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Freundlich and Langmuir adsorption isotherms and kinetics for the removal of Tartrazine from aqueous solutions using hen feathers

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Abstract

Tartrazine, a yellow menace, is widely being used in cosmetics, foodstuffs, medicines and textile. It is carcinogenic and also catalyzes allergic problems. In the present work the ability to remove Tartrazine from aqueous solutions has been studied using waste material—hen feathers, as adsorbent. Effects of pH, concentration of the dye, temperature and adsorbent dosage have been studied. Equilibrium isotherms for the adsorption of the dye were measured experimentally. Results were analyzed by the Freundlich and Langmuir equation at different temperatures and determined the characteristic parameters for each adsorption isotherm. The adsorption process has been found endothermic in nature and thermodynamic parameters, Gibb's free energy (ΔG°), change in enthalpy (ΔH°) and change in entropy (ΔS°) have been calculated. The paper also includes results on the kinetic measurements of adsorption of the dye on hen feathers at different temperatures. By rate expression and treatment of data it has been established that the adsorption of Tartrazine over hen feathers follows a first-order kinetics and a film diffusion mechanism operates at all the temperatures.

Keywords: Tartrazine; Hen feathers; Adsorption; Kinetics; Dye

1. Introduction

Water pollution due to discharge of coloured effluents from textile dye manufacturing and textile dyeing mills are one of the major environmental concerns in the world today. Though dyes impart appealing colours to textile fibers, foodstuffs, etc., however, strong colours imparted by the dyes pose aesthetic and ecological problems to the aquatic ecosystems. Because of their complex molecular structures and large sizes most of the dyes are considered non-oxidizable by conventional physical and biological treatments [1]. Thus their decolourization is one of the indispensable processes in wastewater treatment. A number of techniques aimed at preferential removal of different types of dyes from wastewater have been developed [2,3]. Among these physico-chemical methods like adsorption [4,5], electrochemical coagulation [6] and photocatalytic decolourization [7] are more popular now-a-days. Among all these, adsorption is one of the methods, which is gaining more and more attention because of its easy operations and versatility. It is a useful and simple technique and allows kinetic and equilibrium measurements without any highly sophisticated instrument [8]. Consequently, various potential adsorbents have been implemented for the removal of specific organics from water. Thus researchers are pursuing hard to develop more suitable, efficient, cheap and easily accessible type of adsorbents. Much work has been carried out using peat [9], sugar cane bagasse [10], biomass [11], eucalyptus bark [12], bottom ash, de-oiled soya [13,14] and hen feathers [15] as potential adsorbents.

Present paper is an attempt to remove a hazardous dye, Tartrazine by using hen feathers as adsorbent. Hen feathers have crossed the way of human evolution ever since the first feather landed on the face of the earth. And it will go on until the last bird will shed its feathers. Feathers represent 4–6% of the total weight of mature chickens and are generated in huge quantities as a waste by-product at commercial poultry processing plants [16]. In place of disposing these feathers in landfills, these are usually recycled by converting into animal feed via hydrolyzation [17]. In recent past, feathers have also been successfully used in the removal of heavy metals [18],

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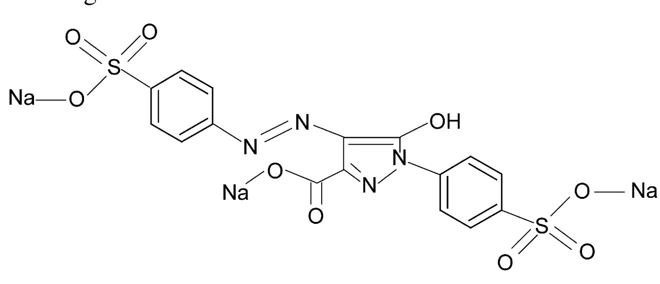
phenol [19] and organic dyes [15,20] from their aqueous solutions.

The dye under investigation, Tartrazine (otherwise known as E102 or FD&C Yellow 5) is a coal-tar derivative that is used to colour foods, cosmetics, and other products, it is a lemon yellow azo dye used as a food colouring. It is found in certain brands of fruit squash, fruit cordial, coloured fizzy drinks, instant puddings, cake mixes, custard powder, soups, sauces, ice cream, ice lollies, sweets, chewing gum, marzipan, jam, jelly, marmalade, mustard, yoghurt and many convenience foods together with glycerine, lemon and honey products. It is cheaper than beta carotene and therefore used as an alternative to beta carotene to achieve similar colour. The water-soluble Tartrazine is used in drugs especially shells of medicinal capsules, syrups and cosmetics. Tartrazine is a yellow menace, whose wide use in industry and its water-soluble nature maximize its chances to be found as contaminant in industrial effluents. Tartrazine is also reputed to catalyze hyperactivity [21] and other behavioral problems [22], asthma [23–27], migranes, thyroid cancer [28], etc. Because of its hazardous health effects, foods and drinks containing Tartrazine are avoided. The present study is devoted to its removal from the wastewater using adsorption technique. The study has been carried out under different variables, like temperature, pH, adsorbent dose and adsorbent concentration and a convenient and economically viable process has been developed by involving a waste material—hen feathers as potential adsorbent.

2. Experimental

Tartrazine(I), trisodium-5-hydroxy-1-(4-sulfonatophenyl)-4-(4-sulfonato phenylazo)-*H*-pyrazole-3-carboxylate is an azo dye (CI Number = 19140, EEC Number = E-102) with molecular formula $C_{16}H_9N_4Na_3O_9S_2$ and molecular weight 534.4 was obtained from M/s Merck. All other reagents were of A.R. grade.



TARTRAZINE

(I)

Studies were carried out by preparing the stock solution of 1 mM concentration in doubly distilled water. Concentrations of the dye aqueous solutions were monitored on UV–vis spectrophotometer, Model 117 (M/s Systronics, Ahmedabad, India) over a wavelength range of 426 nm.

Adsorbent, hen feathers were collected from the local poultry. A typical vaned feather features a main shaft, called the rachis and fused to the rachis are a series of branches or barbs. Before using it as adsorbent, feathers were subjected to thorough washing with detergent and then rinsed with distilled water. Small size barbs of each feather were carefully cut by scissors excluding rachis. To remove adhering organic materials present in feathers barbs were treated by hydrogen peroxide for 24 h and then once again washed in the pool of distilled water and dried in the oven, overnight. The dried material obtained was then stored in desiccators for subsequent use.

2.1. Adsorption studies

The prologue investigations were carried out in batches in different conditions of pH, concentration, time, amount of adsorbent, temperature, etc., to check the propensity of adsorption process. After undergoing meticulous experimental procedures, concentration range of $(1–10) \times 10^{-5}$ M was chosen. In each 100 mL measuring flasks, 25 mL of dye solutions of known concentrations was poured having a known amount of adsorbent. The mixture was sporadically shaken and then kept for 24 h for saturation. Thereafter supernatant liquid was filtered through Whatmann Filter Paper No. 42 and the amount of dye adsorbed was determined spectrophotometrically at the λ_{max} 426 nm.

2.2. Kinetic studies

Present kinetic investigations are carried out to measure the rates of reaction under various experimental conditions; to determine the influence of concentration and temperature on the rates of reaction; and also to determine the time requirement for the attainment of equilibrium during the adsorption process. In different measuring flasks, 25 mL of dye solution of known concentration with definite pH and known amount of adsorbent was taken at different temperatures of 30, 40 and 50 °C with periodic shaking. The solutions were then filtered at different time intervals using Whatmann Filter Paper No. 42 and evaluated spectrophotometrically for the removal of Tartrazine.

3. Results and discussion

3.1. Characterization of adsorbent

A feather has a protein content of around 84% along with the inorganic constituents like calcium, magnesium, selenium, zinc, etc. However, raw feathers are relatively insoluble and have a very low digestibility of 5% due to the high keratin content and the strong disulphide bonding of the amino acids. The feathers are ‘H’ type of adsorbent as the pH of 100 mL distilled water increases, when 1 g of feathers are dipped in it.

3.2. Adsorption studies

The adsorption characteristics of Tartrazine by feathers were studied at varying pH range from 2 to 6. The profile (Fig. 1) concerning pH shows that in the observed pH range the adsorption capacity was much pronounced at lower pH 2, while as the pH increases adsorption decreases. As such all

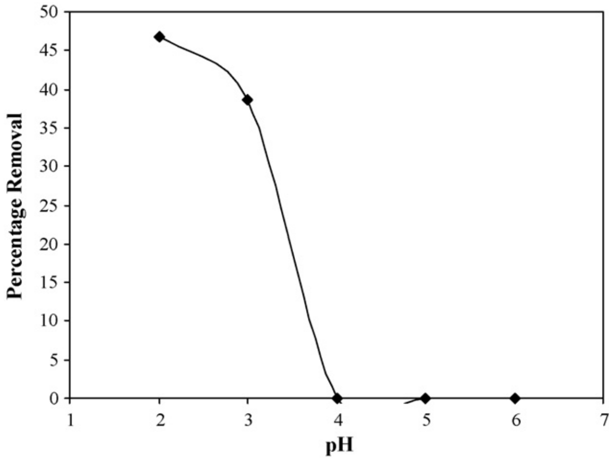


Fig. 1. Effect of pH on uptake of Tartrazine by hen feathers: temperature = 50 °C; concentration = 9×10^{-5} M; amount = 0.01 g; time = 24 h.

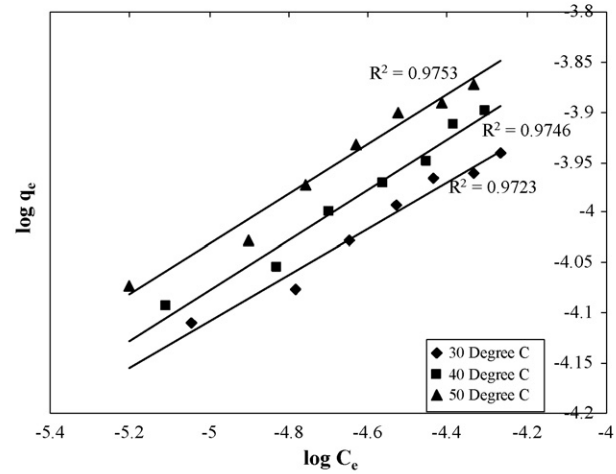


Fig. 3. Freundlich adsorption isotherm for Tartrazine–hen feather system: temperature = 50 °C; pH 2.0; amount = 0.01 g; time = 24 h.

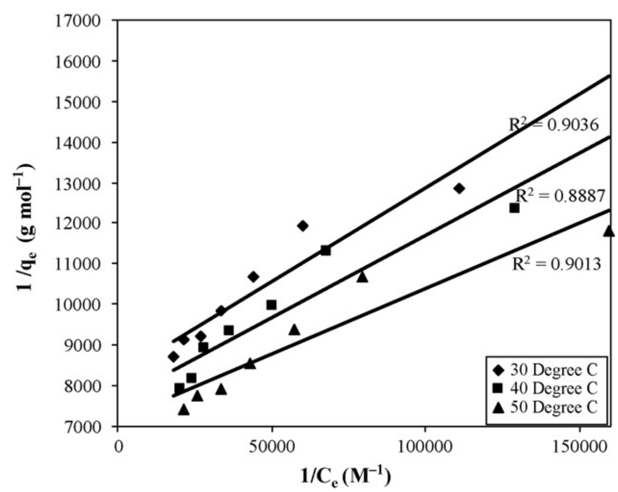


Fig. 4. Langmuir adsorption isotherm for Tartrazine–hen feather system: temperature = 50 °C; pH 2.0; amount = 0.01 g; time = 24 h.

subsequent studies were performed at pH 2.0, which is the optimum value for adsorption.

The adsorption of Tartrazine was also recorded in the concentration range from (1 to 10) $\times 10^{-5}$ M, at a fixed pH of 2.0 and temperatures 30, 40 and 50 °C (Fig. 2). Fig. 2 also indicates that the adsorption of Tartrazine by feathers increases with the increase in temperature, indicating thereby the process to be endothermic in nature. It is also observed that the initial removal of dye is fast and with the rise in concentration the percentage uptake gradually decreases.

The profile obtained from the study of concentration at different temperatures was used to obtain Langmuir and Freundlich adsorption isotherms by using well-known adsorption isotherm equations [29,30]. In both the cases linear plots were obtained, which reveal the applicability of these isotherms on the ongoing adsorption process. Figs. 3 and 4 exhibit Freundlich and Langmuir plots respectively for the adsorption of Tartrazine on feathers and different Freundlich and Langmuir constants derived from these plots are presented in Table 1. The adsorption capacity was found to increase with rising temperature, which is further confirmed by the decline in Q_0 values with decreasing temperature. This once again reveals the endothermic nature of the ongoing process.

To examine the progression of adsorption dimensionless constant, separation factor r [31] was calculated by following

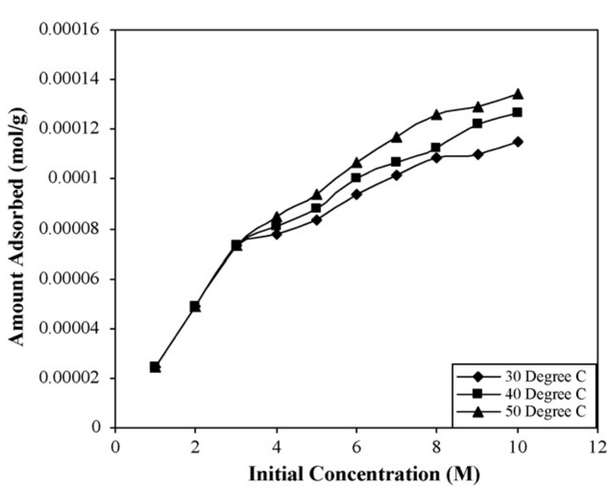


Fig. 2. Effect of concentration for the uptake of Tartrazine on hen feathers at different temperatures: temperature = 50 °C; pH 2.0; amount = 0.01 g; time = 24 h.

Table 1
Freundlich and Langmuir constants of Tartrazine adsorption over hen feathers at different temperatures

	Temperature		
	30 °C	40 °C	50 °C
Langmuir constants			
Q_0 (mol/g)	0.00012	0.00013	0.00014
b ($\times 10^3$ L/mol)	179.137	188.980	220.244
Freundlich constants			
n	4.323	3.989	4.034
K_F	0.0011	0.0015	0.0016

equation:

$$r = \frac{1}{1 + bC_0} \tag{1}$$

where b and C_0 values were derived from Langmuir isotherm. The decline in r values with rising temperatures clearly denotes that the ongoing adsorption process is much favourable at higher temperatures. The parameters indicate the shape of isotherm accordingly.

r value	Type of isotherm
$r > 1$	Unfavourable
$r = 1$	Linear
$0 < r < 1$	Favourable
$r = 0$	Irreversible

The thermodynamic data were evaluated from Langmuir isotherms using following equations:

$$\Delta G^\circ = -RT \ln K \tag{2}$$

$$\Delta H^\circ = R\frac{T_2T_1}{T_2 - T_1}\ln\frac{K_2}{K_1} \tag{3}$$

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} \tag{4}$$

where K, K_1 and K_2 are the equilibrium constants at the temperature 30, 40 and 50 °C respectively and obtained from the slopes of adsorption isotherms at different concentrations.

Evaluated thermodynamic parameters, change in free energy (ΔG°), change in enthalpy (ΔH°) and change in entropy (ΔS°) are presented in Table 2. Negative values of ΔG° establish the feasibility of adsorption process. Further, the decrease in the values of ΔG° with the increasing temperature indicates the spontaneity of the process at higher temperatures. The endothermic nature was also confirmed from the positive values of enthalpy change (ΔH°), while good affinity of Tartrazine towards the adsorbent materials is revealed by the positive value of ΔS°.

3.3. Kinetic studies

For the effectual designing and representation of the ongoing process, kinetics parameters were calculated by monitoring the effects of contact time, amount of adsorbent and concentration of adsorbate solution on adsorption of the dye over hen feathers.

Preliminary studies suggested that 4 h were sufficient for the attainment of equilibrium (Fig. 5). Moreover, the kinetics of adsorption process at different temperatures (30, 40 and 50 °C) exhibited an increase in adsorption with the increase in temperature. The half-life of each process was also calculated and was found to decrease with increase in temperature. These results once again confirm endothermic nature of the ongoing process.

Table 2
Thermodynamic parameters for the adsorption of Tartrazine on hen feathers

$-\Delta G^\circ$ (kJ mol^{-1})	
30 °C	30.471
40 °C	31.616
50 °C	33.037
ΔH° (kJ mol^{-1})	8.497
ΔS° (J K^{-1} mol^{-1})	74.158

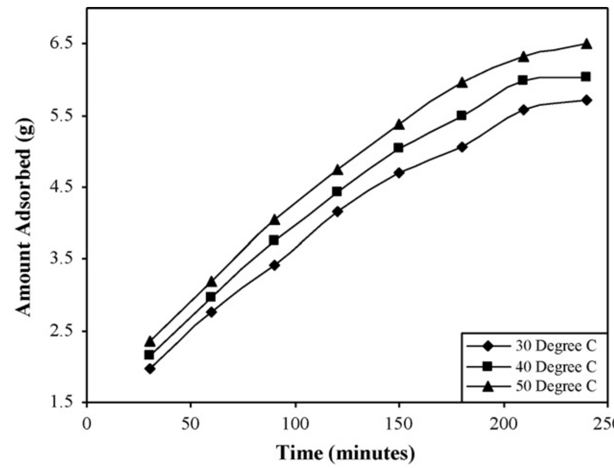


Fig. 5. Effect of contact time for the adsorption of Tartrazine by hen feathers at different temperatures: temperature = 50 °C; concentration = 9 × 10^{-5} M; amount = 0.01 g; pH 2.0.

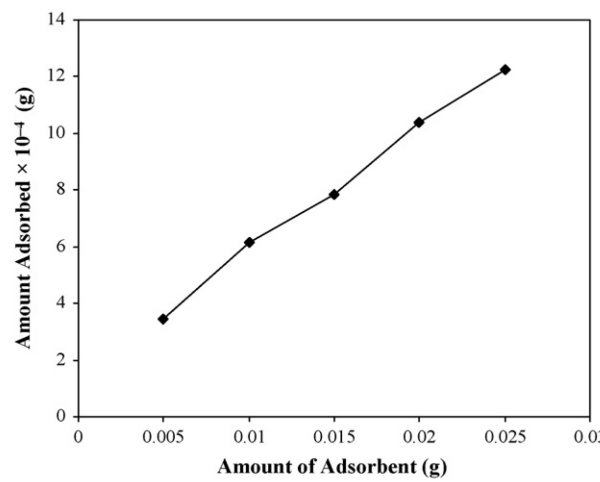


Fig. 6. Effect of amount of adsorbent for the removal of Tartrazine using hen feathers: temperature = 50 °C; concentration = 9 × 10^{-5} M; pH 2.0; time = 24 h.

Fig. 6 shows the results of adsorption study carried out with different adsorbent dose. It was found that with the increasing dosage of adsorbent the rate of removal of adsorbate increases. The data obtained reveals that there is a substantial increase in adsorption when amount of adsorbent is increased from 0.005 to 0.025 g.

3.4. Adsorption rate constant study

In order to study the specific rate constant of Tartrazine–feather system, the well-known Lagergren first-order rate equation was employed [32]. Values of log ($q_e - q_t$) was calculated for each time interval at different temperatures:

$$\log(q_e - q_t) = \log q_e - \frac{k_{ad}}{2.303}t \tag{5}$$

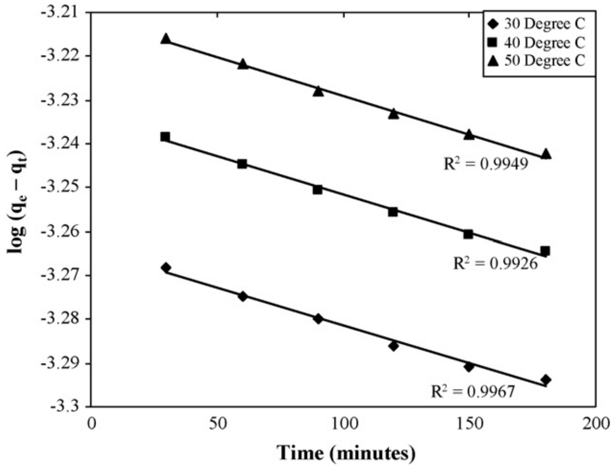


Fig. 7. Lagergren's plot of time vs. $\log(q_e - q_t)$ for Tartrazine adsorption on hen feathers at different temperatures.

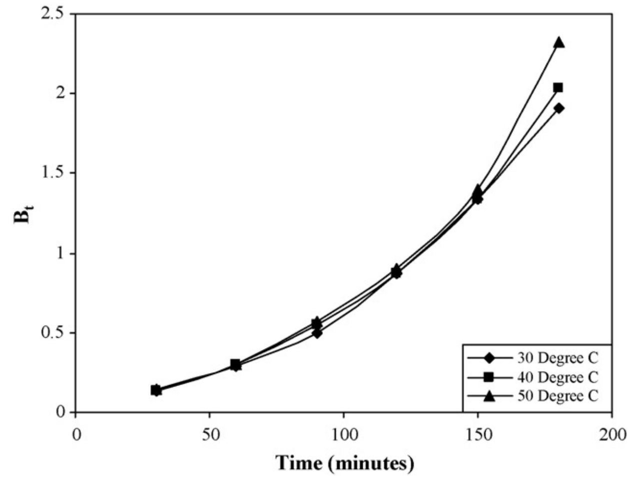


Fig. 8. Plot of time vs. B_t for Tartrazine uptake by hen feathers at different temperatures.

where q_e and q_t signify the amount adsorbed at equilibrium and at any time t. The graph of $\log(q_e - q_t)$ versus t (Fig. 7) exhibits straight lines at 30, 40 and 50 °C and confirm the first-order rate kinetics for the ongoing adsorption process. The k_{ad} values evaluated, from Lagergren plots are found to be 0.00041, 0.00024 and 0.00041 s^{-1} at 30, 40 and 50 °C, respectively.

For an appropriate interpretation of experimental data, it is essential to identify the steps in the adsorption process. The ingenious mathematical treatment recommended by Boyd et al. [33] and Reichenberg [34] has been applied for elucidating the kinetics data. These mathematical treatments were found useful to distinguish between particle diffusion and film diffusion. The successive steps involved in the adsorption of an organic/inorganic compound by an adsorbent are

(i) transport of the ingoing ions (adsorbate) to the external surface of the adsorbent (film diffusion);
(ii) transport of the adsorbates within the pores of the adsorbent except for a small amount of adsorption, which occurs on the external surface (particle diffusion);
(iii) adsorption of the ingoing ion (adsorbate) on the interior surface of the adsorbent.

Out of these, third process is considered very fast and cannot be treated as rate-limiting step for the uptake of organic dye. The remaining two steps impart the following three possibilities:

- *Case I*. External transport > internal transport, where rate is governed by particle diffusion.
- *Case II*. External transport < internal transport, where rate is governed by film diffusion.
- *Case III*. External transport ≈ internal transport, which accounts for the transport of the adsorbate ions to the boundary and may not be possible within a significant rate, which later on give rise to the formation of a liquid film surrounded by the adsorbent particles with a proper concentration gradient.

A quantitative treatment of the sorption dynamics can be applied with the help of the following expressions:

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

where F is the fractional attainment of equilibrium at time t and is obtained by using Eq. (7) and n is Freundlich constant of the adsorbate.

$$F = \frac{Q_t}{Q_\infty} \tag{7}$$

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

With the help of Reichenberg's table [34], B_t values were evaluated from corresponding F values obtained in above case. The graph is plotted between time and B_t, which gives us an idea about the type of step involved during the progress of adsorption process. In this case the B_t versus time plot (Fig. 8) at a concentration of 4×10^{-5} M was found linear without passing through origin. Likewise, at a higher concentration a smooth curve is obtained passing through the origin, thus indicating the adsorption of Tartrazine on feather to be film diffusion in nature.

4. Conclusion

The report predicted from the current paper clearly suggest that use of feathers as adsorbent is much economical, effectual and more viable. It can be efficiently used to remove Tartrazine, a coal-tar derivative without even posing any threat to the quality of water. The different operational parameters observed during the process of investigations reveal that the pH, temperature, contact time, adsorbent dose and concentrations of the adsorbate govern the overall process of adsorption. The batch studies clearly suggest that feathers exhibit almost 100% adsorption at lower concentrations of (1–3) × 10^{-5} M, whereas removal of 47, 52 and 55% of the dye takes place at a concentration of 10 × 10^{-5} M, at 30, 40 and 50 °C, respectively. The results obtained are well fitted in the linear forms of Freundlich and

Langmuir adsorption isotherms. The calculated values of different thermodynamic parameters clearly indicate that the ongoing adsorption process is feasible, spontaneous and endothermic in nature. The kinetic evaluation suggests that the process purely occurs by film diffusion mechanism.

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