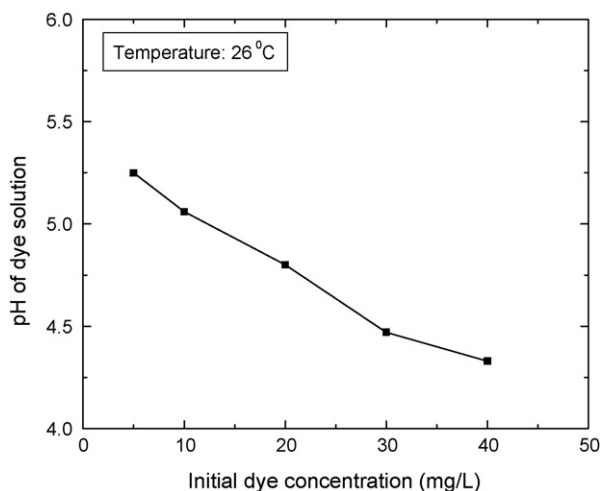
Fig. 3. Variation of pH of the dye solution with initial concentration of brilliant green.

above experiments. Three different agitation speeds of 610, 800 and 1000 rpm are used for observing the effect of turbulence on the dye adsorption.

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).

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 h (to get confirm that the equilibrium has been reached) with constant shaking at ambient temperature of $26 \pm 2\,^\circ$C. After 24 h the solution attains equilibrium and the amount of dye 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 into consideration. The average deviation of duplicate results in the units of concentration is found to vary as $\pm 2\%$. Blank experiments are carried out with dye solution and without adsorbent to ensure that no dye is adsorbed onto the walls of the beakers.

2.2. 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 h. 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 total pore volume. Structural analysis of the kaolin is done by X-ray diffractometer (D8 ADVANCE, Bruker Axs). 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 (PerkinElmer Precisel, Lamda-35) at a wavelength of 625 nm.

3. Results and discussion

3.1. 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 sizes of the kaolin particles are in the range of 0.23–20 μm. More than 90% particles are of below 5 μm. Average particle size of the adsor-
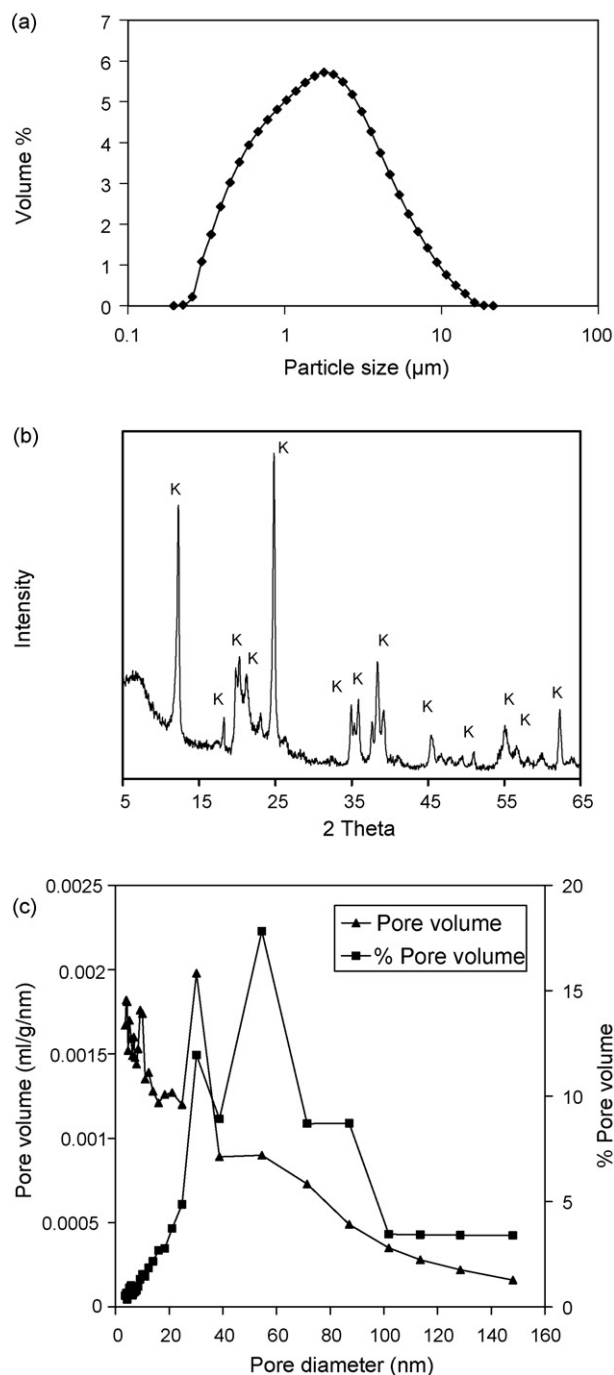

Fig. 4. (a) Particle size distribution of kaolin. (b) XRD diagram of kaolin powder. K: kaolinite (PDF-01-089-6538). (c) Pore size distribution of kaolin particles.
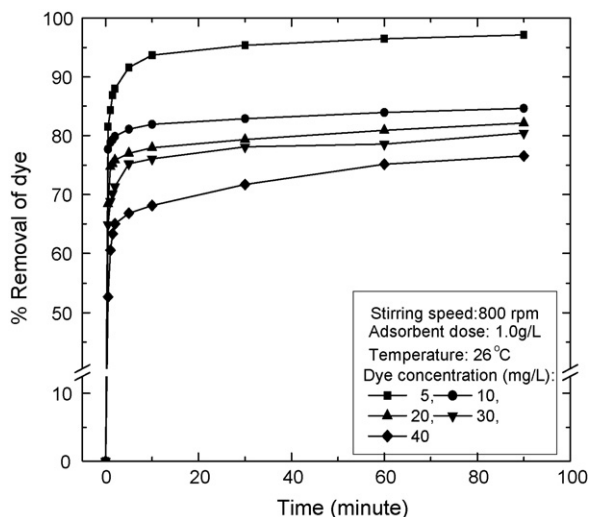
Fig. 5. Effect of contact time and initial concentration of brilliant green on the extent of adsorption.
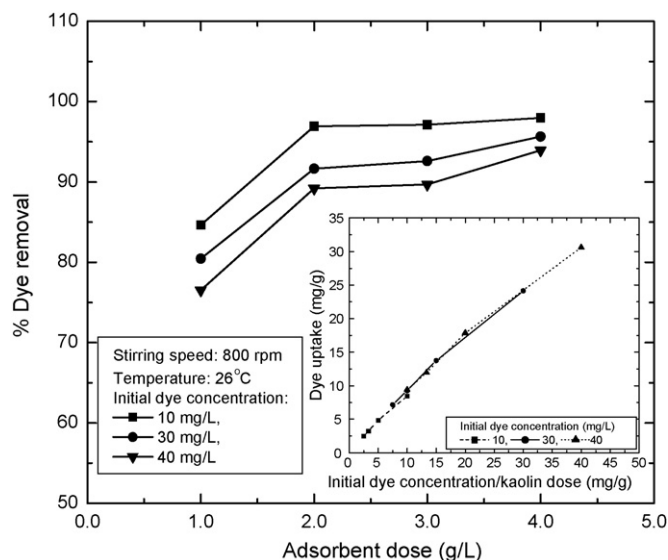

Fig. 6. Variation of dye adsorption with adsorbent dose. Time of adsorption is 90 min.

bent is 2.37 μm. The X-ray diffraction pattern of kaolin is shown in Fig. 4(b). The XRD spectrum is matched with the JCPDS database file (PDF-01-089-6538) which indicates that the kaolin used in our work is ideal kaolinite [$Al_2Si_2O_5(OH)_4$] with anorthic (triclinic) lattice structure. The specific surface area of the kaolin determined from BET surface area analyzer is 13.69 m^2/g. Fig. 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 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 (40–100 nm) pore volume is 0.025 mL/(g nm) with 39% of total pore volume. This indicates the existence of the mesopores in the sample.

3.2. Adsorption studies

3.2.1. Effect of contact time and initial dye concentration

The variation in percentage removal of dye with contact time at different initial concentrations ranging from 5 to 40 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 min and becomes gradual there after. This indicates that the rate of adsorption is very fast. Data has been taken up-to 90 min of operation which close to attain equilibrium. After that no significant change in the extent of adsorption is observed. For the initial concentration of up-to 30 mg/L, more than 80% adsorption has been observed, whereas for 40 mg/L, the percent removal of dye is 76%. 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 slowing down. This explains the more adsorption time for higher concentration.

3.2.2. Effect of adsorbent dose

The effect of kaolin dose (varying from 1.0 to 4.0 g/L) on the dye uptake capacity for four different initial dye concentrations 10, 30 and 40 mg/L is presented in Fig. 6. Initially, rapid increase in adsorption with the increase in adsorbent dose can be attributed to greater surface area and availability of more adsorption sites. After the critical dose (2 g/L) the extent of adsorption is increasingly slow down. This phenomenon is also confirmed by dye uptake versus initial dye concentration/kaolin dose ratio plot shown in the inset of Fig. 6. It is observed from the figure (inset of Fig. 6) that for the constant initial dye concentration, the dye uptake (mg dye/g of kaolin) decreases with increase in kaolin dose (i.e., initial dye/kaolin dose ratio decreases). But at the same time the overall removal efficiency marginally increases. The decrease in dye uptake value (mg dye/g of kaolin) is due to the splitting effect of flux (concentration gradient) between adsorbate and adsorbent. 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. However, dye uptake increases with the increase in initial dye concentration for constant kaolin dose. This is due the presence of more number of dye molecules in the solution.

3.2.3. 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. Fig. 7 shows the percentage removal of brilliant green using kaolin at different agitation speed (610, 800 and 1000 rpm) within contact time of 90 min. From the figure it is clear that with increasing agitation speed from 610 to 1000 rpm, the percentage removal of dye increases from 78% to 87% at the end of 90 min of operation. It is confirmed that a further prolongation of the contact time of 24 h did not increase the dye adsorption significantly. So, the difference in agitation speed cause changes in the kinetics of the adsorption as well as the equilibrium adsorption capacity. The increase in percentage removal 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 percentage dye removal. The change in equilibrium adsorption capacity with agitation speed is surprising since the agitation speed can change the
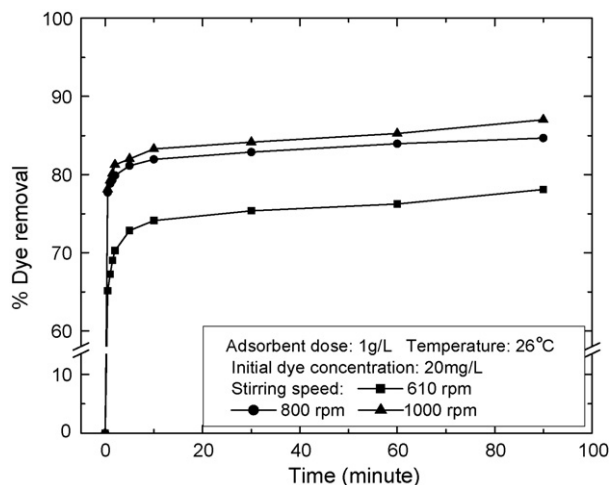
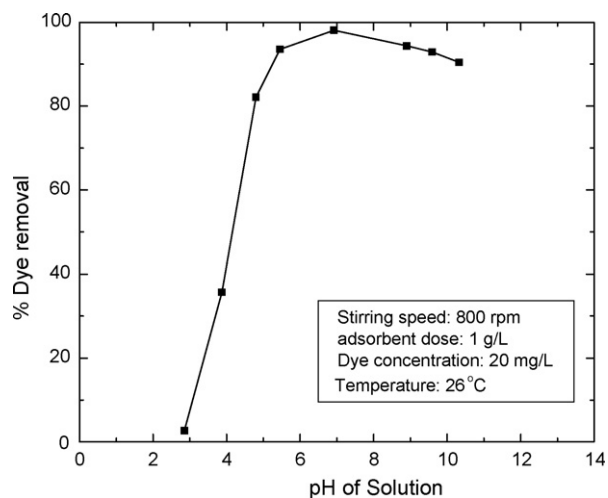Fig. 7. Effect of stirring on the percentage adsorption of brilliant green dye.

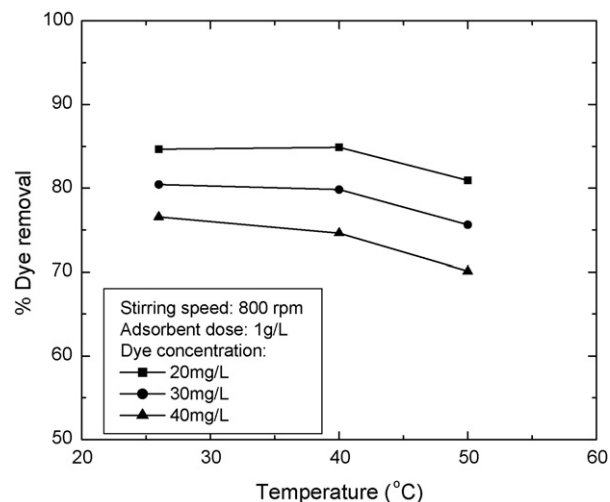Fig. 8. Effect of pH on the percentage adsorption of brilliant green dye.

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

uptake since dye molecule becomes neutral at that pH. At a pH lower than pHZPC the kaolin surface acquires positive charge and dye molecules also become positive charge. Due to this there is an electrostatic repulsion between dye molecules and kaolin that causes decrease in dye uptake.

3.2.5. 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 (26, 40 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 change in Gibb's free energy (ΔG^0), change in entropy (ΔS^0) and change in enthalpy ΔH^0 for the adsorption of brilliant green over kaolin has been determined by using the following equations [25]:

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

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

where m is the adsorbent dose (g/L), q_e is the amount of dye adsorbed per unit mass of kaolin (mg/g), C_e is equilibrium concentration (mg/L) and T is temperature in K. q_e/C_e is called the adsorption affinity. For unit mass of adsorbent dose ($m = 1.0$ g/L) Eq. (4a) becomes:

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

The values of Gibbs free energy (ΔG^0) have been calculated by knowing the enthalpy of adsorption (ΔH^0) and the entropy of adsorption (ΔS^0) and ΔH^0 are obtained from a plot of $\log(q_e/C_e)$ versus $1/T$, from Eq. (4b). 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.

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 12.31, 17.56 and 25.41 J mol^{-1} K^{-1}, respectively, which indicates that the adsorbed

kinetics, not the equilibrium capacity. Similar result is also reported in the literature [24]. 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.

3.2.4. 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 2.85 to 10.32. 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 maximum adsorption takes place at pH value of 7. Fig. 8 also shows that the removal of dye increases with the increase of pH up-to 7 and then it gradually decreases. 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 and point of zero charge (pHZPC) of kaolin (Figs. 1 and 2). For kaolin, the point of zero charge is estimated to be as 7.0. Above this pH, the kaolin particle acquires a negative surface charge leading to a lesser dye

Table 2
Thermodynamic parameters for the adsorption of brilliant green in kaolin at different temperatures

Dye concentration (mg/L)	$-\Delta H^0$ (kJ mol^{-1})	$-\Delta S^0$ (J mol^{-1} K^{-1})	$-\Delta G^0$ (kJ mol^{-1})		
			299 K	313 K	323 K
20	8.04	12.31	4.36	3.60	3.00
30	8.85	17.56	4.19	3.36	2.65
40	10.59	25.41	4.07	3.18	2.39

dye molecules on the kaolin surface are more organized compared to those in the aqueous phase. Similar observations have been reported in the literature [8]. The higher heat of adsorption obtained in this work indicates that chemisorptions rather than the physical adsorption are prevalent in this case. It is reported [26] that the value of ΔH^0 about 8–10.6 kJ/mol signifies chemisorptions rather than physical adsorption. The negative values of ΔH^0 and ΔG^0 indicate that the adsorption process is spontaneous and exothermic in nature. The negative value of ΔS^0 suggests decreased randomness during adsorption [8].

3.3. Adsorption kinetics

In order to investigate the adsorption of brilliant green 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 and adsorption capacity of adsorbent. In this study, pseudo-first-order kinetic model, pseudo-second-order kinetic model and intra-particle-diffusion model are investigated to find the best fitted model for the experimental data.

3.3.1. Pseudo-first-order kinetic model

This model assumes that the rate of change of solute uptake with time is directly proportional to difference in saturation concentration and the amount of solid uptake with time. In most cases the adsorption reaction preceded by diffusion through a boundary, the kinetics follows the pseudo-first-order rate equation. The rate constant of adsorption is expressed as a first-order rate expression given as [25]:

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

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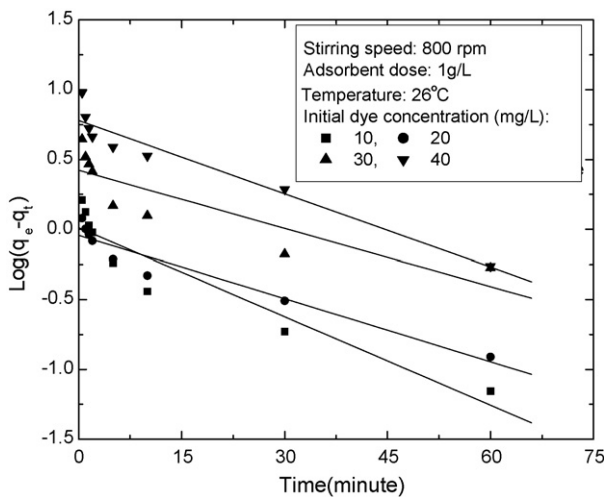
constant (min^{-1}). After integrating with the boundary conditions at initial time ($t = 0$), $q_t = 0$ and at any time ($t > 0$), amount of dye adsorbed is q_t and rearranging Eq. (5), the rate law for a pseudo-first-order reaction becomes:

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

The plot of $\log(q_e - q_t)$ versus t (as shown in Fig. 10) should give a straight line with slope of $-k_1/2.303$ and intercept $\log q_e$ which allows calculation of adsorption rate constant k_1 and equilibrium adsorption capacity $q_{e, cal}$. From Fig. 10, it may be observed that the experimental data point does not fit a straight line. This may be due to the stirring speed used in the present work (610, 800 and 1000 rpm) which reduces the film boundary layer as discussed in Section 3.2.3. Calculated values of k_1 and $q_{e, cal}$ are summarized in Table 3. From Fig. 10 and q_e values (experimental and calculated) in Table 3, it may be concluded that the kinetics of brilliant green adsorption on kaolin is not probably following the pseudo first order kinetic model and hence not a diffusion-controlled phenomena.

3.3.2. Pseudo-second-order kinetic model

Adsorption process with chemisorptions being the rate-control follows pseudo-second-order model. The sorption kinetics may be

Table 3
Different kinetic model parameters at 26 °C

Feed concentration, C_o (mg/L)	$q_{e, expt}$ (mg/g)	$q_{e, cal}$ (mg/g)	k_1 (1/min)	R^2
Pseudo-first order				
5	4.33	0.47	0.03	0.95
10	10.06	1.03	0.05	0.89
20	14.66	0.91	0.03	0.93
30	22.89	2.65	0.03	0.76
40	30.59	6.01	0.04	0.93

Feed concentration, C_o (mg/L)	$q_{e, cal}$ (mg/g)	k_2 (g/mg min)	R^2
Pseudo-second order			
5	4.32	0.71	0.99
10	10.06	0.44	1
20	14.62	0.39	1
30	22.78	0.14	0.99
40	30.49	0.06	0.99

Feed concentration, C_o (mg/L)	$k_{i, 1}$ (mg/(g min$^{1/2}$))	I_1 (mg/g)	R^2
Intra-particle diffusion			
5	0.28	4.07	0.69
10	0.66	8.09	0.94
20	0.52	13.09	0.99
30	2.55	16.81	0.95
40	6.94	16.60	0.93

Feed concentration (C_o) (mg/L)	$k_{i, 2}$ (mg/g min$^{1/2}$)	I_2 (mg/g)	R^2
5	0.05	3.88	0.99
10	0.06	9.54	0.98
20	0.08	13.89	0.99
30	0.19	21.04	0.96
40	0.56	25.53	0.99

Fig. 10. Pseudo-first-order-kinetic model for the adsorption of brilliant green dye on kaolin.

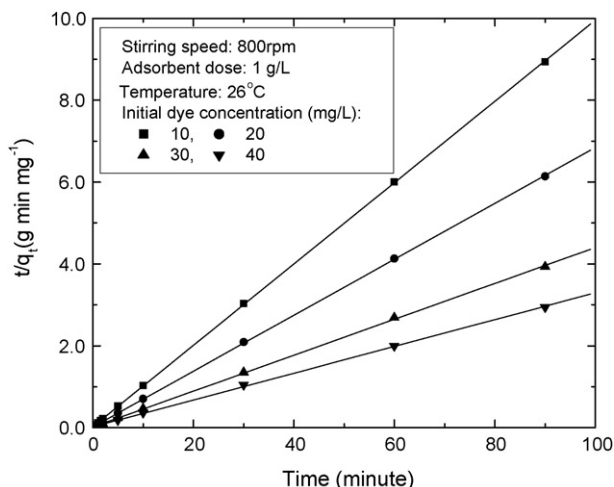**Fig. 11.** Pseudo-second-order-kinetic model for the adsorption of brilliant green on kaolin.

Fig. 12. Intra-particle-diffusion model for adsorption of brilliant green onto kaolin.

represented by pseudo-second-order model [25] 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 any time t, amount of dye adsorbed is q_t and rearranging the rate law for a pseudo-second-order reaction becomes:

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

Fig. 11 shows that the plot of t/q_t versus t is a straight line with slope of $1/q_e$ and intercept $1/k_2 q_e$. 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 regression coefficient is unity for 10 and 20 mg/L and nearly unity (0.99) for 30 and 40 mg/L of brilliant green which confirms that, the sorption kinetics of brilliant green 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 experimentally obtained q_e. Thus, it may be concluded that the adsorption of brilliant green on kaolin can be better explained by pseudo-second-order kinetic model than that of first-order kinetic model and the process is chemisorption controlled.

3.3.3. 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 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; (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. Pore-diffusion models should be formulated so as to consider not only the particle size but also particle shape. The importance of considering particle geometries (shapes and surfaces) in the formulation of pore-diffusion models is reported in the
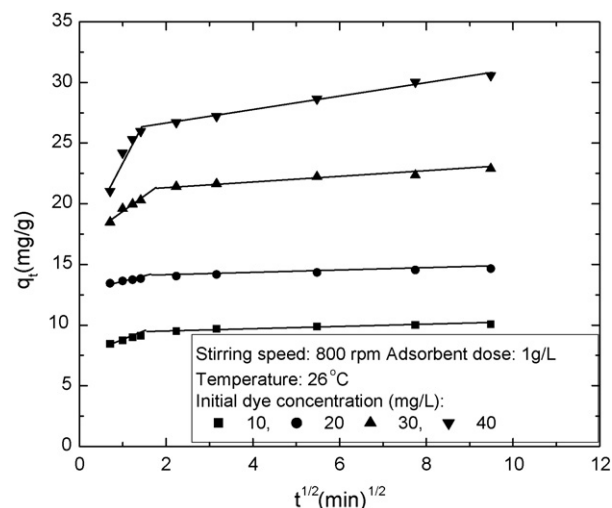
literature [27]. The potential effect of particle shape on the observed extent of adsorption is discussed in Ref. [28]. The adsorption process is a diffusive mass transfer process where the rate can be expressed in terms of the square root of time (t). The intra-particle-diffusion model is expressed as follows [29]:

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

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 I represents the effect of boundary layer thickness. Minimum is the intercept length, adsorption is less boundary layer controlled.

Fig. 12 represents the plot of q_t versus $t^{0.5}$ plot for the initial dye concentration of 10, 20, 30, and 40 mg/L. It seems that for all the four concentrations plots are nonlinear in nature but careful observation infer that data points can be better represented by double linear with difference in slope (k_i) and intercept (I). The values of k_i and I are summarized in Table 3 along with regression constant (R^2) for different initial dye concentrations. In 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, dye molecules are entered into the kaolin particle by intra-particle-diffusion through pore, which is represented in second straight line. Both the line does not pass through the origin that concludes that both film diffusion and intra-particle-diffusion are simultaneously occurring during the adsorption of brilliant green onto kaolin. Similar result is found in the literature [30] for adsorption of cationic dye using silkworm pupa as adsorbent.

3.4. 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 help to provide 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 common types of isotherms are the Langmuir and Freundlich models. The Langmuir isotherm is based on the assumption that
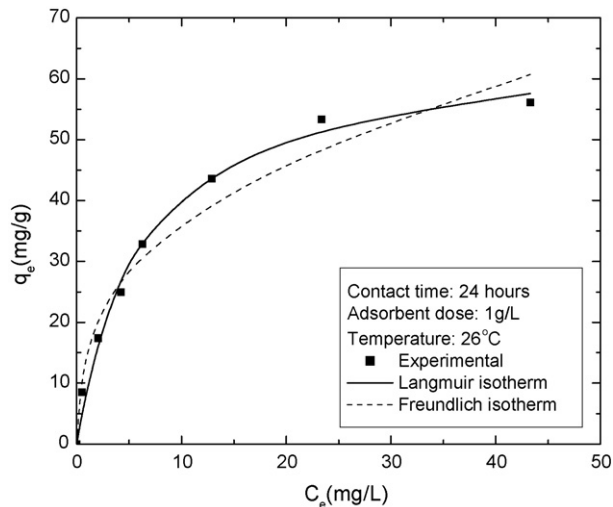
Fig. 13. Langmuir and Freundlich adsorption isotherms for brilliant green using kaolin.

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 adsorbed molecules. The equation of Langmuir isotherm [25] is 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 that 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 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 [25].

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

where K_F is the Freundlich constant K_F [mg/g(L/g)$^{1/n}$] 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 solution concentration and adsorption.

The kaolin particle and dye molecule exists as anion and cation in aqueous medium, respectively. As a result, chemisorp-

tions rather than physical adsorption prevails which is already discussed in Section 3.2.5. Since the adsorption is supposed to be the chemisorptions in nature, it may be proposed that monolayer coverage of dye molecule is taking place over the kaolin surface. Therefore, adsorption process should be better represented physically by Langmuir isotherm model than Freundlich isotherm model.

Both the isotherms for brilliant green—kaolin system at 26 °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 brilliant green 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 also found from the correlation coefficients (R^2) that adsorption isotherm for the present system is explained better by Langmuir isotherm model.

4. Conclusion

Kaolin is identified to be an effective adsorbent for the removal of brilliant green dye from aqueous medium. The adsorption is highly dependent on various operating parameters, like; adsorbent dose, contact time, pH, initial dye concentration, stirring speed and temperature. It has been observed that the percentage adsorption increases with an increase in the agitation time and becomes gradual after 5 min. As for example, about 91% adsorption is observed within 5 min and there after extent of adsorption becomes marginal for the initial dye concentrations of 10 mg/L. The percentage adsorption is maximal at pH value of 7 and decreases with acidic and or basic strength of the dye solution. The percentage adsorption decreases from about 98% to 2.67% for the initial dye concentrations of 20 mg/L at the end of the experiment when the pH is gradually decreased from 7 to 2.85. Adsorption kinetic follows pseudo-second-order kinetics. Adsorption capacity decreases with temperature. The temperature effect is used to calculate the change in activation enthalpy (ΔH^0), free energy of adsorption (ΔG^0) and entropy (ΔS^0). The analysis of these thermodynamic parameters suggests that adsorption is: (a) spontaneous and ΔG^0 is negative, and (b) mainly chemisorptions because of the high ΔH^0 values. Negative value of ΔS^0 dictates that adsorbed dye molecules remaining on the kaolin surface is decreased in a random fashion. The equilibrium data are analyzed against Langmuir and Freundlich isotherm equations. The result shows that the experimental data are best correlated by 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 brilliant green dye using kaolin. Further study is under investigation to develop a suitable regeneration method to reuse kaolin for multioperational cycles.

Table 4
Langmuir and Freundlich isotherm constants for the adsorption of brilliant green on kaolin at 26 °C, 40 °C and 50 °C

Langmuir constant	
Q_0 (mg/g)	65.42
b (L/mg)	0.17
R^2	0.99
Freundlich constant	
K_F [mg/g(L/g)$^{1/n}$]	16.24
n	0.35
R^2	0.97

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