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Use of hen feathers as potential adsorbent for the removal of a hazardous dye, Brilliant Blue FCF, from wastewater

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Abstract

Waste material, hen feather, a biosorbent, was successfully utilized in removing a water-soluble hazardous triphenylmethane dye, Brilliant Blue FCF from wastewater. The paper incorporates effect of pH, temperature, amount of adsorbent, contact time, concentration of adsorbate, etc. The adsorption data validates Langmuir and Freundlich adsorption isotherms and on the basis of these isotherms thermodynamic parameters like Gibb's free energy, change in enthalpy and entropy were calculated. Kinetics of the ongoing adsorption was also monitored and specific rate constants for the involved process were calculated at different temperatures. Kinetic measurements suggest a first order adsorption kinetics and adsorption was found to be applicable via film diffusion process in the entire concentration range.

Keywords: Hen feather; Brilliant Blue FCF; Adsorption; Kinetics; Waste material; Biosorbent

1. Introduction

Ever since the adsorption technique has been used for the removal of toxic chemicals from wastewater there has been a struggle to uncover some new, economic and competent adsorbents, particularly waste materials. Thus, many waste materials like, shells, husks, plant leaves, etc., have been tried as adsorbents. But still the question mark on the economics involved in the developed process persists. Moreover, most of these materials are also utilized in some other useful purposes and this makes their availability difficult.

Recently, our laboratory explored the use of waste material, hen feathers, as biosorbent to remove a toxic triphenylmethane dye, Brilliant Blue FCF and found these quite proficient and economic. Literature survey reveals that surprisingly very little attention has been paid so far, to use chicken feathers as adsorbent and only few reports are available, which only describe removal of metal impurities from wastewater [1–4]. Thus, the idea to use hen feathers as adsorbent to remove hazardous dyes seems to be an innovative one for the appropriate, valuable and necessitous utilization of such a waste material for the mankind.

The dye under consideration is Brilliant Blue FCF, which is a popular colorant in the textile and leather industries. Earlier it was also used as a common food additive to color confectionary and dairy products but because of its toxic effects towards human and animals it was banned. It is carcinogenic [5], causes reproductive and neurological disorders [6,7], severe allergies [8], anaphylactic reactions [9] including rashes, swelling and trouble in breathing in human being. Even behavioural—convulsions [10], gastrointestinal tumors, blood-lymphoma, etc. [11] have also been found in rodents.

Availability of three sulfonic acid groups with the Brilliant Blue FCF molecule makes it highly ionic and soluble in aqueous medium and due to this reason the dye tenders tremendous mobility in the soils. Moreover, development of bright greenish blue hue with water in soil and rock materials, distinguishes the dye from other red and yellow dyes and that is why Brilliant Blue FCF is also used as tracer dye to visualize flow pathway of water in the vadose zone [12,13].

Despite its adverse effects and variety of uses not much attention has been paid to remove it from the water and may be because of its complex structure very limited techniques have been explored. Reports are available to remove this dye through electrochemical [14] and photochemical [15] degradation techniques, but unfortunately degradation of the Brilliant Blue FCF leads amino products and toxicity in the water. Adsorption of

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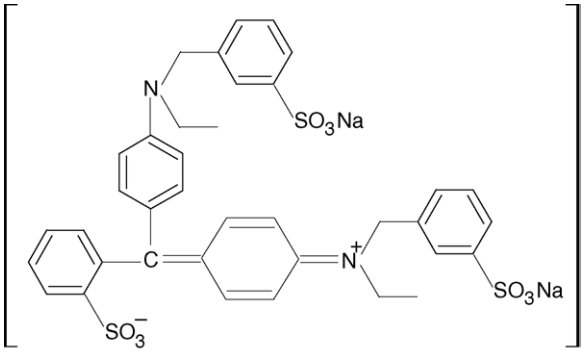
Brilliant Blue FCF over porous xerogels [16] and polymeric resins [17] has also been tried but both the materials are costly adsorbents.

Keeping all this in view, it was considered worthwhile to develop a systematic and economic procedure to remove the hazardous dye, Brilliant Blue FCF from the wastewater by adsorbing over the waste material and biosorbent, hen feather.

2. Materials and methods

Brilliant Blue FCF, bis{4-(*N*-ethyl-*N*-3-sulfophenylmethyl) aminophenyl}-2-sulfophenyl methylium disodium salt (molecular formula $C_{37}H_{34}O_9N_2S_3Na_2$), was obtained from M/s Merck and its stock solution (1 mM) was prepared in doubly distilled water. All other reagents used were of A.R. grade. Hen feathers were collected from local poultry farm and activated before use.

The pH of each solution was measured by using microprocessor based pH meter; model number HI 8424 (M/s Henna Instruments, Italy) and absorbance measurements were carried out on UV–vis spectrophotometer model number 117 (M/s Systronics, Ahmedabad, India) over the wavelength range 200–710 nm:



BRILLIANT BLUE FCF

Hen feathers procured from the local poultry farm were first thoroughly agitated in the pool of distilled water and then rinsed several times by doubly distilled water. These wet feathers were then dried. From each dried feather, soft barbs were cut with the help of scissors and hard middle rachis was removed and discarded. The barbs thus obtained were about 1 cm of length, which were now cut into small pieces of approximately 0.1 mm length each, with the help of sharp blade. The dried material was then treated with hydrogen peroxide (30%, w/v) for 24 h to oxidize all possible adhering organic material. Now for the removal of moisture, the material obtained was kept in an oven at 100 °C for 12 h and activated adsorbent thus obtained was stored in a vacuum desiccator until used.

Adsorption studies with the feathers were carried out by batch technique at 30, 40 and 50 °C temperatures. A series of 100 mL graduated conical flasks containing 25 mL of adsorbate solutions of varying concentrations and required amount of the hen feathers were employed at a desired pH and temperature. These flasks were agitated intermittently for about 1–3 h to achieve equilibration, however, shaking for 3–10 h gave practically the same uptake in each case. Once the equilibrium is thought to be reached, solution was carefully filtered by using Whatman filter paper No. 42 and concentration of the dye in the solution after equilibrium adsorption was determined spectrophotmetrically by measuring the absorbance at λ_{max} of 630 nm. The wavelength was recorded before and after the adsorption and in all the cases no shift in the absorbance peak (λ_{max} = 630 nm) was observed.

For kinetic studies 25 mL solution of Brilliant Blue FCF of known concentration and a known amount of adsorbent were taken in an airtight 100 mL conical flask. Keeping the flask in a water bath, maintained at desired temperature, mixture was mechanically agitated. After a definite interval of time, the solution of the flasks was filtered and filtrate of each was analyzed for the uptake of dye. The kinetic studies were also performed at different adsorbate concentrations.

3. Results and discussion

3.1. Adsorption studies

Removal of Brilliant Blue FCF over hen feathers was carried out in the pH range 2–6 and it was found that the adsorption decreases with increase in pH (Fig. 1). The variation in the removal of the Brilliant Blue FCF with respect to pH can be explained by considering the surface charge of the adsorbent materials. The higher adsorption of the dye over the adsorbent hen feathers at low pH may be due to neutralization of the negative charge at its surface, which increases the protonation. This facilitates diffusion to provide more of the active surface of the adsorbent resulting thereby enhanced adsorption at its surface. Decrease in the adsorption of the dye with increasing pH may be due to deprotonation, which hinders the diffusion and as a result of which adsorption of the dye decreases till pH 4.0 and then remains constant. Maximum uptake of the dye takes place at around pH 2.0, which was therefore selected for all subsequent studies.

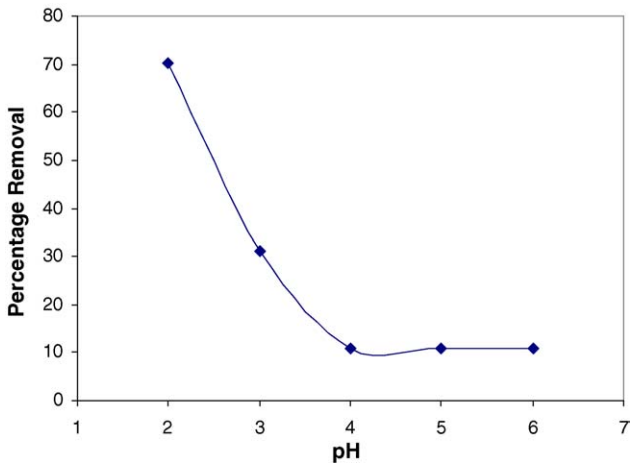


Fig. 1. Effect of pH on uptake of Brilliant Blue FCF (1×10^{-4} M) by hen feathers (0.01 g) at 30 °C.

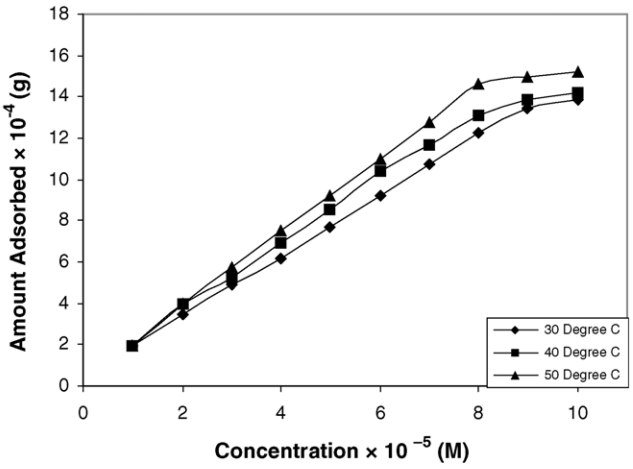


Fig. 2. Effect of concentration for the removal of Brilliant Blue FCF by hen feathers (0.01 g) at pH 2.0 and at different temperatures.

The effect of concentration of the dye on adsorption was monitored in the concentration range 1×10^{-5} to 1×10^{-4} M at pH 2.0 and temperatures 30, 40 and 50 °C. Fig. 2 exhibits that the adsorption of the dye increases with increasing temperature, indicating thereby the process to be endothermic in nature.

Sorption data obtained in the concentration range $3–8 \times 10^{-5}$ M was correlated with following linear forms of the Langmuir (Eq. (1)) and Freundlich (Eq. (2)) models:

$$\frac{1}{q_e} = \frac{1}{Q_0} + \left(\frac{1}{bQ_0}\right)\left(\frac{1}{C}\right) \quad (1)$$

$$\log q_e = \log K_f + \frac{1}{n}\log C \quad (2)$$

where C is measured molar concentration in solution at equilibrium, Q_0 the number of moles of solute adsorbed per unit weight of adsorbent, q_e the number of moles of solute adsorbed per unit weight at concentration C and b, K_f and n are constants.

Best fitted straight lines obtained in case of Langmuir (Fig. 3) and Freundlich (Fig. 4) plots confirm the applicability of both the adsorption models in the present studies. The value of Langmuir and Freundlich constants derived from the respective plots are presented in the Table 1. The data indicates that the values of K_f and n are almost constant at all the temperatures. However, values of Q_o increases with increase in temperature, which further indicates the processes to be endothermic in nature.

The favorablility of the ongoing adsorption process was confirmed on the basis of method applied by Weber and Chakravorti [18], which suggests that the linear, favorable or irreversible nature of isotherm is dependent on the obtained value of separation factor (r) as unity, between 0–1 and zero, respectively. The separation factor 'r' [19], a dimensionless constant, was

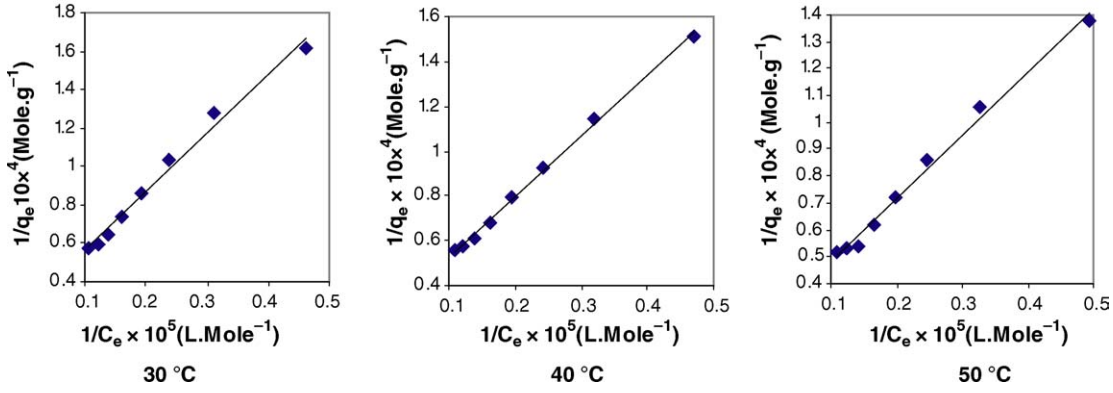


Fig. 3. Langmuir adsorption isotherms for adsorption of Brilliant Blue FCF over hen feathers (0.01 g) at pH 2.0.

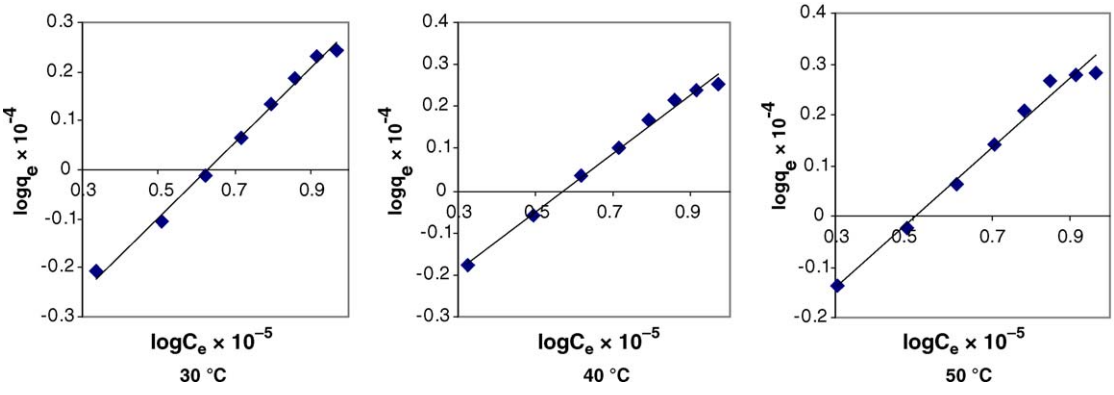


Fig. 4. Freundlich adsorption isotherms for adsorption of Brilliant Blue FCF over hen feathers (0.01 g) at pH 2.0.

Table 1
Freundlich and Langmuir constants and separation factor for the adsorption of Brilliant Blue FCF over hen feathers (0.01 g) at pH 2.0 and different temperatures

Temperature (°C)	Q_0 ($\times 10^{-4}$ mol g^{-1})	b ($\times 10^3$ L mol^{-1})	n	K_f	r
30	3.9984	8.104	0.132	0.9999	0.925
40	3.9463	9.352	0.142	0.9999	0.914
50	3.9020	10.678	0.145	0.9999	0.904

calculated by following equation:

$$r = \frac{1}{1 + bC_0} \quad (3)$$

where, values b and C_0 were obtained from Langmuir isotherm. In the present case the values of r (Table 1) were found less than unity at all temperatures and validate the ongoing process a highly favorable one.

Langmuir isotherms were also used for calculating thermodynamic parameters on the basis of following equations:

$$\Delta G^\circ = -RT \ln b \quad (4)$$

$$\Delta H^\circ = -R \left(\frac{T_2 T_1}{T_2 - T_1} \right) \ln \left(\frac{b_2}{b_1} \right) \quad (5)$$

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} \quad (6)$$

where b, b_1, b_2 are the equilibrium constants at different temperatures and obtained from the slopes of Langmuir adsorption isotherms at different concentrations.

Obtained values of the thermodynamic parameters are presented in Table 2. At all the temperatures negative values of ΔG° were obtained, which indicates the nature of adsorption feasible and spontaneous. It may also be observed that the ΔG° values decreases with the increasing temperature, which suggest more amount of adsorption of the dye at higher temperature. Positive values of enthalpy change (ΔH°) further authenticate endothermic nature of the present adsorption, while positive entropy change (ΔS°) values reflect the affinity of the feathers towards Brilliant Blue FCF.

3.2. Kinetic studies

In order to formulate an effective and applicable adsorption model, kinetics of the adsorption process was monitored very carefully by observing effects of contact time, amount of adsorbent and concentration of adsorbate solution on the uptake of the dye.

Contact time studies suggest that at 5×10^{-5} M adsorbate concentration (Fig. 5) about 28, 29 and 40% Brilliant Blue FCF adsorbs within initial one hour of adsorption over hen feathers at 30, 40 and 50 °C, respectively. While at 9×10^{-5} M adsorbate concentration (Fig. 6) the amount adsorption achieved was only 12, 14 and 17% at the three temperatures, respectively. Thus, in the lower concentration range equilibrium was established within 200 min, whereas, at higher concentration 300 min were found sufficient for attaining the equilibrium. Further, kinetics of the process at different temperatures (30, 40 and 50 °C) exhibits marginal increase in adsorption with the increasing temperature (Figs. 5 and 6). The half-life of each process was also calculated and was found to decrease with increase in temperature. This trend once again confirms the endothermic nature of the ongoing process.

Table 2
Thermodynamic parameters for the uptake of Brilliant Blue FCF over hen feathers (0.01 g) at pH 2.0

$-\Delta G^\circ$ (kJ mol^{-1})			ΔH° (kJ mol^{-1})	ΔS° (J K^{-1} mol^{-1})		
30 °C	40 °C	50 °C		30 °C	40 °C	50 °C
22.672	23.793	31.093	11.22	111.85	111.86	130.99

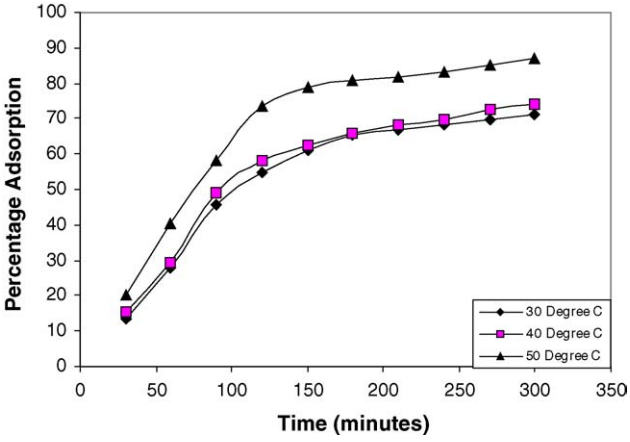


Fig. 5. Effect of contact time for the uptake of Brilliant Blue FCF (5×10^{-5} M) by hen feathers (0.01 g) at pH 2.0 and at different temperatures.

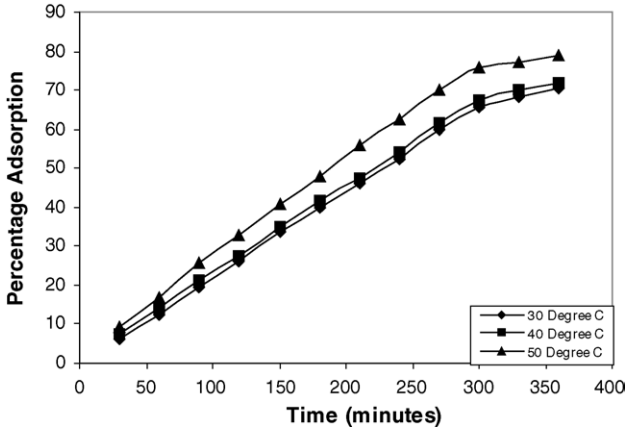


Fig. 6. Effect of contact time for the uptake of Brilliant Blue FCF (9×10^{-5} M) by hen feathers (0.01 g) at pH 2.0 and at different temperatures.

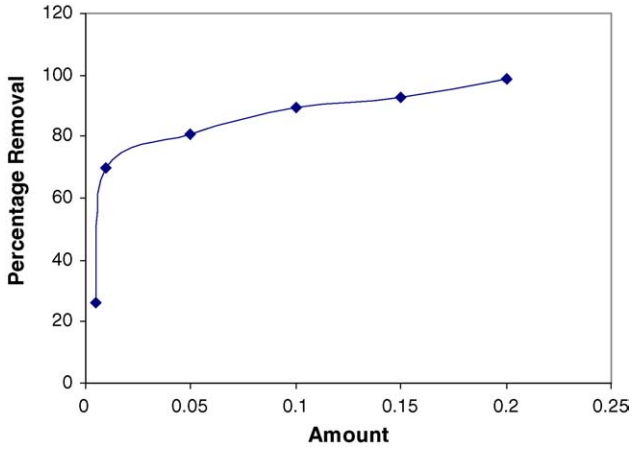


Fig. 7. Effect of amount of adsorbent for the removal of Brilliant Blue FCF (1×10^{-4} M) at 30 °C and pH 2.0.

Uptake of the dye was also monitored through observing the effect of amount of adsorbent (Fig. 7) and it was found that the most substantial increase in adsorption was observed when amount of adsorbent is increased by two times (0.005–0.01 g), however this effect was not prominent, when more adsorbent was introduced in the solution. Rate of uptake of the dye over adsorbent was also found to follow the same pattern. Since fairly good adsorption was achieved by using 0.01 g of feathers, hence all the studies were made with this amount only. By increasing the amount of adsorbent the half-life was found decreasing at all the temperatures, which confirms the dependency of amount of adsorbent on rate of adsorption.

3.2.1. Adsorption rate constant study

The specific rate constants of Brilliant Blue FCF—hen feather adsorption at different temperature was evaluated by using following Lagergren's first order rate expression [20]:

$$\log(q_e - q_t) = \log q_e - \frac{k_{ads}}{2.303} \times t \quad (7)$$

where q_e and q_t are the amount adsorbed at equilibrium and time t, respectively. Straight lines obtained in the time versus $\log(q_e - q_t)$ plot (Fig. 8), confirm the first order nature of the process at each temperature. The value of the rate constant, k_{ads}, obtained from the slop of straight lines of Fig. 8, were found to increase from 2.11×10^{-2} to 2.90×10^{-2} min^{-1} from 30 to 50 °C at 5×10^{-5} M concentration of Brilliant Blue FCF further confirms the increase in uptake of dye by increasing temperature.

3.2.2. Rate expression and treatment of data

In order to identify the mechanistic steps involved in the ongoing adsorption process, the obtained kinetic data has been treated by ingenious mathematical treatment suggested by Boyd et al. [21] and Reichenberg [22]. This helped in judging the nature of overall rate of the dye removal and ascertaining that whether the on-going process is particle diffusion or film diffusion.

During the adsorption of an organic/inorganic compound by a porous adsorbent following three possible consecutive steps are thought to be operative:

a. Film diffusion
b. Particle diffusion
c. Adsorption of adsorbate on the interior surface of the adsorbent.

Out of these three processes the third one is considered quite rapid and that is why cannot be treated as rate-limiting step [23]. However, remaining two steps give rise to following three distinct cases:

- Case I, when external transport > internal transport, where rate is governed by particle diffusion.
- Case II, when external transport < internal transport, where rate is governed by film diffusion.
- Case III, when external transport ≈ internal transport, where formation of a liquid film surrounding the adsorbent particles with a proper concentration gradient as transport of ions to the boundary may not be possible at a significant rate.

To examine the actual process involved in the present adsorption, following quantitative treatment of the sorption dynamics [22] was employed:

$$F = 1 - \frac{6}{\pi^2} \sum_{1}^{\infty} \left(\frac{1}{n^2}\right) \exp(-n^2 B_t) \quad (8)$$

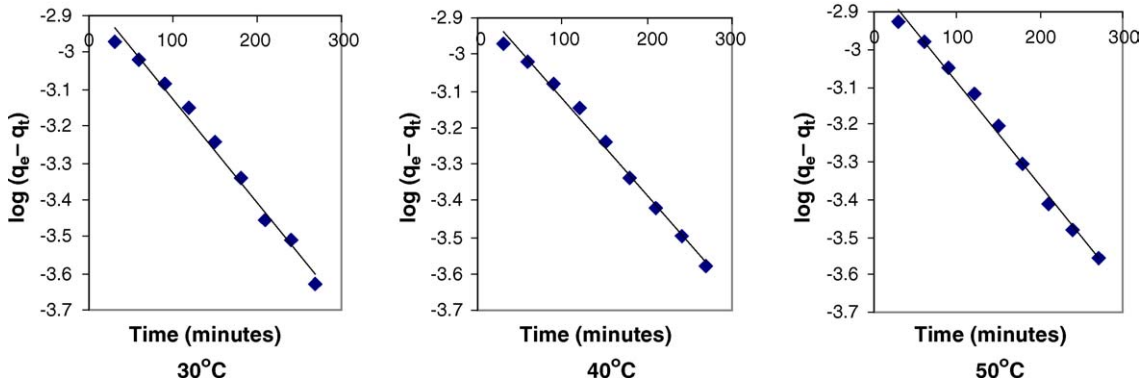


Fig. 8. Lagergren plot for Brilliant Blue FCF (9×10^{-5} M)—hen feather system at different temperatures.

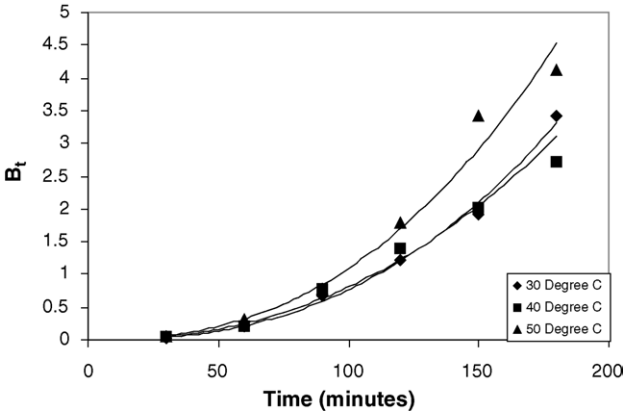


Fig. 9. Time vs. B_t plot for the Brilliant Blue FCF (5×10^{-5} M) adsorption over hen feathers at different concentrations and at 30 °C.

where F is the fractional attainment of equilibrium at time 't' and is obtained by using Eq. (9), n is Freundlich constant of the adsorbate and B_t is a calculated mathematical function of F (and vice versa) derived from the Reichenberg's table [22]:

$$F = \frac{Q_t}{Q_\infty} \tag{9}$$

where Q_t and Q_∞ are amounts adsorbed after time t and after infinite time, respectively.

With the help of Reichenberg's table [22] values of B_t was derived from every observed value of F and a graph between time and B_t was plotted. Typical time versus B_t plots at (5 and 9) $\times 10^{-5}$ M concentration of the Brilliant Blue FCF are presented in Figs. 9 and 10, respectively, which confirm involvement of film diffusion mechanism as the rate-controlling steps, because of deviation from linearity.

Further validation of the above observations was carried out by Mckay's graph by plotting $\log(1-F)$ versus time graphs at different concentrations of the dye. Curved lines (Figs. 11 and 12) were obtained at all the temperatures and concentrations, which support the fact that rate of adsorption of Brilliant Blue FCF at hen feathers, take place by internal transport at all the concentrations [24].

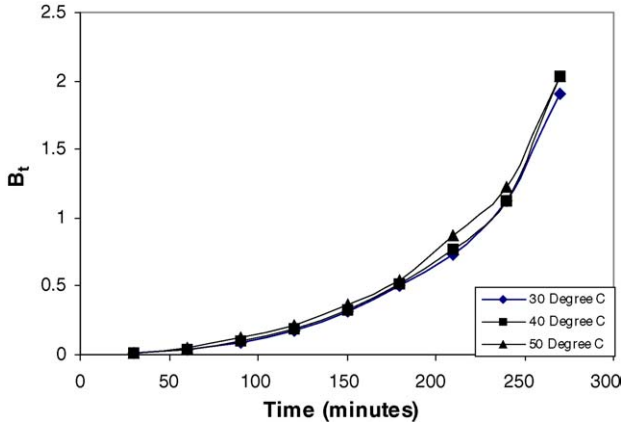


Fig. 10. Time vs. B_t plot for the Brilliant Blue FCF (9×10^{-5} M) adsorption over hen feathers at different concentrations and at 30 °C.

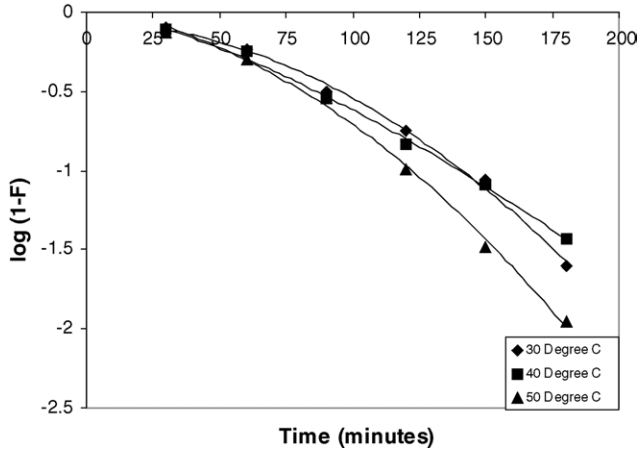


Fig. 11. Time vs. $\log(1-F)$ Graph for Brilliant Blue FCF (5×10^{-5} M)—hen feather system.

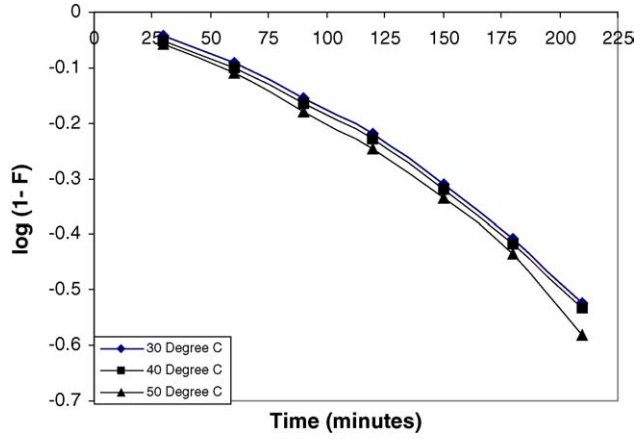


Fig. 12. Time vs. $\log(1-F)$ graph for Brilliant Blue FCF (9×10^{-5} M)—hen feather system.

4. Conclusions

The research carried out in the present paper clearly suggests that the waste material, hen feathers acts as excellent biosorbent for the removal of Brilliant Blue FCF from wastewater. Batch studies clearly suggest that 100–70% of the dye could be adsorbed by hen feathers in the concentration range 1×10^{-5} to 1×10^{-4} M, at 30, 40 and 50 °C. Well-fitted straight lines obtained for the Freundlich and Langmuir adsorption isotherm models indicate a feasible, spontaneous and endothermic adsorption. Kinetic studies suggest that the adsorption of Brilliant Blue FCF over hen feathers undergo purely, through film diffusion mechanisms at all concentrations and rate of adsorption takes place by internal transport mechanism.

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