CHAPTER 5
ADSORPTION TECHNIQUE FOR DECOLORIZATION OF
BRILLIANT GREEN AND CONGO RED DYE BEARING WATER

5.1 INTRODUCTION

Various researches have been performed to develop effective treatment technologies for wastewaters containing dyes; however, no single solution has been satisfactory for remediating the broad diversity of textile wastes [Moussavi and Mahmoudi, 2009]. Different physico-chemical processes like adsorption, electro-kinetic coagulation, ion-exchange, membrane filtration, electrochemical oxidation, and photo-catalytic degradation process have shown considerable success in treating these wastewaters [Gupta and Suhas, 2009; Laszlo, 1996; Gemea et al., 2003; Grimau and Gutierrez, 2006; Cisneros et al., 2002; Hachem et al., 2001] however, there are certain short comings. Coagulation process produces large amount of sludge leading to high disposal costs [Moussavi and Mahmoudi, 2009]. Ion-exchange process has no loss of adsorbent on regeneration; however, it cannot accommodate wide range of dyes, and is expensive [Srivastava et al., 2006]. Membrane separation process is also effective in removal of dyes, however, due to relatively high investment and membrane fouling problem, its application is restricted [Gupta and Suhas, 2009]. As there is a wide range in pH and dyes are difficult to decompose biologically, conventional biological methods are not effective to treat dye bearing wastewaters [Rajkumar and Kim, 2006]. Moreover, all these processes are costly and cannot be used by small industries to treat the wide range of dye wastewater [Gupta and Suhas, 2009; Rajkumar and Kim, 2006].
The adsorption process provides an attractive alternative treatment, especially if the adsorbent is inexpensive and readily available [Dogan et al., 2009]. This process is becoming an attractive and promising technology because of its simplicity, ease of operation and handling, sludge free operation, and regeneration capacity. Adsorption produces a high quality product, and is a process which is economically feasible [Choy et al., 1999]. Almost complete removal of impurities with negligible side effects explains its wide application for the treatment of dye bearing wastewaters [Mittal et al., 2008]. Activated carbon (AC) is the most popular adsorbent, which has been used with great success. However, AC is expensive and its regeneration and reuse make it more costly [Afkhami et al., 2010].

Many researchers have studied the feasibility of using low cost materials, such as saw dust (SD) [Kalavathy and Miranda, 2010; Sharma et al., 2009; Ahmad et al., 2009], bagasse fly ash [Mane et al., 2007a], rice husk ash [Mane et al., 2007b], waste orange peel [Namasivayam et al., 1996], banana pith [Namasivayam et al., 1998] and bottom ash [Gupta et al., 2004; Gupta et al., 2009; Mittal et al., 2005]. The other researchers also utilized adsorbents like deoiled soya [Mittal et al., 2008], rice husk [McKay et al., 1986], kaolin [Nandi et al., 2009], bentonite clay [Ramkrishna and Viaraghavan, 1997], neem leaf powder [Bhattacharya and Sharma, 2003], powdered activated sludge [Kargi and Ozmuhe, 2004], perlite [Dogan and Alkan, 2004], powdered peanut hull [Gong et al., 2005], Natural and modified clays like sepiolite [Mahir et al., 2005] and zeolite [Armagan et al., 2004]. The bamboo dust [Kannan and Sundaram, 2001], coconut shell [Manju et al., 1998], groundnut shell [Kannan and Sundaram, 2001], rice straw [Hameed and Khaiary 2008], duck weed [Waranusantigul et al., 2003] and sewage sludge [Otero et al., 2003] have also utilized as low cost adsorbent by earlier researches.
Other researchers have utilized sawdust carbon [Jadhav and Vanjara, 2004], agricultural waste and timber industry waste carbons [Bansal et al., 2009] and gram husk [Jain and Sikarwar, 2006] as adsorbents for removal of various dyes from wastewaters. Critical review of low cost adsorbents for wastewater treatment has been presented by earlier researchers [Gupta and Suhas, 2009; Mall et al., 1996; Bailey et al., 1999; Demirbas, 2009].

The by-products from the forestry and agricultural industries could be assumed to be low-cost adsorbents since they are abundant in nature, inexpensive, require little processing and are effective materials [Demirbas, 2009]. Saw dust is an abundant by-product of the wood industry that is either used as cooking fuel or as packing material [Garg et al 2004]. Saw dust is easily available at negligible price [Hameed and Khaiary, 2008]. The role of saw dust in the removal of pollutants from aqueous solutions has been reviewed [Shukla et al., 2002]. Sawdust has proven to be a promising effective material for the removal of various dyes. Various researchers have utilized saw dust for removal of dyes like beech sawdust [Batzias and Sidiras, 2007], Oak wood saw dust [Ferrero, 2007], Neem sawdust (*Azadirachta indica*) [Khattri and Singh, 2009] and Pine wood saw dust [Khattri and Singh, 2009; Ozacar and Sengil, 2005]. Saw dust also utilized for heavy metals removal like teakwood saw dust [Naiya et al., 2005], saguan (*Tectona grandis*) wood saw dust [Sharma et al., 2009], Raw saw dust (RSD) [Kalavathy and Miranda, 2010], Meranti tree sawdust [Ahmad, et al., 2009] and Indian Rosewood saw dust (*Dalbergia sissoo*) [Garg et al., 2004]. Timber of Indian eucalyptus wood tree is widely used for furniture making and the waste sawdust so produced is generally used as cooking fuel due to its zero or negligible cost. The other industrial waste, bagasse fly ash (BFA) and rice husk ash
(RHA) was successfully utilized for the removal of BG from aqueous solution [Mane et al., 2007a, b]. The other researchers have also successfully removed BG by utilizing low cost adsorbents like kaolin [Nandi et al., 2009], bottom ash and deoiled soya [Mittal et al., 2008], neem leaf powder [Bhattacharya and Sharma, 2003] and modified peat-resin particles [Sun and Yang, 2003]. This study is yet another attempt to explore the possibility of utilizing NaOH treated saw dust (SD) of Indian eucalyptus wood for the removal of hazardous BG from aqueous solution by performing batch studies. The effect of factors such as initial pH ($pH_0$), adsorbent dose ($m$), contact time ($t$), initial concentration ($C_0$) and temperature ($T$) was investigated. The kinetics of adsorption has been studied, and various kinetic models, such as pseudo-first-order, pseudo-second-order, and diffusion models have been tested with experimental data for their validity. The equilibrium sorption behavior of the adsorbents has been studied using the adsorption isotherm technique. Experimental data have been fitted to various isotherm equations to determine the best isotherm to correlate the experimental data. Thermodynamics of adsorption process has been studied and the changes in Gibbs free energy, enthalpy and the entropy have been determined.

5.2 EXPERIMENTAL

This section deals with the materials and methods of analysis, and the experimental procedure.

5.2.1 MATERIALS

5.2.1.1 Adsorbent

Saw dust of eucalyptus ($Eucalyptus globulus$) wood was collected from a saw mill at Nashik, Maharashtra, India. The saw dust was washed with distilled water to
remove muddy materials and dried in sunlight until all the moisture evaporated. The material was grounded and sieved to desired particle sizes such as ((<53 BSS mesh), (53–75 BSS mesh), (75–106 BSS mesh), (106–180 BSS mesh), (180–212 BSS mesh), (212-300 BSS mesh), (300-425 BSS mesh), (425-600 BSS mesh), and (600-850 BSS mesh)). The ground powder was treated with 1% sodium hydroxide in the ratio of 1:5 (sawdust: sodium hydroxide, w/v) at 50 °C for 4 h to remove lignin based color materials. The sawdust was filtered out, washed with distilled water to remove free sodium hydroxide and activated at 80 °C in a hot air oven for 24 h. The material was placed in an airtight container for further use.

5.2.1.2 Adsorbates

The adsorbates, BG dye [Color index = 42040, chemical formula = $C_{27}H_{34}N_2O_4$ S, FW = 482.62; nature = basic green 4] and CR dye [Color index. = 22120, chemical formula = $C_{32}H_{22}N_6Na_2O_6S_2$, FW = 696.7, $\lambda_{max} = 500$ nm] were used. The dye was of analytical reagent grade, and of 99.8% purity. Stock solution (1000 mg/l) of dye was prepared by dissolving an accurately weighed quantity of dye in distilled water. Experimental solutions of the desired concentrations were then obtained by successive dilutions with distilled water.

5.2.2 Characterization of adsorbent

The physico-chemical characteristics of the Saw dust (SD) were determined using standard procedures as discussed below:

Proximate analysis of the SD were carried out using the procedure as per IS 1350:1984. The Bulk density of SD was determined using MAC bulk density meter. Particle size analysis of the SD was made using standard sieve as per IS 2720 (Pt 4):
1985. The specific surface area and pore diameter was measured by N$_2$ adsorption isotherm using an ASAP 2010 Micromeritics instrument and by the Brunauer-Emmet-Teller (BET) method, using the software of Micromeritics. Nitrogen was used as cold bath (4.35 °C). The Barrett-Joyner-Halenda (BJH) method [Barret et al., 1951] was used to calculate the mesopore distribution for the SD. FT-IR (FTIR RX-1, Perkin Elmer, USA) spectrometer was employed to determine the type of functional groups in saw dust responsible for adsorption of BG and CR. Pellet (pressed-disk) technique has been used for this purpose. The sample was mixed with KBr (IR spectroscopy, grade) thoroughly and pellet was made by using a special mold provided to make pellet under the pressure of 15 tonne. The spectral range was from 4000 to 400 cm$^{-1}$. X-ray diffraction analysis of SD was carried out with a diffraction unit (Model PW 1140/90, Phillips, Holland), using copper target with nickel as a filter medium, and K radiation maintained at 1.542 A$^\circ$. Goniometer speed was kept at 2° min$^{-1}$. The range of scanning angle (2θ) was kept at 10–90°.

The ultimate analysis was performed on finely ground and oven-dried SD to determine the weight fractions of carbon, hydrogen and nitrogen. The weight fractions of carbon, hydrogen and nitrogen were determined by using Perkin Elmer CHN elemental analyzer. SEM analysis of SD was carried out by using LEO 435 VP Scanning electron microscope. The thermogravimetric analysis (TGA), differential thermal analysis (DTA) and derivative thermogravity (dTG) were performed using a Perkine Elmer Pyris Diamond TG/TGA instrument at a fixed heating rate of 20 °C/min over a temperature range of 30-1000 °C and using alpha alumina (0 mg) as reference.

5.2.3 Analytical Measurement
The BG and CR in the aqueous solution were analyzed by using a UV spectrophotometer (Perkin Elmer Lambda 35). Standard solutions of the BG maintained at different pH values were scanned to determine the wavelengths ($\lambda_{\text{max}}$) corresponding to maximum absorbance. The wavelengths corresponding to maximum absorbance were different for different pH values. By using these wavelengths the calibration graphs of absorbance versus concentration of BG and CR for different pH values were prepared for accurate determination of the BG and CR residual concentration at equilibrium pH values.

5.2.4 EXPERIMENTAL PROCEDURE

5.2.4.1 Batch Adsorption Experiments

Adsorption studies were mainly carried out by batch technique to obtain rate and equilibrium data. The experiments were performed to observe the effect of important parameters like initial pH ($pH_0$), adsorbent dose ($m$), initial concentration ($C_0$) and contact time ($t$) on the adsorptive removal of BG and CR, batch experiments were conducted at 30 ± 1 °C. For each experimental run, 50 ml of dye solution of known concentration, and $pH_0$ and a known amount of the adsorbent were taken in a 100 ml stoppered conical flask. This mixture was agitated in a temperature-controlled orbital shaker at a constant speed of 150 rpm at 30 ± 1 °C. Samples were withdrawn at appropriate time intervals. Some SD particles remain suspended and do not settle down easily. Therefore, all the samples were centrifuged at 8000 rpm for 10 min to settle down suspended particles. After centrifugation, clear supernatant samples were obtained and analyzed of the residual dye concentration. The effect of $pH_0$ on dye removal was studied for $pH_0$ values of 2 to 13. $pH_0$ was adjusted by the addition of dilute aqueous solutions of 0.1N H$_2$SO$_4$ or 0.1N NaOH. The effect of
equilibrium pH was studied in comparison with the initial pH (pH₀) of the dye solution. For the optimum amount of adsorbent per unit mass of adsorbate, a 50 ml dye solution was contacted with different amounts of SD till equilibrium was attained. The kinetics of adsorption was determined by analyzing adsorptive uptake of the dye from the aqueous solution at different time intervals. For adsorption isotherms, dye solutions of different C₀ were agitated with the known amount of adsorbent till the equilibrium was achieved. The effect of temperature on the sorption characteristics was investigated by determining the adsorption isotherms at 288, 303 and 318 K. The solutions of different initial concentrations were obtained by successive dilutions with distilled water from stock solution (1000 mg/l) of dye prepared by dissolving an accurately weighed quantity of dye in distilled water. The residual dye concentration (Cₜ) of the solution was then determined. Blank experimental runs, with only the adsorbent in 50 ml of distilled water, were conducted simultaneously at similar conditions to account for any color leached by the adsorbents and adsorbed by glass containers.

5.2.4.2 Column Studies

A Pyrex glass column of 100 cm length and 2.54 cm internal diameter with 0.2 cm wall thickness was used to contain SD as a fixed-bed adsorber. A fine mesh was introduced at the bottom of column over which a layer of ceramic beads was spread to prevent the escape of adsorbent. Synthetic dye solution was fed through the bed of SD in up-flow mode to avoid channeling of the effluent. A peristaltic pump was used to control the flow rate. Samples of the treated effluent were collected periodically and analyzed for (Cₜ). The flow through the tested column was continued until the dye concentration of column effluent approached 0.9, Cₜ/C₀, which indicated the
exhaustion point \( (C_x) \). The curve of \( C_t/C_0 \) versus volume treated between the concentration at 10% break through \( (C_b) \) and concentration at exhaustion \( (C_x) \) is called the breakthrough curve.

(a) Studies of variable flow rate and bed depth

The effect of bed height (15, 30 and 45 cm) and flow velocity (9 and 11 l/h) on the breakthrough for SD was studied. The \( C_o \) was kept constant at 50 mg/l for BG and 20 mg/l for CR. The experiments were performed at natural pH for BG and at 7 for CR and temperature 30 °C. Bohart Adams model is used for the predication of model specific parameters.

5.3 RESULTS AND DISCUSSION

5.3.1 Introduction

This section has been divided into the following sub sections:

1. Characterization of adsorbent
2. Batch adsorption
3. Column adsorption study

5.3.2 CHARACTERIZATION OF ADSORBENT

5.3.2.1 Physico-chemical characterization of adsorbent

The particle sizes of SD were <53 (5.5%), 53-75 (6.6%), 75-106 (9.2%), 106-180 (24%), 180-212 (10.8%), 212-300 (5.8%), 300-425 (27.2%), 425-600 (7.0%) and 600-850 (4.0%) and >850(0.4%) μm. Average particle size of SD was 182.8 μm. Proximate analysis showed presence of 2.1681, 4.633, 59.33 and 33.8689 percent moisture, volatile matter, ash and fixed carbon, respectively, in SD. Thus very high amount of ash was present in SD. The CHN analysis of SD showed 47.78, 8.18, 5.0 percent carbon, hydrogen and nitrogen respectively and rest others. Bulk density of
SD was 212 kg/m³. Scanning electron microscopic photograph (Fig. 5.1) of SD reveals surface texture and porosity. This photomicrograph shows fibrous structure of saw dust. It shows very fine particle size of the order of a millimeter or less and that there are pores within the particle of varying size. The FTIR technique is an important tool to identify some characteristic functional groups, which are capable of adsorbing dye ions. The spectra of the adsorbents were measured by an FTIR spectrometer within the range of 400–4000 cm⁻¹ wave number. The FTIR spectrum of SD (Fig. 5.2) studied using KBr pellets shows peaks at 3488 cm⁻¹ due to NH stretching and peaks at 2923 cm⁻¹ (stretch), 1465.95 attributed to CH₂ group. C = 0 stretching is observed at 1654 cm⁻¹ and another band at 1425.44 cm⁻¹ due to C–N stretching, thereby showing the presence of –CONH₂ group. X – Ray spectra (Fig. 5.3) reflect the presence of cellulose and minerals like goethite, Mullite, hematite, keolinite, α-quartz, γ-alumina etc. in the material. Thermal analysis (Fig. 5.4) shows there is no moisture after 150 °C. The net weight loss is of 9.5859% for temperature range of 415 to 618 °C. For the temperature range of 112.73 to 413 °C, weight loss is 49.0687%. The active pyrolysis zone is from 200 to 1000 °C. Maximum energy change occurs at temperature of 359.8 °C and exothermic change at this temperature. The Brunauer-Emmett-Teller (BET) surface area, pore volume and average pore diameter of SD was 0.3742 m²/g, 0.00836 cm³/g and 893.6 Å, respectively. The analysis of the BJH desorption pore distribution shows that the mesopores (13 Å < d < 1526.04 Å) have a total pore area of about 99% and the macropores of about 1%. The SD, thus, is found to consist of mesopores predominantly. This is what is desirable for the liquid phase adsorptive removal of BG and CR dye.
Fig. 5.1 Scanning electron micrograph of blank SD

Fig. 5.2 FTIR of blank SD
Fig. 5.3 XRD of blank SD
Fig. 5.4 TGA of blank SD
5.3.3 BATCH ADSORPTION STUDIES

Batch adsorption studies have been conducted for the decolorization of BG and CR dye bearing water. Effect of various parameters viz. initial pH ($pH_0$), adsorbent dose ($m$), initial concentration ($C_0$), contact time ($t$) and temperature ($T$) on the adsorption of BG and CR onto SD have been discussed in this section.

5.3.3.1. Effect of initial pH ($pH_0$)

The initial pH of the dye solution is an important parameter, which controls the adsorption process particularly the adsorption capacity [Nandi et al., 2009]. The pH value affects the structural stability of BG and, therefore, its concentration [Mittal et al., 2008]. Fig. 5.5 shows the BG removal trend from aqueous solution with (with dose, dye solution with adsorption) and without SD (Blank, Dye solution without adsorption without dose) for $pH_0$ values of 2, 2.9, 4, 6, 7, 9 and 11. The effect of $pH_0$ was studied with blank solutions of $C_0 = 50$ mg/l having natural $pH_0 = 2.9$. The solution was kept for 1 h, after which the absorbance of the solution was determined. There was insignificant change in absorbance of BG solution after 1 h with respect to that after 15 min. Therefore, stability of BG was examined only for solutions held for 1 h. It is inferred that the BG solution is stable at the natural $pH_0 = 2.9$ and it becomes unstable if the solution pH is either increased or decreased. BG instability due to pH change alone may be due to the structural changes taking place in the BG molecules. The change in natural pH of BG solution, therefore, changes the structure of BG and, hence, destabilizes the solution. It can also be inferred from Fig. 5.5 that the BG removal due to adsorption on SD is maximum and nearly constant for
$pH_0$ greater than or equal to 2.9. The ion-exchange mode of adsorption might be operative [Mall et al., 2005]. The solution is most stable at this $pH_0$. Therefore, further adsorption experiments were carried out at $pH_0 2.9$.

The system pH changes during the adsorption process. Fig. 5.6 shows the final pH values ($pH_f$) as a function of $pH_0$. The $pH_f$ values are higher than the $pH_0$ values for $pH_0 < 7.0$ for $C_0 = 50$ mg/l. Although the BG removal increases sharply with an increase in $pH_0$, the $pH_f$ values were almost constant for $4.5 \leq pH_0 \leq 9.0$. The $pH_f$ values are, therefore, considered to indicate the equilibrium pH values [Kwon et al., 2005]. The increase in pH of the solution during sorption process appears to be due to the adsorption of $H^+$ ions onto SD, and the hydrolysis of SD to release basic cations in solution [Srivastava et al., 2006a, b]. The degree of pH variation was small in higher $pH_0$ solutions because of their higher buffering capacities [Srivastava et al., 2006a, b; Dimitrova and Mehandgiev, 1998].
Fig. 5.5 Effect of $pH_0$ on the adsorption of BG by SD ($T=303$ K, $t=3$ h, $C_0=50$ mg/l, $m=4$ g/l).

Fig. 5.6 The variation in equilibrium system $pH_f$ with $pH_0$ during the adsorption of BG by SD ($T=303$ K, $t=3$ h, $C_0=50$ mg/l, $m=4$ g/l).
Fig. 5.7 shows the CR removal trend from aqueous solution with (with dose, dye solution with adsorption) and without SD (Blank, Dye solution without adsorption without dose) for $pH_0$ range of 3 to 13. The effect of pH was studied with blank CR solutions of concentration 10 mg/l having the natural $pH_0 = 6.8$. The solution was kept for 1 h after the pH adjustment and, thereafter, the absorbance of the solution was found out. It is inferred that the CR solution is stable at $pH_0$ around 7, and it becomes unstable if the solution pH is either increased or decreased. More than 80% color removal is observed in the $pH_0$ range 4–10. When $pH_0$ is increased from 4 to 7, the color removal increases slightly from 80% to 85% and then decreases slightly up to $pH_0$ 10. There is significant decrease of 16% in color removal, in the pH range of 10–12. It can also be inferred from Fig. 5.7 that the CR removal is maximum at $pH_0 = 7$ and also the solution is most stable at this $pH_0$. Therefore, further adsorption experiments were carried out at $pH_0 = 7$. 
Effect of adsorbent dosage ($m$)

Adsorbent dosage is an important parameter because this factor determines the capacity of an adsorbent for a given initial concentration of the adsorbate [Bulut and Aydin, 2006]. The effect of $m$ on the uptake of BG onto SD was studied at $T = 30 \, ^\circ\text{C}$ and $C_0 = 100 \, \text{mg/l}$ and the results are shown in Fig. 5.8. The removal of BG was found to be increasing with an increase in $m$ from 1 to 30 g/l. Initially, rapid increase in adsorption with the increase in adsorbent dose can be attributed to greater surface area and availability of more adsorption sites [Nandi et al., 2009]. The removal remained unchanged for $m > 4 \, \text{g/l}$ for SD. At $m < 3.5 \, \text{g/l}$, the SD surface becomes saturated with BG and the residual BG concentration in the solution is large. With an increase in $m$, the BG removal increases due to increased BG uptake by the increased amount of SD. For $m = 3.5 \, \text{g/l}$, the incremental BG removal became low. At about $m = 4 \, \text{g/l}$, the percent removal became almost constant.

Fig. 5.7 Effect of $pH_0$ on the adsorption of CR by SD ($T= 303 \, \text{K}, \ t = 4 \, \text{h}, \ C_0 = 10 \, \text{mg/l}, \ m = 4 \, \text{g/l}$).
The effect of $m$ on the uptake of CR onto SD was studied at $T = 30^\circ$C and $C_0 = 10$ mg/l and the results are shown in Fig. 5.9. The removal of CR was found to be increasing with an increase in the $m$ from 1 to 4 g/l. The removal remained unchanged for $m > 4$ g/l for SD. The increase in the adsorption with the SD dosage can be attributed to the availability of greater surface area and more adsorption sites [Cisneros et al., 2002]. At $m < 3.5$ g/l, the SD surface becomes saturated with CR and the residual CR concentration in the solution is large. With an increase in $m$, CR removal increases due to increased CR uptake by the increased amount of SD. For $m > 3.5$ g/l, the incremental CR removal became low. At about $m = 4$ g/l, the removal efficiency becomes almost constant.

Fig. 5.8 Effect of adsorbent dose on the adsorption of BG by SD ($T=303$ K, $t =3$ h, $C_0 = 100$ mg/l).
Fig. 5.9 Effect of adsorbent dose on the adsorption of CR by SD (T=303 K, \( t = 4 \) h, \( C_0 = 10 \) mg/l).

5.3.3.3 Effect of contact time (\( t \)) and initial dye concentration (\( C_0 \))

Effect of contact time for the removal of BG by the SD at \( C_0 = 50, 100 \) and 200 mg/l for \( m = 4 \) g/l (Fig. 5.10) (three top curves for % removal Vs. \( t \)) showed rapid adsorption of dye in the first 15 min and, thereafter, the adsorption rate decreased gradually and the adsorption reached equilibrium in about 3 h. Increase in contact time up to 24 h showed that the BG removal by about 0.6% over those obtained for 3 h contact time. This is the reason why an insignificant enhancement in adsorption is effected in 24 h as compared to that in 3 h. Since the difference in the adsorption values at 3 h and at 24 h is very small, after 3 h contact a steady-state approximation was assumed and a quasi-equilibrium situation was accepted. Further experiments were conducted for 3 h contact time only. Accordingly all batch experiments were conducted with a contact time of 3 h under shaking speed of 150 rpm. 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 [Nandi et al., 2009; Kalavathy and Miranda, 2010; Srivastava et al.,
2008]. Besides, the BG is adsorbed into the macro- and meso-pores that get almost
saturated during the initial stage of adsorption. Thereafter, the BG molecules have to
traverse farther and deeper into the micro-pores encountering much larger resistance
[Srivastava et al., 2008]. This results in the slowing down of the adsorption during the
later period of adsorption [Srivastava et al., 2006].

The effect of $C_0$ on the removal of BG by SD is shown in Fig. 5.10. It is
evident from the figure (three bottom curves for $q_t$ Vs $t$) that the amount of BG
adsorbed per unit mass of SD ($q_t$) increased with the increase in $C_0$, although
percentage BG removal decreased with the increase in $C_0$. The values of amount BG
adsorbed per unit mass of SD ($q_t$) with time are mentioned in Table A.1- A.3 for
adsorption of BG. The $C_0$ provides necessary driving force to overcome the
resistances to the mass transfer of BG between the aqueous and the solid phases. The
increase in $C_0$ also enhances the interaction between BG and SD. Therefore, an
increase in $C_0$ of BG enhances the adsorption of BG. The rate of adsorption also
increases with the increase in $C_0$ due to increase in the driving force [Kalavathy and
Miranda, 2010]. On changing the initial concentration of BG from 50 mg/l to 200
mg/l, the amount adsorbed increases from 12.4890 mg/g to 45.3534 mg/g respectively
(Table 5.1). Similar trend has been reported in literature for effect of time and $C_0$ for
removal of BG by adsorbents like kaolin [Nandi et al., 2009], bottom ash and deoiled
soya [Mittal et al., 2008], neem leaf powder [Bhattacharya and Sharma, 2003] and
modified peat-resin particles [Sun and Yang, 2003].
The effect of contact time on the removal of CR by SD at $C_0 = 10, 20$ and $30$ mg/l is given in Fig. 5.11. The contact time curves shows rapid adsorption of CR in the first 15 min, thereafter, the adsorption rate decreases gradually and the adsorption reaches equilibrium in 4 h (optimum contact time). Increase in contact time up to 24 h showed that the CR removal increases slightly over those obtained for optimum contact time. This is the reason why an insignificant enhancement in adsorption is effected in 24 h as compared to that in 4 h. Since the difference in the adsorption values at 4 h and at 24 h is very small, after 4 h contact a steady-state approximation was assumed and a quasi-equilibrium situation was accepted. Further experiments were conducted for 4 h contact time only.

Fig. 5.10 Effect of contact time on adsorption of BG by SD ($T = 303$ K, $m$ =4 g/l).
The effect of $C_0$ on the removal of CR by SD is shown in Fig. 5.11. It is also evident from the figure that the percentage CR removal decreased with the increase in $C_0$, although, CR adsorbed per unit mass of SD ($q_e$) increased with the increase in $C_0$. The values of amount of CR adsorbed per unit mass of SD ($q_t$) with time are mentioned in Table A.4-A.6. The $q_e$ increased with the increase in $C_0$ as the resistance to the uptake of CR from the solution decreases with the increase in CR concentration. The rate of adsorption also increases with the increase in $C_0$ due to increase in the driving force [Table 5.2] [Kalavathy and Miranda, 2010]. Similar trend has been reported in literature for effect of time and $C_0$ for removal of CR by various adsorbents [Ahmad and Kumar, 2010; Mall et al., 2005; Mittal et al., 2009; Afkhami et al., 2010; Lian et al., 2009].

![Graph](image)

**Fig. 5.11** Effect of contact time on adsorption of CR by SD ($T= 303$ K, $m =4$ g/l).
5.3.3.4 Effect of temperature

Temperature has a pronounced effect on the adsorption capacity of the adsorbents. Fig. 5.12 shows the plots of adsorption isotherms, $q_e$ versus equilibrium liquid phase concentration ($C_e$) for BG-SD system at different temperatures, 288, 303, and 318 K. It shows that with the increase in temperature, the adsorptivity of BG by SD decreases. This figure also shows that at lower adsorbate concentrations, $q_e$ rises sharply and thereafter the increase is gradual with solute concentration in the solution. Since sorption is an exothermic process, it would be expected that an increase in temperature of the adsorbate-adsorbent system would result in decreased sorption capacity of SD. The increase in BG sorption capacity with the decrease in temperature has also been reported by other investigators on kaolin [Nandi et al., 2009] and neem leaf powder [Bhattacharya and Sharma, 2003].

![Equilibrium adsorption isotherms at different temperatures for BG-SD system](image)

*Fig. 5.12 Equilibrium adsorption isotherms at different temperatures for BG-SD system ($t = 3 \text{ h}, C_0 = 50-200 \text{ mg/l}, m = 4 \text{ g/l}).*
Fig. 5.13 shows the plots of adsorption isotherms, $q_e$ versus equilibrium liquid phase concentration ($C_e$) for CR-SD system at different temperatures, 288, 303, and 318 K. It is found that the sorption of CR increases with an increase in temperature. If the adsorption process controlled by the diffusion process (intra-particle transport pore diffusion), the sorption capacity will increase with an increase in temperature due to endothermicity of the diffusion process [Weber, 1972]. An increase in temperature results in an increased mobility of the adsorbate and a decrease in the retarding forces acting on the diffusing adsorbates. This results in the enhancement in the sorptive capacity of the SD. However, the diffusion of the CR into the pores of the SD is not the only rate-controlling step, and the diffusion resistance can be ignored with adequate contact time. Therefore, an increase in sorptive capacity with an increase in temperature may be attributed to chemisorptions [Srivastava et al., 2005]. The increase in CR sorption capacity of various adsorbents with an increase in temperature has also been reported by other investigators [Yang et al., 2011; Ahmad and Kumar, 2010; Xia et al., 2011; Panda et al., 2009; Jain and Sikarwar, 2008; Wang and Wang, 2008].

![Fig. 5.13 Equilibrium adsorption isotherms at different temperatures for CR-SD system ($t=4$ h, $C_0 = 10-30$ mg/l, m = 4 g/l).](image-url)
5.3.4 Adsorption kinetic study

Pseudo-first-order, pseudo-second-order and intraparticle diffusion models are used models, for the kinetic study.

5.3.4.1 Pseudo-first-order and pseudo-second-order models

The adsorption of dye molecules from liquid phase to the solid phase can be considered as a reversible process with equilibrium being established between the solution and the solid phase. Assuming non-dissociating molecular adsorption of dye molecules on SD particles with no dye molecules initially present on the adsorbent, the uptake of the dye molecules by the SD at any instant \( t \) is given as [Srivastav et al 2009]

\[
q_t = q_e [1 - \exp(-k_f t)]
\]  

(5.1)

where, \( q_t \) is the amount of adsorbate adsorbed at time \( t \) (mg/g), \( q_e \) is the adsorption capacity at equilibrium (mg/g), \( k_f \) is the pseudo-first-order rate constant (min\(^{-1}\)), and \( t \) is the contact time (min). The pseudo-second-order model is represented as: [Blanchard et al., 1984; Ho and McKay; 1999]

\[
q_t = \frac{tk_s q_e^2}{1 + tk_s q_e}
\]  

(5.2)

The initial sorption rate, \( h \) (mg/g min), at \( t \to 0 \) is defined as

\[
h = k_s q_e^2
\]  

(5.3)

The prediction of the batch adsorption kinetics is necessary for the design of
industrial adsorption columns. In the present study, the frequently used kinetic models, namely pseudo-first-order and pseudo-second-order models have been tested to investigate the adsorption of BG and CR onto SD.

The experimental value of solid phase concentration of adsorbate at equilibrium ($q_{e,exp}$) and the calculated value of solid phase concentration of adsorbate at equilibrium ($q_{e,calc}$) for the pseudo-first-order model and pseudo second-order models are also shown in Table 5.1 for BG and Table 5.2 for CR. The $q_{e,exp}$ and the $q_{e,calc}$ values from the pseudo-second-order kinetic model are very close to each other, and also, the calculated correlation coefficient, $R^2$ are also closer to unity for pseudo-second-order kinetics than that for the pseudo first-order kinetics for BG and CR removal. Therefore, the sorption can be approximated more appropriately by the pseudo-second-order kinetic model than the first-order kinetic model for the adsorption of BG and CR by SD [Fig. 5.14, Fig 5.15 for BG and Fig. 5.16 and Fig. 5.17 for CR]. Similar results reported by earlier researchers for removal of BG by various adsorbents [Nandi et al., 2009; Mittal et al., 2008; Bhattacharya and Sharma, 2003; Sun and Yang, 2003]. Also similar results reported by earlier researchers for removal of CR by various adsorbents [Ahmad and Kumar, 2010; Xia et al., 2011; Panda et al., 2009; Mall et al., 2005; Mittal et al., 2009; Lian et al., 2009].
Table 5.1 Kinetic parameters for the removal of BG by SD, Initial concentration \((C_0) = 50-200\text{mg/l}\), Temperature \((T) = 303 \text{K}\), Shaking \((t) = 5 \text{h}\), Adsorbent dose \((m) = 4 \text{g/l}\).

<table>
<thead>
<tr>
<th>(C_0) mg/l</th>
<th>(q_{e,\text{exp}}) (mg/g)</th>
<th>(q_{e,\text{calc}}) (mg/g)</th>
<th>( kf ) (min(^{-1}))</th>
<th>( R^2 )</th>
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<tbody>
<tr>
<td>50</td>
<td>12.4890</td>
<td>1.2019</td>
<td>0.01635</td>
<td>0.826</td>
</tr>
<tr>
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<td>45.3534</td>
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<td>0.03319</td>
<td>0.993</td>
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<table>
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<tr>
<th>(C_0) mg/l</th>
<th>( h ) (mg/g min)</th>
<th>(k_s ) (g/ mg min)</th>
<th>( R^2 )</th>
</tr>
</thead>
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<td>50</td>
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<tr>
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<td>46.5100</td>
<td>6.8639</td>
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<table>
<thead>
<tr>
<th>(C_0) mg/l</th>
<th>(k_{id} ) (mg/ g min(^{1/2}))</th>
<th>( I ) (mg/g)</th>
<th>( R^2 )</th>
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<tbody>
<tr>
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<th>(k_{id} ) (mg/ g min(^{1/2}))</th>
<th>( I ) (mg/g)</th>
<th>( R^2 )</th>
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</thead>
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<td>200</td>
<td>0.3502</td>
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Table 5.2 Kinetic parameters for the removal of CR by SD, Initial concentration \((C_o) = 10-30 \text{ mg/l}\), Adsorbent dose \((m) = 4 \text{ g/l}\).

<table>
<thead>
<tr>
<th>Pseudo-first-order model</th>
<th>(C_o \text{ mg/l} )</th>
<th>(q_{e,\text{exp}} \text{ (mg/g)} )</th>
<th>(q_{e,\text{calc}} \text{ (mg/g)} )</th>
<th>(k_f \text{ (min}^{-1}) )</th>
<th>(R^2 )</th>
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<tr>
<td>20</td>
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<table>
<thead>
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<th>(C_o \text{ mg/l} )</th>
<th>(q_{e,\text{calc}} \text{ (mg/g)} )</th>
<th>(h \text{ (mg/g min)} )</th>
<th>(k_s \text{ (g/mg min)} )</th>
<th>(R^2 )</th>
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<td></td>
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<tr>
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<td>1</td>
<td></td>
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<td>0.0124</td>
<td>0.9998</td>
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</tbody>
</table>

<table>
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<tr>
<th>W-M Intra-particle diffusion model</th>
<th>(C_o \text{ mg/l} )</th>
<th>(k_{id,1} \text{ (mg/g min}^{1/2}) )</th>
<th>(I \text{ (mg/g)} )</th>
<th>(R^2 )</th>
</tr>
</thead>
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<tr>
<td>20</td>
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<td>1.580</td>
<td>0.9782</td>
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<td>1.692</td>
<td>0.9747</td>
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\(C_o \text{ mg/l} \)

<table>
<thead>
<tr>
<th>(k_{id,2} \text{ (mg/g min}^{1/2}) )</th>
<th>(I \text{ (mg/g)} )</th>
<th>(R^2 )</th>
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<tr>
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</tr>
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<td>30</td>
<td>0.068</td>
<td>5.016</td>
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</table>
Fig. 5.14 Lagergren first order kinetic plot for the removal of BG by SD (T= 303 K, \( m = 4 \text{ g/l} \)).

Fig. 5.15 Pseudo second order kinetic plot for the removal of BG by SD (T= 303 K, \( m = 4 \text{ g/l} \)).
Fig. 5.16 Lagergren first order kinetic plot for the removal of CR by SD (T= 303 K, m = 4 g/l).

Fig. 5.17 Pseudo second order kinetic plot for the removal of CR by SD (T= 303 K, m = 4 g/l).
5.3.4.2 Weber-Morris intra-particle diffusion equation

For the interpretation of experimental kinetics data, from a mechanistic viewpoint, prediction of the rate-limiting step is an important consideration. The adsorbate transport from the solution phase to the surface of the adsorbent particles occurs in several steps. The overall adsorption process may be controlled either by one or more steps, e.g. film or external diffusion, pore diffusion, surface diffusion and adsorption on the pore surface, or a combination of more than one step [Lakshmi et al., 2009]. The possibility of intra-particle diffusion was explored by using the intra-particle diffusion model [Weber, 1963].

\[ q_t = k_{id} t^{1/2} + I \]  

(5.4)

Where \( k_{id} \) is the intra-particle diffusion rate constant (mg/g min\(^{1/2}\)) and \( I \) (mg/g) is a constant. If the Weber-Morris plot of \( q_t \) versus \( t^{1/2} \) satisfies the linear relationship with the experimental data, then the sorption process is found to be controlled by intra-particle diffusion only. However, if the data exhibit multi-linear plots, then two or more steps influence the sorption process. The first, sharper portion is attributed to the diffusion of adsorbate through the solution to the external surface of adsorbent or boundary layer diffusion of solute molecules. The second, linear portion is the gradual equilibrium stage with intra-particle diffusion dominating. The third portion is attributed to the final equilibrium stage for which the intra-particle diffusion starts to slow down due to the extremely low adsorbate concentration left in the solution [Kalavathy and Miranda, 2010; Crank, 1965]. The mathematical dependence of fractional uptake of adsorbate on \( t^{1/2} \) is obtained if the sorption process is considered to be influenced by diffusion in the cylindrical (or spherical) and
convective diffusion in the adsorbate solution. Fig. 5.18 shows a representative $q_t$ versus $t^{1/2}$ plot for BG adsorption onto SD for $C_0 = 50$, 100 and 200 mg/l at 30 °C. In the figure, the plots are not linear over the whole time range, implying that the more than one process is controlling the sorption process. If the two steps are independent of one another, the plot of $q_t$ versus $t^{1/2}$ appears as a combination of two or more intersecting lines [Wu et al., 2000]; the first of the lines represents surface adsorption and the second intraparticle diffusion. The presence of such distinctive features in the plots of the present work could be interpreted as due to distinction between the two steps. Surface adsorption and intraparticle diffusion were likely to take place separately [Gad and Sayed, 2009]. The first portion (line not drawn for the clarity of picture) in Fig. 5.18 gives boundary layer diffusion, and further linear portions depict intra-particle diffusion. For $C_0 = 100$ and 200 mg/l, there are two linear portions - the first straight portion depicting mesopore diffusion and the second representing micropore diffusion [Lakshmi et al., 2009]. These show only the pore diffusion data. For $C_0 = 50$ mg/l, there is only one linear portion depicting combined mesopore diffusion.

Extrapolation of the linear portions of the plots back to the y-axis gives the intercepts, i.e. the value of $I$, which provides the measure of the boundary layer thickness. If the intercept is large, the boundary layer effect will also be large. 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 [Lakshmi et al., 2009]. Further, such deviation of straight line from the origin indicates that the pore diffusion is not the sole rate controlling step [Naiya et al., 2009]. Therefore, the adsorption proceeds via a complex mechanism. It seems that the intra-particle diffusion of BG dye into
pores (mesopore diffusion for $C_0 = 50$ mg/l and micropore diffusion for $C_0 = 100$ and 200 mg/l) is the rate-controlling step in the adsorption process. The amount of adsorbate and the driving force for BG adsorption is less for $C_0 = 50$ mg/l, as compared to that for $C_0 = 100$ and 200 mg/l; therefore, BG gets adsorbed in mesopores only, and adsorption into mesopores is the rate-limiting step. For $C_0 = 100$ and 200 mg/l, the driving force increases and overcomes the resistance for getting adsorbed into micropores; and therefore, adsorption into micropores is the rate-limiting step for higher $C_0$. Also, slopes of second and third portions ($k_{id,1}$ and $k_{id,2}$) are higher for higher $C_0$, which corresponds to an enhanced diffusion of BG through meso- and micropores at higher $C_0$. This is due to the higher driving force at higher $C_0$. Similar results reported in the literature for adsorption of BG on kaolin [Nandi et al., 2009], bagasse fly ash [Mane et al., 2007a] and rice husk ash [Mane et al., 2007b].

![Fig. 5.18 Weber and Morris intra-particle diffusion plot for the removal of BG by SD (T= 303 K, m = 4 g/l).](image)
Fig. 5.19 shows a representative $q_t$ versus $t^{1/2}$ plot for CR adsorption onto SD for $C_0 = 10, 20$ and $30$ mg/l at $30^\circ$C. In the figure, the plots are not linear over the whole time range, implying that the more than one process is controlling the sorption process. If the two steps are independent of one another, the plot of $q_t$ versus $t^{1/2}$ appears as a combination of two or more intersecting lines; the first of the lines represents surface adsorption and the second intraparticle diffusion. The presence of such distinctive features in the plots of the present work could be interpreted as due to distinction between the two steps. Surface adsorption and intraparticle diffusion were likely to take place separately. The first portion (line not drawn for the clarity of picture) in Fig. 5.19 gives boundary layer diffusion, and further linear portions depict intra-particle diffusion. For $C_0 = 10, 20$ and $30$ mg/l, there are two linear portions - the first straight portion depicting mesopore diffusion and the second representing micropore diffusion. These show only the pore diffusion data. It seems that the intra-particle diffusion of CR dye into pores is the rate-controlling step in the adsorption process. The values of $k_{id,1}$ and $k_{id,2}$ as obtained from the slopes of the straight lines are listed in Table 5.2. Similar results reported in the literature for adsorption of CR on bagasse fly ash and activated carbon [Mall et al., 2005], cattail root [Hua et al., 2010] and Penicillium YW 01 [Yang et al., 2011].

![Weber and Morris Intra-particle Diffusion Plot](image.png)

**Fig. 5.19** Weber and Morris intra-particle diffusion plot for the removal of CR by SD ($T= 303$ K, $m = 4$ g/l).
5.3.5 Adsorption equilibrium study

To optimize the design of an adsorption system for the adsorption of adsorbates, it is important to establish the most appropriate correlation for the equilibrium curves. Various isotherm equations have been used to describe the equilibrium characteristics of adsorption.

5.3.5.1 Freundlich and Langmuir isotherms:

Linearized form of Freundlich and Langmuir isotherm equations are given as

\[ \ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad \text{(Linear form)} \quad (5.5) \]

\[ \frac{C_e}{q_e} = \frac{1}{K_A q_m} + \frac{C_e}{q_m} \quad \text{(Linear form)} \quad (5.6) \]

Fig. 5.20 and 5.25 shows the Freundlich isotherm plots (\( \ln Q_e \) vs \( \ln C_e \)) for adsorption of BG and CR, respectively, onto SD at 288, 303 and 318 K. Langmuir isotherm plot (\( C_e/Q_e \) versus \( C_e \)) are shown in Fig. 5.21 and 5.26, respectively for adsorption of BG and CR, respectively, onto SD. Freundlich and Langmuir isotherm parameter along with linear and non-linear correlation coefficients are given in Tables 5.3 and 5.4, respectively. At all temperatures, Langmuir isotherm represents a better fit of the experimental data then Freundlich isotherm equation. The essential characteristics of a Langmuir isotherm can be expressed in terms of a dimensionless factor, \( R_L \), which describes the type of pattern and is defined as \( R_L=1/(1 + K_A C_0) \) indicates the nature of adsorption as

If \( R_L > 1 \) Unfavorable

\( R_L = 1 \) Linear

\( 0 < R_L < 1 \) Favorable

\( R_L = 0 \) Irreversible
The value of $R_L$ is found to be less than 1 for adsorption of BG and CR on SD, so adsorption onto SD is favorable. The values of $1/n$ were also found to be less than 1 showing favorable nature of adsorption.

### 5.3.5.2 The Temkin isotherm:

It is given as

$$q_e = \frac{RT}{b} \ln(K_T C_e) \quad (5.7)$$

This can be linearized as:

$$q_e = B_1 \ln K_T + B_1 \ln C_e \quad (5.8)$$

Where $B_1 = \frac{RT}{b}$

Temkin isotherm contains a factor that explicitly takes into account adsorbing species-adsorbent interactions. This isotherm assumes that (i) the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbent-adsorbate interactions, and that (ii) the adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy [Temkin and Pyzhev, 1940; Kim et al., 2004]. A plot of $q_e$ versus $\ln C_e$ enables the determination of the isotherm constants $B_1$ and $K_T$ from the slope and the intercept, respectively. $K_T$ is the equilibrium binding constant (l/mol) corresponding to the maximum binding energy and constant $B_1$ is related to the heat of adsorption. Fig. 5.21 and 5.28 shows the Temkin isotherm plot for BG and CR removal, respectively, at 288, 303 and 318 K. The Temkin isotherm parameters are listed in Tables 5.3 and 5.4.

### 5.3.5.3 Redlich-Peterson isotherm

Redlich and Peterson (1959) model has a linear dependence on concentration in the numerator and an exponential function in the denominator. It approaches the Freundlich model at high concentration and is in accord with the low concentration
limit of the Langmuir equation. Furthermore, the R–P equation incorporates three parameters into an empirical isotherm, and therefore, can be applied either in homogenous or heterogeneous systems due to the high versatility of the equation.

It can be described as follows:

\[ Q_e = \frac{K_R C_e}{1 + a_R C_e^\beta} \]  

(5.9)

Where \( K_R \) is R–P isotherm constant (L/g), \( a_R \) is R–P isotherm constant (L/mg) and \( \beta \) is the exponent which lies between 1 and 0, where \( \beta=1 \)

\[ Q_e = \frac{K_R C_e}{1 + a_R C_e} \]  

(5.10)

It becomes a Langmuir equation. Where \( \beta=0 \)

\[ Q_e = \frac{K_R C_e}{1 + a_R} \]  

(5.11)

i.e. the Henry’s Law equation

It can be converted to a linear form by taking logarithms:

\[ \ln \left( \frac{K_R}{Q_e} \frac{C_e}{Q_e} - 1 \right) = \ln a_R + \beta \ln C_e \]  

(5.12)

Plotting the left-hand side of equation against \( \ln C_e \) to obtain the isotherm constants is not applicable because of the three unknowns, \( a_R, K_R \) and \( \beta \). Therefore, a minimization procedure was adopted to solve equation by maximizing the correlation coefficient between the theoretical data for \( Q_e \) predicted from equation and experimental data. Therefore, the parameters of the equations were determined by minimizing the distance between the experimental data points and the theoretical model predictions with the solver add-in function of the Microsoft excel. Fig. 5.23
and 5.28 shows the R-P isotherm plot for BG and CR removal, respectively, at 288, 303 and 318 K. The R-P isotherm parameters and the correlation coefficients, $R^2$, for the R-P isotherms are listed in Tables 5.3 and 5.4 for BG and CR, respectively.

### 5.3.5.4 Dubinin-Radushkevich (D-R) isotherm:

It is given as [Dubinin and Radushkevich, 1947]

$$q_e = q_s \exp(-B\varepsilon^2)$$

(5.13)

Where, $q_s$ is the D-R constant and $\varepsilon^2$ can be correlated as

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e}\right)$$

(5.14)

The constant $B$ gives the mean free energy $E$ of sorption per molecule of sorbate when it is transferred to the surface of the solid from infinity in the solution and can be computed using the following relationship [Hasany and Chaudhary, 1996]:

$$E = \sqrt[3]{2B}$$

D-R isotherm plots for decolorization of BG and CR at 288, 303 and 318 K are shown in Fig. 5.24 and Fig. 5.29, respectively. The estimated values of the D-R constants for the adsorption of BG and CR are shown in Table 5.3 and 5.4 respectively. It may be observed that the sorption energy value is the lowest for adsorption of BG at lower temperatures. The values of correlation coefficients are the lowest in comparison to the values for all other isotherms investigated. Thus, the D-R equation does not represent the experimental data satisfactorily for decolorization of BG.
Table 5.3 Isotherm parameters for removal of BG by SD. Initial Concentration ($C_0$) = 50-200 mg/l, Shaking time ($t$) = 3 h, Adsorbent dose ($m$) = 4 g/l.

**Freundlich**: $q_e = K_F C_e^{1/n}$

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$K_F$ ((mg/g) (mg/l)$^{1/n}$)</th>
<th>$1/n$</th>
<th>$R^2$</th>
<th>MPSD</th>
</tr>
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<tr>
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<td>11.66024</td>
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<tr>
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<td>13.06713</td>
<td>0.295</td>
<td>0.9968</td>
<td>4.091748</td>
</tr>
</tbody>
</table>

**Langmuir**: $q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$K_L$ (l/mg)</th>
<th>$q_m$ (mg/g)</th>
<th>$R^2$</th>
<th>MPSD</th>
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</tbody>
</table>

**Temkin Constants**: $q_e = B_t \ln K_T + B_t \ln C_e$

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$K_T$ (l/mg)</th>
<th>$B_t$</th>
<th>$R^2$</th>
<th>MPSD</th>
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<td>0.9739</td>
<td>17.79075</td>
</tr>
</tbody>
</table>

**Redlich-Peterson Constants**: $q_e = \frac{K_R C_e}{1 + a_RC_e^\beta}$

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$K_R$ (g/l)</th>
<th>$a_R$ (l/mg)</th>
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**Dubinin-Radushkevich Constants**: $q_e = q_s \exp(-Be^{2})$

<table>
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<tr>
<th>$T$ (K)</th>
<th>$q_s$</th>
<th>$\beta$</th>
<th>$R^2$</th>
<th>MPSD</th>
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Table 5.4 Isotherm parameters for removal of CR by SD. Initial Concentration \((C_0) = 10-30\text{ mg/l}\), Adsorbent dose \((m) = 4\text{ g/l}\).

<table>
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<tr>
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<th>1/n</th>
<th>(R^2)</th>
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Freundlich \(q_e = K_F C_e^{\frac{1}{n}}\)

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<tr>
<th>T (K)</th>
<th>(K_L) (L/mg)</th>
<th>(q_m) (mg/g)</th>
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Langmuir \(q_e = \frac{q_m K_F C_e}{1 + K_F C_e}\)

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<tr>
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</table>

Temkin \(q_e = B_1 \ln K_T + B_1 \ln C_e\)

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<th>(q_R) (L/mg)</th>
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Redlich-Peterson \(q_e = \frac{K_R C_e}{1 + q_R C_e^\beta}\)

<table>
<thead>
<tr>
<th>T (K)</th>
<th>(q_s)</th>
<th>(\beta)</th>
<th>(R^2)</th>
<th>MPSD</th>
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</table>

Dubinin-Radushkevich constants: \(q_e = q_s \exp(-B e^\beta)\)

128
Fig. 5.20 Freundlich isotherm plots for the removal of BG (t = 3 h, SD dose = 4 g/l).

Fig. 5.21 Langmuir isotherm plots for the removal of BG (t = 3 h, SD dose = 4 g/l).
Fig. 5.22 Temkin isotherm plots for the removal of BG (t = 3 h, SD dose = 4 g/l).

Fig. 5.23 R-P isotherm plots for the removal of BG (t = 3 h, SD dose = 4 g/l).
Fig. 5.24 D-R isotherm plots for the removal of BG (t = 3 h, SD dose = 4 g/l).

Fig. 5.25 Freundlich isotherm plots for the removal of CR (t = 4 h, SD dose = 4 g/l).
Fig. 5.26 Langmuir isotherm plots for the removal of CR (t = 4 h, SD dose = 4 g/l).

Fig. 5.27 Temkin isotherm plots for the removal of CR (t = 4 h, SD dose = 4 g/l).
Fig. 5.28 R-P isotherm plots for the removal of CR (t = 4 h, SD dose = 4 g/l).

Fig. 5.29 D-R isotherm plots for the removal of CR (t = 4 h, SD dose = 4 g/l).
5.3.6 Choosing best-fit isotherm based on error analysis:

The values of the five error functions are presented in appendix A (Tables A.7 and A.8). By comparing the results of the values of the error functions, it is found that R-P and Temkin isotherm best-fitted the isotherm data for BG adsorption on SD. Similarly, the $R^2$ values for R-P and Temkin isotherms are closer to unity (Table 5.3). Therefore, any one of the R-P and Temkin isotherm could be used to represent the equilibrium adsorption of BG on SD at all temperatures.

Comparison of various isotherm equations plots for the adsorption of BG and CR by SD at 303 K is shown in Fig. 5.30 and 5.31, respectively. By comparing the results of the values of the error functions for CR removal for R-P and Temkin isotherms are smaller than other isotherms for all temperatures (Table 5.4). It may, however, be noted that the correlation coefficient, $R^2$ values for R-P isotherm are closer to unity in comparison to the values obtained for Temkin isotherms and hence R-P isotherms could be used for CR adsorption on SD. For BG adsorption, the $R^2$ values of D-R isotherm are not closer to unity in comparison to values obtained for other isotherm (Table 5.3). Therefore the D-R isotherm is not considered for comparison for BG adsorption in Fig. 5.30.
Fig. 5.30 Comparison of various isotherm equations for the adsorption of BG by SD at 303 K ($t = 3$ h, $C_0 = 50-200$ mg/l, $m = 4$ g/l).

Fig. 5.31 Comparison of various isotherm equations for the adsorption of CR by SD at 303 K ($t = 4$ h, $C_0 = 10-30$ mg/l, $m = 4$ g/l).
5.3.7 THERMODYNAMIC STUDY

The Gibbs free energy change of the adsorption process is related to the equilibrium constant by the classic Van’t Hoff equation

\[ \Delta G^0 = -RT \ln K \]  
(5.20)

According to thermodynamics, the Gibbs free energy change is also related to the entropy change and heat of adsorption at constant temperature by the following equation:

\[ \Delta G^0 = \Delta H^0 - T \Delta S^0 \]  
(5.21)

Combining above two equations, we get

\[ \ln K = \frac{-\Delta G^0}{RT} = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{R} \frac{1}{T} \]  
(5.22)

Where, \( \Delta G^0 \) is the free energy change (KJ/mol), \( \Delta H^0 \) is the change in enthalpy (KJ/mol), \( \Delta S^0 \) is the entropy change (KJ/mol K), \( T \) is the absolute temperature (K) and \( R \) is the universal gas constant (8.314 J/mol K). Thus \( \Delta H^0 \) can be determined by the slope of the linear Van’t Hoff plot i.e. as \( \ln K \) versus \( (1/T) \), using equation:

\[ \Delta H^0 = \left[ R \frac{d \ln K}{d(1/T)} \right] \]  
(5.23)

\( \Delta H^0 \) obtained here corresponds to isosteric heat of adsorption (\( \Delta H_{st,0} \)) with zero surface coverage (i.e. \( q_e = 0 \)) [Suzuki and Fujii, 1982]. Fig. 5.32 and 5.33 show the Van’t Hoff’s plots for Freundlich, Langmuir, Temkin and Redlich-Peterson
isotherms, from which $\Delta H_{st,0}$ and $\Delta S^0$ values have been obtained (Table 5.5 for BG and 5.6 for CR). The $\ln K$ calculated from Freundlich, Langmuir, Temkin and Redlich-Peterson isotherms constants. For significant adsorption to occur, the free energy changes of adsorption, $\Delta G^0$ must be negative [Srivastav et al., 2009]. The thermodynamics relation among $\Delta G^0$, $\Delta H^0$ and $\Delta S^0$ suggests that either (a) $\Delta H^0$ is positive and $\Delta S^0$ is positive and that the value of $T\Delta S$ is much larger than $\Delta H^0$, or (b) $\Delta H^0$ is negative and $\Delta S^0$ is positive or that the value of $\Delta H^0$ is more than $T\Delta S$. BG adsorption is exothermic in nature, giving a negative value of $\Delta H^0$. Hence, $\Delta S^0$ has to be positive or that the value of $\Delta H^0$ is more than $T\Delta S$. $\Delta G^0$ values were negative indicating that the sorption process led to a decrease in Gibbs free energy. Negative $\Delta G^0$ indicates the feasibility and spontaneity of the adsorption process. The earlier researchers reported the exothermic adsorption of BG on kaolin [Nandi et al., 2009] and neem leaf powder [Bhattacharyya and Sharma, 2003]. These results are in agreement with the present work.

The positive value of $\Delta H^0$ indicates that the process is endothermic in nature for CR adsorption on SD. The negative values of $\Delta G^0$ showed the spontaneous adsorption of CR on SD and the positive values of $\Delta S^0$ suggest that the increased randomness at the solid-solution interface during the adsorption of CR in aqueous solution on SD. The earlier researchers reported the endothermic adsorption of CR on bael shell carbon [Ahmad and Kumar, 2010] and modified hectorite [Xia et al., 2011]. These results are in agreement with the present work.
Fig. 5.32 Van’t Hoff plot for the adsorption of BG onto SD

Fig. 5.33 Van’t Hoff plot for the adsorption of CR onto SD.
Table 5.5 Thermodynamic parameters for adsorption of BG by SD

<table>
<thead>
<tr>
<th>Thermodynamic Properties</th>
<th>ΔG(KJ/mol)</th>
<th>ΔH(KJ/mol)</th>
<th>ΔS(J/mol K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>288 K</td>
<td>303 K</td>
<td>318 K</td>
</tr>
<tr>
<td>Langmuir</td>
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<td>R-P</td>
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Table 5.6 Thermodynamic parameters for adsorption of CR by SD

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<th>Thermodynamic Properties</th>
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<th>ΔH(KJ/mol)</th>
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5.3.8 COLUMN STUDY

5.3.8.1 MATERIALS AND METHODS

A Pyrex glass column of 100 cm length and 2.54 cm internal diameter with 0.2 cm wall thickness was used to contain SD as a fixed-bed adsorber. Schematic diagram of experimental set up is shown in Fig. 5.34. A fine mesh was introduced at the bottom of column over which a layer of ceramic beads was spread to prevent the escape of adsorbent. Synthetic dye solution was fed through the bed of SD in up-flow mode to avoid channeling of the effluent. A peristaltic pump was used to control the flow rate of dye with initial concentration \( C_0 \). Samples of the treated effluent were collected periodically and analyzed for concentration at time \( t \) \( (C_t) \). The flow through the tested column was continued until the dye concentration of column effluent approached 0.9, \( C_t/C_0 \), which indicated the exhaustion point \( (C_x) \) [Gupta et al., 2004; Sharma and Forster, 1995; Volesky and Prasetyo, 1994]. The curve of \( C_t/C_0 \) versus volume treated between the concentration at 10% break through \( (C_b) \) and concentration at exhaustion \( (C_x) \) is called the breakthrough curve [Gupta et al., 2004]. The effects of variation in flow rate and bed depth on the bed performance were studied. The \( C_0 \) was kept constant at 50 mg/l for BG and 20 mg/l for CR. All the experiments were performed at natural pH for BG and that of 7 for CR and temperature 30 \(^\circ\)C.
Fig. 5.34 Schematic diagram of Column study adsorption
5.3.8.2 RESULTS AND DISCUSSION

(a) Effect of flow rate on breakthrough curve

Figs. B.3-B.5 show the breakthrough profiles for the adsorption of BG removal in the continuous-flow fixed column at different bed depth at 30 °C. The flow rate was varied between 9-11 l/h, while the inlet BG concentration in the feed was held constant at 50 mg/l. Figs. B.8-B.10 show the breakthrough profiles for the adsorption of CR removal in the continuous-flow fixed column at different bed depth at 30 °C. The flow rate was varied between 9-11 l/h, while the inlet CR concentration in the feed was held constant at 20 mg/l. When the adsorption zone moves up and the upper edge of this zone reaches the top of the column, the effluent concentration starts to rise rapidly [Faust and Aly, 1987]. This point is called the breakthrough point, which indicates the $t_b$. Results show that a decrease in the flow rate at a constant bed depth increases the $t_b$ and, therefore, the $V_b$ (volume of the solution treated at breakthrough point), due to an increase in the empty bed contact time (EBCT) [Goel et al., 2005; Ko et al., 2000; Othman et al., 2001]. Using a smaller flow rate, the front of the adsorption zone reaches the top of the column later, thereby giving higher $t_b$. An increase in the flow rate appears to increase the sharpness of the breakthrough curves. These results indicate that as the flow rate increases the shape of the breakthrough curve drastically changes from S-shape to that of a downwardly concave shape. The curves exhibit a sharp leading edge and a broad trailing edge. The broadness of the trailing edge is most likely due to slow intraparticle diffusion within the pores of the SD. According to Cooney (1991), the ‘tailing’ of a breakthrough curve (i.e. a slow approach of $C/C_0$ towards 1) is commonly observed in liquid phase sorption where intraparticle diffusion is the rate-limiting transport process [Ko et al., 2000].
As the flow rate through the bed increases, the depth of the adsorption zone increases and the time of contact of the solution with the adsorption zone decreases [Ko et al., 2000; Vijayaraghavan et al., 2004]. In designing a column, the length of the adsorption zone represents the minimum bed depth needed to produce a low effluent BG and CR concentration. This result suggests that a lower flow rate or a longer contact time may be required for BG and CR adsorption by a column filled SD.

(b) Effect of bed depth on breakthrough curve

Figs. B.1 and B.2 show the breakthrough curves for bed depths of 15, 30 and 45 cm and feed flow rates of 9 and 11 l/h for BG removal. Figs. B.6 and B.7 show the breakthrough curves for bed depths of 15, 30 and 45 cm and feed flow rates of 9 and 11 l/h for CR removal. The time required for the effluent to reach breakthrough concentration, $t_b$, increased with increasing bed depth. This may be attributed to the increase in binding sites on the adsorbent [Zulfadhlly et al., 2001]. Although an increasing bed depth increases $t_b$, very high bed depth is not useful for a single column. The shape and gradient of the breakthrough curves were slightly different with the variable bed depths. As the bed height increases from 15 cm to 45 cm the curves change their profile from steep concave to flatter concave (i.e., the steepness changes). The breakthrough curves of the longer beds (45 cm) tended to be more gradual, meaning that the column was difficult to be completely exhausted [Goel et al., 2005; Vijayaraghavan et al., 2004]. Here, breakthrough time is taken as the time of operation at which the ratio of the effluent to inlet BG and CR concentrations becomes 0.1.

(c) Bed depth service time (BDST) equation (Model)

The BDST model is based on physically measuring the capacity of the bed at
different breakthrough values. This simplified design model ignores the intraparticle mass transfer resistance and external film resistance such that the adsorbate is adsorbed onto the adsorbent surface directly. With these assumptions, the BDST model works well and provides useful modeling equations for the changes of the system parameters [Ko et al., 2000]. The BDST model parameters can be helpful to scale up the process for other flow rates without further experimental run [Goel et al., 2005]. It is used for predicting the relationship between bed depth (x) and service time ‘t’, in terms of process concentrations and adsorption parameters [Zulfadhly et al., 2001].

\[
\ln\left(\frac{C_0}{C} - 1\right) = KN_0 \frac{x}{V} - KC_0 t
\]  

(5.24)

Where \(C_0\) is the initial concentration of solute (mg/m\(^3\)), \(C\) is the desired concentration of solute at breakthrough (mg/m\(^3\)), \(K\) is the rate constant (m\(^3\) liquid/mg hr), \(x\) is the depth of bed (m), \(N_0\) is the adsorptive capacity of adsorbent (mg/m\(^3\)), \(V\) is the linear flow velocity of feed to bed (m/hr) and ‘t’ is the service time of column under above conditions.

After the \(V\) and \(t\) are determined, the BDST curves are plotted between \(t\) versus \(x\). According to Bohart-Adams model, the relationship between \(t\) and \(x\) is described as in [Goel et al., 2005; Ko et al., 2000; Othman et al., 2001].

\[
t = \frac{N_0 x}{C_0 V} - \left(\frac{1}{KC_0}\right)\ln\left(\frac{C_0}{C} - 1\right)
\]  

(5.25)

This equation predicts linear BDST plots. The adsorptive capacity of the system, \(N_0\) and the rate constant can be evaluated from the slope of the plot of \(t\) versus
x, which yields a straight line (refer Figs. B.11 and B.13). The numerical value of the slope is $N_0/C_0V$ where upon $N_0$ can be calculated. The rate constant is in turn calculated from the intercept by using:

$$b = \left( \frac{1}{KC_0} \right) \ln \left( \frac{C_0}{C} - 1 \right)$$  \hspace{1cm} (5.25)

The minimum bed depth ($x_{\text{min}}$) can be calculated from the relationship of Eq. 5.24 by letting $t=0$ and solving for $x$ [Volesky and Prasetyo, 1994].

The plots were linear, indicating the validity of BDST model when applied to a fixed bed of SD. Table 5.7 for BG and Table 5.8 for CR show the slope and intercept calculated using a flow rate of 9.0, 11 l/h and BDST model parameters are calculated for the above flow rates at 90% breakthrough. Table 5.7 for BG and Table 5.8 for CR show the BDST model parameters: adsorption capacity ($N_0$), rate constant ($K$) and critical bed depth ($x$) calculated from slope and intercept of BG studied.

At 50% breakthrough is reduced to

$$\left( \frac{C_0}{C} = 2 \right)$$  \hspace{1cm} (5.26)

Thus the logarithmic term reduces to zero and the expression can be written as

$$t_{50} = \frac{N_0x}{C_0V}$$  \hspace{1cm} (5.27)

or  \hspace{1cm} $t_{50} = \text{constant (x)}$

Figs. B.12 and B.14 show the plot of the service time ‘$t$’, against bed height ($x$), at 50% breakthrough curve for the adsorption of BG and CR by SD respectively. Theoretically, a 50% breakthrough curve between $t$ and ($x$) must result in a straight line passing the origin. However, Figs. B.12 and B.14 clearly show that the straight line did not pass through the origin. The failure of $t_{50}$ versus ($x$) curve indicates that
the phenomena occurring during the treatment of BG and CR by SD is quite complex and involve more than one rate-limiting step [Goel et al., 2005; Ko et al., 2000; Othman et al., 2001].

Table 5.7 Bed depth service time parameter for adsorption of BG using SD

<table>
<thead>
<tr>
<th>Flow rate (L/hr)</th>
<th>Linear flow rate (m/hr)</th>
<th>Slope (hr/m)</th>
<th>Intercept (hr)</th>
<th>N₀ (g/m²)</th>
<th>K (m³/gm-hr⁻¹)</th>
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Table 5.8 Bed depth service time parameter for adsorption of CR using SD

<table>
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<th>Flow rate (L/hr)</th>
<th>Linear flow rate (m/hr)</th>
<th>Slope (hr/m)</th>
<th>Intercept (hr)</th>
<th>N₀ (g/m²)</th>
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<tr>
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<td>2097*10⁻²</td>
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<td>2042*10⁻²</td>
</tr>
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</table>

5.4 SUMMARY

The results presented herein show that NaOH treated sawdust (SD) enhances its adsorption properties considerably for the decolorization of BG and CR dye bearing water. A higher percentage of BG and CR removal by SD was possible provided that the C₀ in the solution was low. The optimum adsorbent dose was 4 g/l of solution for both BG and CR removal. Adsorption kinetics was found to follow a second-order rate expression. The adsorption of BG onto SD was found to be exothermic in nature and that of CR onto SD was endothermic in nature. Equilibrium
adsorption data for BG on SD were well represented by the R-P and Temkin isotherm models. Equilibrium adsorption data for CR on SD were well represented by the R-P isotherm model. Adsorption of BG on SD is favorably influenced by a decrease in the temperature of the operation. Adsorption of CR on SD is favorably influenced by an increase in the temperature of the operation. The adsorption capacities of SD for CR dye were obtained as 5.10, 31.25 and 66.67 mg/g at 288, 303 and 318 K, respectively. Similar trend has also been reported by other investigators for CR dye [Yang et al., 2011; Ahmad and Kumar, 2010; Xia et al., 2011; Panda et al., 2009; Jain and Sikarwar, 2008; Wang and Wang, 2008]. The adsorption capacities of SD for BG dye were obtained as 58.4795, 55.8659 and 52.6315 mg/g at 288, 303 and 318 K, respectively. Similar results reported by other investigators for adsorption of BG on kaolin [Nandi et al., 2009] and neem leaf powder [Bhattacharya and Sharma, 2003]. The negative value of $\Delta G^0$ indicates spontaneous adsorption of BG and CR on SD. This study concludes that the SD could be employed as low-cost adsorbent for decolorization of BG and CR dye bearing water. Break through time increased with increase in bed height and decrease in flow rate for the adsorption of BG and CR by SD fixed-bed. Bohart-Adams equation was found to be applicable for the column study.

5.5 COMPARISON OF ADSORPTION, COAGULATION, ELECTROCOAGULATION AND ELECTROCHEMICAL TECHNIQUES

The coagulants magnesium chloride/lime, ferrous sulphate-lime and alum were used for the treatment of BG and CR dyes. Synthetic wastewaters containing BG were removed by 99 percent using the magnesium chloride-lime and ferrous sulphate-lime. The wastewater containing CR dye was also removed by 99 percent using magnesium
chloride-lime, ferrous sulphate-lime and alum. Higher dose of coagulants was needed for the treatment of a high concentration of dyes. It was observed that alum alone with small dosage is more efficient for color removal efficiency of CR. Small quantities of highly polluted wastewaters were successfully purified by the coagulation method [Boon et al., 1999]. By coagulation the high sludge generation takes place and cost for disposal increases [Torres et al., 2010, Szygula et al., 2009]. From the present study it has been observed that electrocoagulation technique is very much effective for the decolorization of BG and CR dye bearing water. Electrocoagulated sludge contains less bound water besides being more shear resistant and readily filterable [Aleboyeh et al., 2008; Kabdas et al., 2009; Davila et al, 2000]. The results of the present studies showed that electrochemical process could be efficiently used to degrade the BG and CR from aqueous solution. But the energy consumption is high in electrocoagulation and electrochemical techniques [Raghu et al., 2009; Vlyssides et al., 1999; Davila et al, 2000; Aleboyeh et al., 2008]. Adsorption techniques have gained favor recently due to their efficiency in the removal of pollutants too stable for conventional methods [Gupta et al., 2004; Gupta et al., 2009; Mittal et al., 2005]. Adsorption produces a high quality product, and is a process which is economically feasible [Nandi et al., 2009]. Decolorization is a result of two mechanisms: adsorption and ion exchange [Slokar and Marechal surface area, particle size, temperature, pH, and contact time [Kargin and Ozmihc, 2004; Dogan and Alkan, 2004]. Adsorption is well recognized as a unit operation for the removal of impurities present in trace amounts from wastewater which otherwise cannot be removed efficiently. These include heavy metals, non-biodegradable organic compounds like phenols, toxic substances, dyes etc. It has been used for taste and odor control in water and wastewater treatment
[Namasivayam et al., 1998]. Almost complete removal of impurities with negligible side effects explains its wide application in tertiary treatment stages and polishing stages [Hameed and EI-Khaiary 2008]. The adsorption study concludes that the SD could be effectively employed as low-cost adsorbent for decolorization of BG and CR dye bearing water. Numbers of technology is available for treatment of dye bearing wastewater. Attempts may be made to develop simple to use technology, cost effective based on these methods. All the techniques are not suitable for all conditions, proper justification is necessary for choosing the particular technique for the given condition.