

Sorption of Eosine Y dye onto pre-treated hen feathers in aqueous solution

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Abstract

The present study reports Eosine Yellow (EosineY) dye removal by adsorption method. For this purpose hen feathers (HF) are used as sorbent. After optimization of various parameters, it was observed that 75.7% removal of dye (25ppm) occurs at pH 4, contact time 1 h using 1.25 g of adsorbent. Adsorption isotherm studies shows that Langmuir model is best fitted for sorption of the dye on selected sorbent. The kinetics and thermodynamics studies revealed that adsorption process follows pseudo second order kinetics and is exothermic in nature. Use of hen feathers for removal of Eosin Y is found to be efficient and cost effective.

Key words: Eosin Y, hen feathers, batch adsorption, kinetics, thermodynamics

Introduction

Effluents from dye industry affect flora and fauna to a greater extent. Number of methods are in use for treatment of these effluents^{1,2}. Among all, adsorption is found to be the simplest, effective and environment friendly method. Survey of the literature shows that biosorption provides an economically viable sustainable technology for treatment of wastewater^{3,4}.

Use of waste biomaterial as sorbent (biosorption) is newly developed technique for removal of dyes due to its low initial cost, simple design, ease of operation and efficiency⁵. A large number of low cost bioadsorbents based on natural material such as rice husk⁶, Mangrove bark⁷, wool and cotton fiber⁸, activated carbon prepared from pistachio nutshell⁹, delonix regia pod¹⁰, rice hull ash¹¹, have been investigated for removal of dyes from aqueous solution. Biological materials such as chitosan¹² bacterial biomass¹³, yeast¹⁴, fungi¹⁵, have been used as bioadsorbent for removal of dyes from solution. Present study deals with the biosorption characteristics of hen feathers (HF) for removal of Eosine Y from aqueous solution. Amino acids in feathers have number of functional groups which render interesting

physicochemical sorption of inorganic and organic compounds¹⁶. Feathers are waste product generated in abundant amount in commercial poultry plants.¹⁷

Material and method

AR grade chemicals and Eosine Y (C.I. No. 45380, MF $C_{20}H_6Br_4Na_2O_5$) were used in the present work. The initial pH of the desired Eosine Y concentration was measured with pH meter and maintained using 0.01 M H_2SO_4 and 0.01M NaOH solution. Structure of Eosine Y is shown in Fig. 1.

Material development

Hen feathers collected from local market were washed several times with detergent and tap water. Feathers were dried completely in the oven at $100^{\circ}C$. The barbs were cut into small pieces with scissor and middle rachis was removed. Dried sample was finely powdered in the mixer and stored until further use.

Characterization of Sorbent

Chemical analysis of hen feathers was done by SEM-EDS (scanning electron microscope with energy dispersive X- ray spectroscopy) method of elemental analysis. Surface structure of the biosorbent was analysed using scanning electron microscope (JSM-6360 A, JOEL, Japan.) at an electron voltage of 20 kV. The SEM image (Fig. 2) of the bioadsorbent shows large surface area that could possibility entrap and bioadsorb Eosine Y by surface functional groups.

For FTIR analysis finely powdered sample of hen feathers was used. Scanning range was selected between wavenumber $4000-400\text{ cm}^{-1}$. The FTIR spectrum of hen feathers (Fig. 3) shows the bands at $1,600 - 1,700\text{ cm}^{-1}$ (amide I) and $1,500-1,560\text{ cm}^{-1}$ (amide II). Band appears at stretching vibrations of C-H ($2960 - 2874\text{ cm}^{-1}$) and that of CO ($2960 - 2874\text{ cm}^{-1}$ and 1159.26 cm^{-1}).

Batch Sorption

Batch adsorption technique was used for the removal of Eosin Y from its aqueous solution. Maximum removal of Eosin Y was achieved by optimization of different parameters Viz. pH, contact time, dosage, concentration of dye and temperature. For adsorption studies fixed amount of powdered HF was shaken with fixed volume (25mL) of dye at desired concentration in 100 mL RB flask on magnetic stirrer to achieve equilibrium. After acquiring

equilibrium condition, solution was filtered and concentration of the dye in filtrate was measured spectrophotometrically at λ_{max} 517 nm.

Calculations

The following equation was used to calculate amount of residual dye per unit quantity of biosorbent

$$q_e = \frac{C_o - C_e}{M} \times V \quad (1)$$

Where C_o and C_e indicate initial and equilibrium dye concentration (mg L^{-1}) respectively, V is volume (L) of the dye solution and M is mass (g) of bioadsorbent. The Following equation is used to find % removal.

$$\% \text{ Removal} = \frac{C_i - C_a}{C_i} \times 100 \quad (2)$$

Results and discussion

Effect of pH

Effect of pH on Eosine Y removal is shown in Fig.4. As can be seen, Maximum removal was found to be 60.69 % at pH 4 and then it decreases with pH reaching minimum removal (21.79 %) at pH 10. Hence pH 4 was selected as an optimum pH. At lower pH, adsorption increases as protonation increases which causes neutralization of negative charges at the surface of hen feathers. Lower pH is responsible for more degree of protonation causing neutralization of negative charges at the surface of adsorbent leading to more adsorption. Degree of protonation is less at higher pH causing preferential adsorption of dye on active sites and enhances the diffusion process. At higher pH, protonation decreases thus repulsive forces becomes operative, which retards adsorption and diffusion¹⁸.

Effect of contact time

Fig. 5 shows variation of % removal of dye with contact time (1-4 h) at pH 4. Maximum removal of dye occurs in about 1 h. Initially, removal was found to be high but it reaches a constant value as contact time increases. This can be attributed to saturation of adsorption sites with time¹⁹.

Effect of amount of adsorbent

The amount of adsorbent was varied between 0.25g - 1.25g at fixed pH and concentration. From the results (Fig.6) it is observed that % removal of Eosine Y increases with increase in adsorbent dosage. This may be due to the increased surface area with amount of adsorbent making more adsorption sites available²⁰

Effect of initial dye concentration

Fig. 7 shows effect on initial dye concentration (5-25 ppm) on its removal. As can be seen from this Fig, percentage removal increases from 5ppm to 25ppm. This was expected due to fact that with higher initial dye concentration the driving force of the concentration gradient increases resulting in favorable condition for adsorption of dye²¹.

Adsorption isotherm

In the present study, experimental data for Eosine Y - hen feathers equilibrium was examined with Freundlich and Langmuir isotherm models.

A Langmuir equation^{22,23} is as follows

$$\frac{1}{q_e} = \frac{1}{a_b} \frac{1}{C_e} + \frac{1}{b} \quad (3)$$

Where, q_e = amount of dye per unit mass of HF (mg/g), a = constant related to affinity of binding sites (L/g), b = maximum amount of dye per g of HF (mg/g), C_e = equilibrium dye concentration. Plots of $1/q_e$ vs $1/C_e$ gives straight line with slope of $1/ab$ and intercept $1/b$ (Fig.8).

Freundlich model can be expressed by following equation²⁴⁻²⁶,

$$\log q_e = \frac{1}{n} \log C_e + \log K_f \quad (4)$$

Where, q_e = amount of dye per unit weight of adsorbent (mg/g) C_e = equilibrium dye concentration per unit weight (mg/g) K_f = Freundlich constant $1/n$ = Freundlich Isotherm constant related to adsorption intensity. A plot of $\log q_e$ vs $\log C_e$ is shown in Fig.9

For the adsorption of Eosine Y onto HF, the Freundlich constant K_f indicates the sorption capacity of adsorbent. The value of n (closer to 1) indicates favorable adsorption process.

Correlation coefficients reveal that Langmuir model is better fitted than the Freundlich model. Experimental data is presented in Table 2.

Biosorption kinetics

The kinetics of adsorption process was studied by varying the contact time. In order to study adsorption process, it is necessary to establish most appropriate correlation for equilibrium data²⁷. Kinetic data was examined in the light of pseudo first order equation²⁸ and pseudo second order equation²⁹.

Plot of t/q_t against t is shown in Fig.10. The different values for pseudo first and pseudo second order kinetics are shown Table 3. The obtained data reveals that adsorption process obeys pseudo second order kinetics and overall process may be controlled by chemisorption^{30, 31}.

Thermodynamics studies

The various thermodynamic parameters were calculated using following equations^{32,33},

$$K = \frac{q_e}{c_e} \quad (5)$$

$$\Delta G^0 = -RT \ln K \quad (6)$$

Where all the symbols have their usual meanings. Positive ΔG^0 at all the temperatures indicates that adsorption of Eosine Y is not a spontaneous phenomenon and sorption of Eosine Y onto hen feathers may be due to physical process of diffusion³⁴.

The thermodynamics adsorption parameters ΔH^0 , ΔS^0 are calculated from Fig.11 using the equation:

$$\log K = \frac{\Delta S^0}{2.303R} - \frac{H^0}{2.303RT} \quad (7)$$

ΔH^0 and ΔS^0 were calculated from Fig.12 and the obtained results are shown in Table 4.

The exothermic nature of adsorption is indicated by negative value of ΔH^0 and positive ΔG reveals non-spontaneous process of adsorption. Further, decreased disorder at the solid solution interface during adsorption is revealed by negative value of entropy change ΔS^0 . With increasing temperature mobility of the dye molecules increases which is responsible for escape of adsorbent molecules from the solid phase causing decrease in the adsorption

capacity of Eosine Y. Similar results were reported by Mahanashi et al.³⁵ for adsorption of E 120 dye onto activated carbon

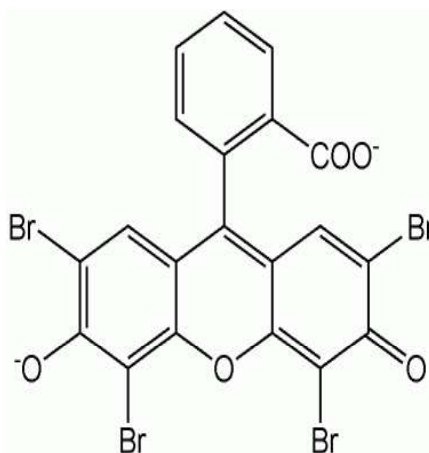
Conclusion

Maximum removal (75.7%) of Eosine Y (25ppm) was seen at pH: 4, contact time: 1h, adsorbent dosage: 1.25 g and concentration: 25 ppm. Langmuir model is best fitted for the biosorption of Eosin Y on hen feathers. Adsorption of Eosine Y on HF can be described by pseudo second order kinetics model. On the basis of thermodynamic parameters it can be revealed that biosorption process is exothermic. As hen feathers are naturally available and cheap animal residue, proposed method can be considered as economical method for the removal of Eosine Y.

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Figures:



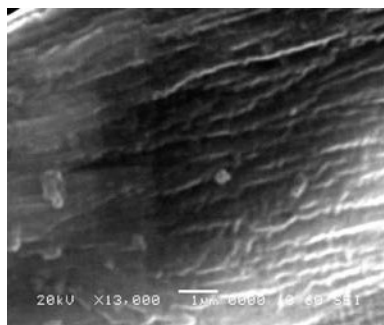


Fig.2: SEM of HF

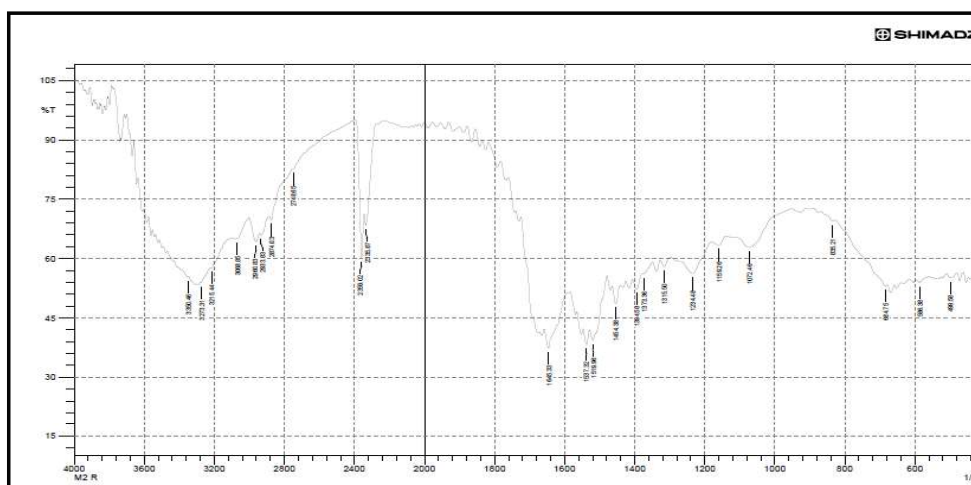


Fig.3: FTIR analysis of hen feathers

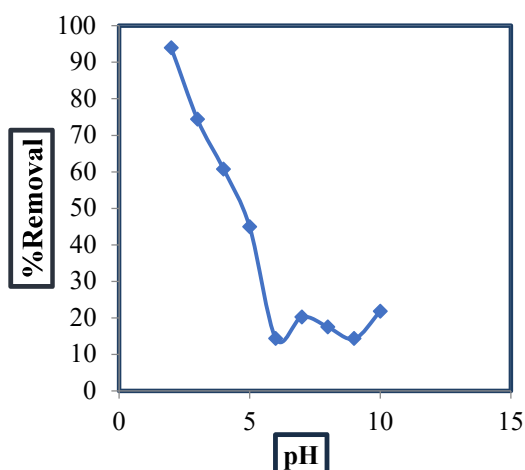


Fig. 4: Effect of pH on uptake of Eosine Y by HF (Experimental condition: Eosine Y concentration = 15 ppm, dosage =0.5 g, contact time = 1h)

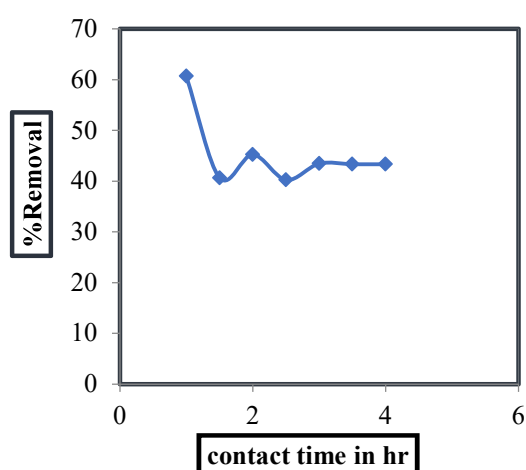


Fig.5: Effect of contact time on uptake of Eosine Y by HF (experimental condition: Eosine Y concentration = 15 ppm, dosage = 0.5 g, pH=4)

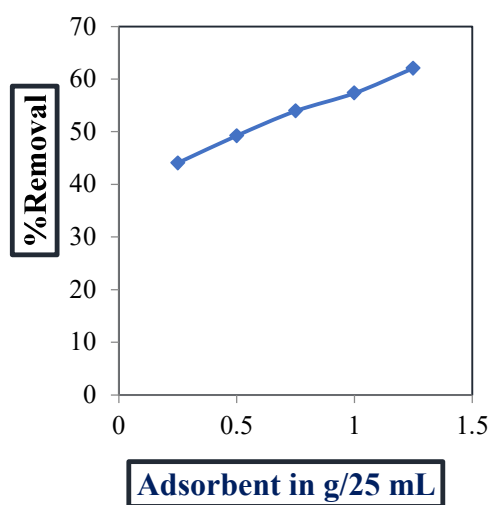


Fig.6: Effect of dosage on uptake of EosineY by HF
(Experimental condition: Eosine Y concentration = 15 ppm, contact time = 1 hr, pH = 4)

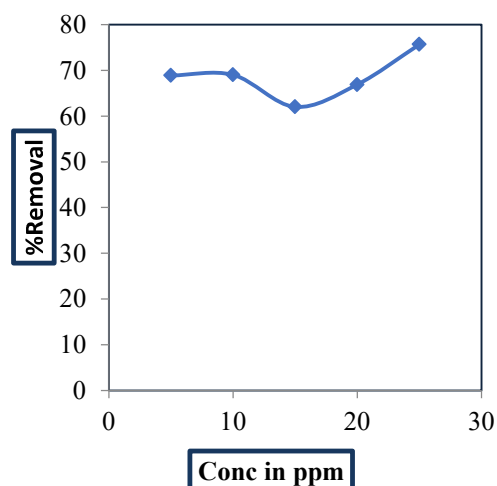


Fig.7: Effect of concentration on uptake of Eosine (experimental condition: contact time = 1 h, pH = 4, dosage = 1.25 g)

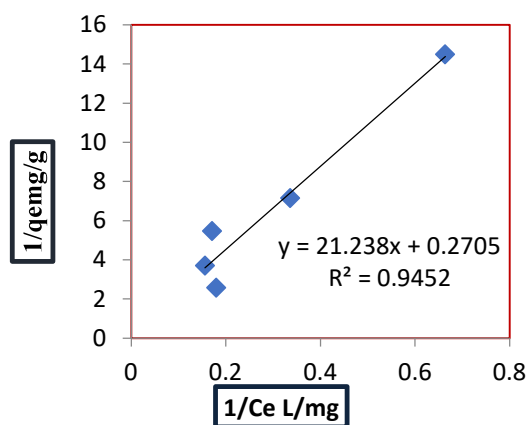


Fig.8: Langmuir plot for adsorption of Eosine Y onto HF.

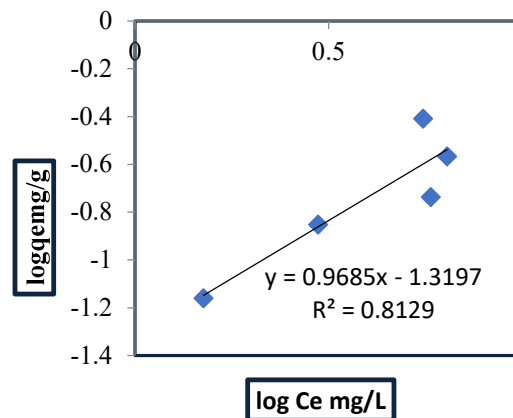


Fig.9: Freundlich plot for adsorption of Eosine Y onto HF

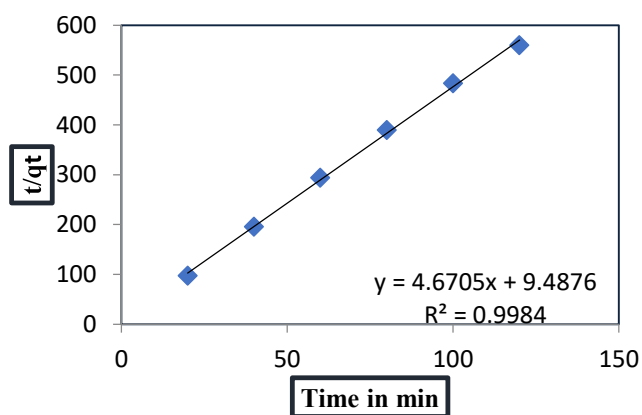


Fig.10: Pseudo second order plot of t/q_t Vs time

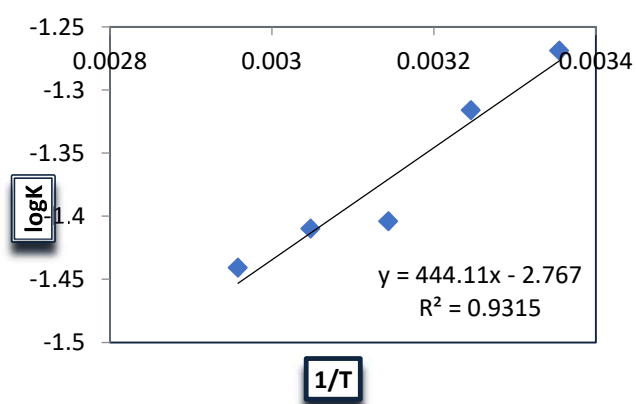


Fig. 11: Plot of $\log K$ vs $1/T$

Tables:

Table 1: Elemental essay of feathers used in adsorption experiment,

Element	(keV)	Mass%
C K	0.277	35.09
N K	0.392	51.38
O K	0.525	4.41
S K	2.307	1.27
Cu K	8.040	3.07
Zr L	2.042	4.78

Table 2: Values of different constants for biosorption of Eosine Y by HF

Langmuir isotherm			Freundlich isotherm		
a(mg/L)	b(mg/g)	R ²	K _f	N	R ²
0.0127	3.703	0.945	0.047	1.033	0.812

Table 3: Kinetic parameters for adsorption of Eosine Y onto hen feathers

Pseudo first order kinetics				Pseudo second order kinetics		
q _{exp}	q _{ecal}	K ₁	R ²	q _{ecal}	K ₂	R ²
(mg/g)	(mg/g)	Time		(mg/g)	g/mg/min	
0.2145	0.010	--	0.149	0.2141	2.342	0.998

Table 4: Estimated values of ΔG^0 , ΔS^0 and ΔH^0 for adsorption of Eosine Y onto hen feathers.

ΔG^0					ΔS^0	ΔH^0
kJ/mol					kJ/(mol K)	kJ/mol
298K	308K	318K	328K	338K		
7.2	7.758	8.547	8.851	9.324	-0.052	-8.510

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