Removal of Orange G from aqueous solution by hematite: Isotherm and mass transfer studies

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Abstract−The efficiency of hematite for the removal of Orange G from aqueous solution has been studied at various concentrations as a function of time, temperatures and pH. It was found that the low initial concentration, low temperature and low pH favor the removal process. The maximum adsorption of the dye on hematite has been recorded at 25 mg/*l* concentration, 303 K temperature and pH 3. The negative values of change in free energy and enthalpy indicate the spontaneous and exothermic nature of the process, respectively. Fixation and immobilization of the dye molecules at the surface of hematite as a result of adsorption are responsible for the negative entropy effect. The effect of pH was described by considering coulombic attraction and aqua complex formation approaches. The applicability of various adsorption isotherms--Langmuir, Freundlich and Jossens--was tested in order to find the most suitable isotherm. The Freundlich isotherm was fitted with the data of the present study.

Key words: Orange G, Hematite, Adsorption Isotherm, Thermodynamic Parameters, Mass Transfer, Aqueous Solution

INTRODUCTION

Most industries use dyes and pigments to color their products. Orange G (dye content 95%, Mol.wt. 452.382, C.I. 16230, λ_{max} 475 nm) is frequently used in the pulp and paper industries. The dye is also important to pathologists [1]. Colored dye waste frequently contains a spectrum of metals and other toxic organic pollutants [2] including dyes and the presence of dye colors may indicate the existence of toxicants [3]. It is the disodium salt of benzene-azo-6:8-disulphuric acid and its molecular structure is shown in Fig. 1. Many dyes are inert and non-toxic at concentrations discharged into receiving waters. Nevertheless some are not so innocuous and in either case the color they impart is very undesirable to the water use [4]. Besides aesthetical problems of colored waters, it also increases the BOD of the aquatic system and thus disturbs the aquatic ecosystem [5]. The treatment of such waters economically is still a crucial problem. Various physico-chemical methods were applied to treat the

above waste water, but adsorption was found the best among all the methods owing to its low cost, easy handling and simple technology [6-9]. Use of activated carbon as an adsorbent does not suit a developing country like India due to its high cost. Thus, there is an imperative need to treat such effluents prior to being discharged due to growing concern of environmental issues. Hematite (α-Fe$_2$O$_3$) was found as the suitable material for removal of heavy metal from contaminated drinking water [10]. Moreover, hematite was also used for adsorption and subsequent catalytic combustion of reactive dye Uniblue A [11]. Keeping all these points in mind, the present study is designed to explore the feasibility of hematite, an iron ore that is plentiful in India, in the purification of waters rich in Orange G. The effects of time, initial dye concentration, temperature and pH onto adsorption of dye, isotherm and transfer of mass studies were investigated.

EXPERIMENTAL

The dye Orange G was supplied by Aldrich Chemical Co. Inc., USA. The chemicals used were of AR grade and were supplied by BDH, Bombay. The hematite was obtained from Noamundi Mine, Bihar, India and was used as such without any processing just after being passed through 53 μm sieve. The characterization of hematite was performed by the methods described earlier [12] and results are reported in Table 1. The point of zero charge of the adsorbent (hematite) was determined by the solid addition method [13]. A 50 ml of 0.1 M KNO$_3$ solution transferred into a series of 100 ml conical flask. The initial pH values of the solution were adjusted from 1.0 to 10.0 by adding either fixed strength of 0.1 N HNO$_3$ or 0.1 N KOH. The 1.0 g of hematite was added to each flask which was securely capped immediately. The flasks were then placed into a constant temperature water bath shaker and shaken for 24 h. The pH values of the supernatant liquid were noted after 24 h.
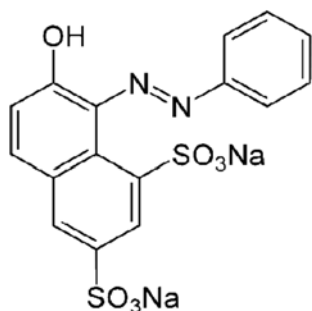

Fig. 1. The molecular structure of Orange G.

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Table 1. Characterization of hematite

Constituents	% By weight
Fe_2O_3	80.80
Al_2O_3	2.10
SiO_2	4.00
CaO	4.80
FeO	1.49
P	0.05
MnO	0.08
TiO_2, MgO, P_2O_5 etc	6.68
pH_{pzc}	3.2
Mean particle diam	$48*10^{-4}$ cm
Surface area	14.40 m^2g^{-1}
Density	5.10 g cm^{-3}
Porosity	0.41

Batch adsorption experiments were carried out by agitating 1.0 g of the hematite with 50 ml of dye solution of desirable concentration and pH in different bottles kept in a temperature controlled shaking machine. As a result, the concentration of hematite in each bottle was kept constant at 20 g/*l*. At the end of pre-determined time intervals the bottles were taken out of the shaker, reaction mixtures were centrifuged and supernatant liquid was analyzed spectrophotometrically (Spectronic-20, BAUSCH and LOMB, USA) at λ_{max} 475 nm to determine the residual dye concentration. The effects of contact time (5-100 min), concentration of dye (15-30 mg/*l*), initial pH (1-10), and temperature (293-313 K) were studied. The initial pH of the adsorbate solution was adjusted by using concentrated HNO_3 and NaOH.

RESULTS AND DISCUSSION

1. Characterization of Hematite

It is clear from Table 1 [14] that hematite mainly contains the oxides of iron, silicon and aluminium while other oxides were present in traces. It is thus expected that the dye will be removed mainly by Fe_2O_3. It is known that oxides form surface hydroxyl compounds with dye, which gives a positively or negatively charged surface. The adsorbent behaves as neutral at pH zero charge. To understand the adsorption mechanism, it is necessary to determine the point of zero charge (pH_{pzc}) of the adsorbent. Adsorption of cation is favored at pH>pH_{pzc}, while the adsorption of anion is favored at pH<pH_{pzc}. It is observed that the point of zero charge of haematite is 3.2 (Table 1).

2. Effect of Contact Time and Concentration

The effect of contact time on amount of adsorption of Orange G is shown in Fig. 2. For different concentrations in the range of 15-30 mg/*l* at 303 K, the adsorbed amount of Orange G increases sharply with time in the initial stage and then gradually increases to reach equilibrium value in approximately 60 min. After this the amount of adsorption becomes constant. The equilibrium time was 60 min irrespective of various initial concentrations used. The amount of adsorption of Orange G increases as the initial concentration of Orange G is increased. At low initial concentration the ratio of active surface of the adsorbent to the total Orange G in the solution is high; therefore, the Orange G may interact easily with the adsorbent and
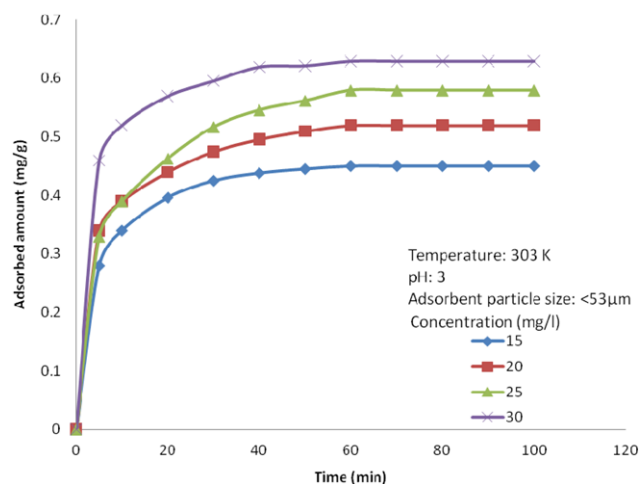
Fig. 2. Effect of time on adsorption amount of Orange G by hematite for different concentrations.

Table 2. Thermodynamic parameters for the removal of Orange G by Hematite

Temperature (K)	ΔG^0 (kJ mol^{-1})	ΔH^0 (kJ mol^{-1})	ΔS^0 (J mol^{-1} K^{-1})	Mass transfer coefficient (β_t) (cm s^{-1})
293	−1.076	−6.477	−18.3	$11.45*10^{-5}$
303	−1.520	−11.928	−34.35	$7.42*10^{-8}$
313	−1.784	-	-	$6.44*10^{-8}$

thus be removed from the solution. However, the adsorbed amount of Orange G per unit mass of the adsorbent is higher at high concentrations as shown in Fig. 2 (Table 2). This may be due to the probability of collision between adsorbate molecules and adsorbent particles.

3. Effect of Temperature

As the temperature can influence the final value of adsorption, the study of its effects on the adsorption process becomes an important aspect in waste water treatment. The effect of temperature on the adsorption of Orange G has been studied by varying the temperature from 293 to 313 K. The results are shown in Fig. 3. The
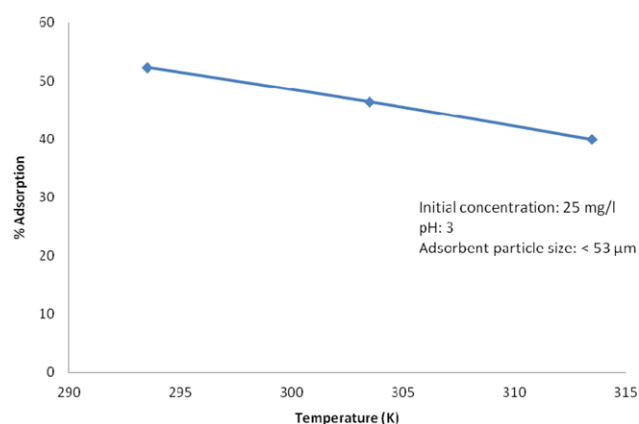
Fig. 3. Effect of temperature on the removal of orange G by hematite.

result shows that the maximum adsorption is accrued at 293 K and it also decreases as the temperature is increased. The increase in adsorption with decrease in temperature indicates the exothermic nature of the adsorption process. The variation was explained on the basis of thermodynamic approach. The thermodynamic parameters, ΔG^0, ΔH^0 and ΔS^0, were calculated with the help of following Eqs. (1)-(3):

$$\Delta G^0 = -RT \ln k_c \qquad (1)$$

$$\Delta H^0 = R (T_1 T_2/T_1 - T_2) \ln k_{c2}/k_{c1} \qquad (2)$$

$$\Delta S^0 = \Delta H^0 - \Delta G^0/T \qquad (3)$$

Where R is the gas constant, T is the temperature on the absolute scale and k_c, k_{c1} and k_{c2} are the equilibrium constants at temperatures T, T_1 and T_2, respectively. The values of k_c, k_{c1} and k_{c2} are calculated graphically.

The values of ΔG^0, ΔH^0 and ΔS^0 are reported in Table 2. The negative values of ΔG^0 indicate the spontaneous and exothermic nature of the process. Also, the negative values of ΔS^0 suggest that the adsorbed species are stable. Immobilization of the dye molecules as a result of adsorption, will decrease the degree of freedom of the dye molecules and that is why the ΔS^0 values are negative [15].

4. Effect of pH

Waste water treatment using conventional and nonconventional adsorbents is highly dependent on the pH of waste water under treatment as it may affect the surface charge of adsorbents as well as the degree of ionisation of different pollutants. The adsorption of Orange G was studied over a range of pH from 1.0 to 10.0 and the results are given in Fig. 4. From Fig. 4, it is observed that the percentage of adsorption increases slowly as the initial pH is increased and attains a maximum value at pH 3. After that it decreases more rapidly up to the pH of 10. At higher pH, Orange G may be forming an aqua cationic species due to the hydrolysis of dye in the solution and therefore the separation may not be due to adsorption.
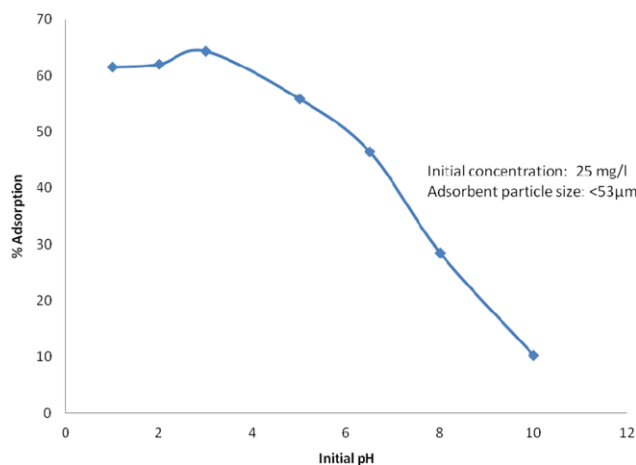
5. Adsorption Isotherm Study

Equilibrium data were tried to fit with several isotherms [16], i.e.,
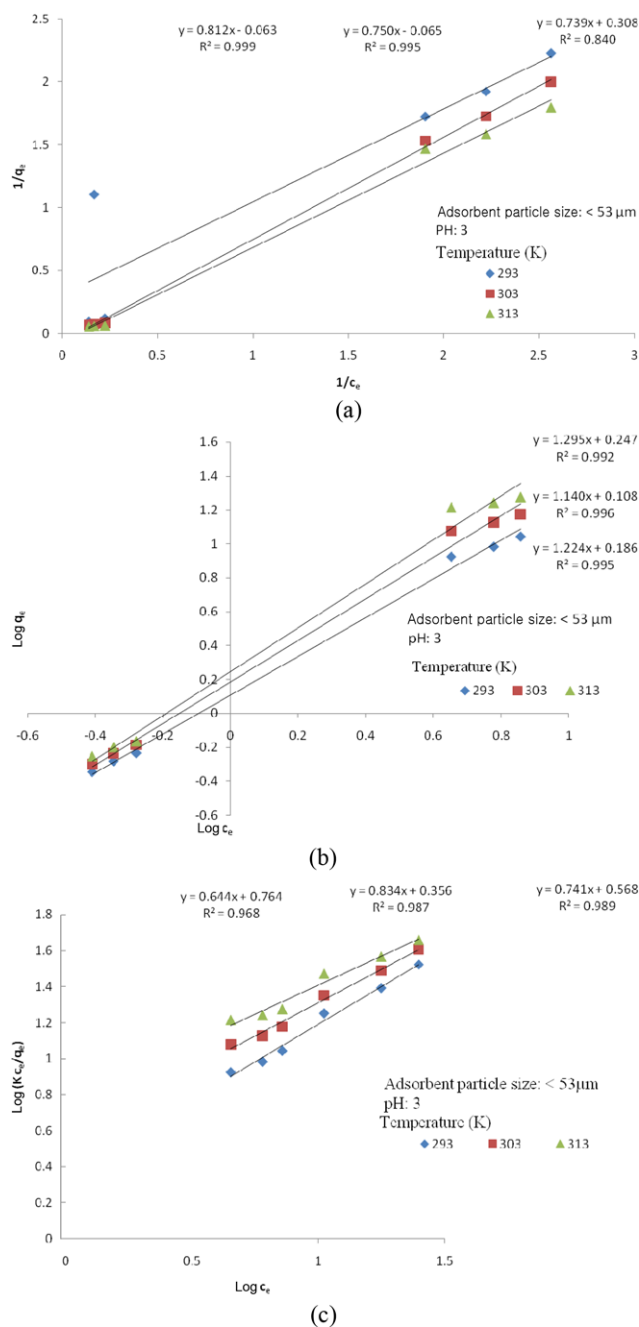
(a)

(b)

(c)

Fig. 5. (a) Langmuir Isotherm for the adsorption of Orange G on hematite. (b) Freundlich isotherm for the adsorption of Orange G on hematite. (c) Jossens Isotherm for the adsorption of Orange G on hematite.

Fig. 4. Effect of pH on the removal of Orange G by hematite.

Table 3. Adsorption isotherm parameters for removal of Orange G by Hematite at 303 K

Langmuir parameters		Freundlich parameters		Jossens parameters		
k_l ($l\,g^{-1}$)	b ($l\,mg^{-1}$)	k_f ($mg\,g^{-1}$)	n	k ($l\,g^{-1}$)	m ($mg\,l^{-1}$)	β
0.1660	0.2092	0.2678	3.4075	0.1660	0.2010	1.0152

Langmuir, Freundlich and Jossens which are as follows, respectively:

$$q_e = k_l C_e/(1+bC_e)$$
Or, $C_e/q_e = 1/k_l + b\, C_e/\, k_l$ (4)

$$q_e = k_f C_e^{1/n}$$
Or, $\log q_e = \log k_f + 1/n \log C_e$ (5)

$$k'C_e/q_e = m\, C_e^{\beta}$$
Or, $\log(k\, C_e/q_e) = \log m + \beta \log C_e$ (6)

Where C_e (mg/l) and q_e (mg/l) are the concentration and adsorbed amount of the dye at equilibrium, k and b are the Langmuir constants, k_l and n are the Freundlich constants while k', m and β are Jossens constants. Initially, k' is assumed to be equal as K. The regression values of all the above constants are given in Table 3. The experimental data and three theoretical isotherms for various temperatures are plotted in Figs. 5(a)-(c). The correlation between the theoretical and experimental is reasonable for all cases, but the Freundlich gives the best overall agreement for removal of Orange G by hematite, which is also confirmed from the data of correlation coefficients (R^2).

6. Mass Transfer Study

A mass transfer phenomenon was studied with the help of the following Eq. (7) [17]:

$$\ln[(C_t/C_0-1)/(1+mk)] = \ln[mk/(1+mk)] - [(1+mk)/mk]\,\beta_l.S_s.t$$ (7)

where C_0 (mg/l) and C_t (mg/l) are the initial concentration and concentration at time t of the adsorbate species, respectively, m (mg/l) is the mass of adsorbent per unit volume, k (l/g) is the Langmuir constant, β_l (cm/s) is the mass transfer coefficient and S_s (1/cm) is the outer surface of the adsorbent per unit volume. According to above Eq. (7), surface mass transfer is controlling when t tends to zero. A plot of $\ln[(C_t/C_0-1)/(1+mk)]$ and t results in a straight line (Fig. 6). The values of β_l have been calculated from slope and intercept of the line. The β_l values (Table 2) indicate that the transfer of dye from bulk of the liquid to adsorbent surface is very rapid and the adsorption is suitable for removal of Orange G from aqueous solution. Similar findings have been reported earlier [17,18]. The β_l values in the present study are less than the values for malachite green-activated carbon [19], malachite green-activated slug [19], crystal violet-walla stonite [20], chrome dye-mixed adsorbent [8],

Fig. 6. Mass transfer plot for adsorption of Orange G on hematite.

and astrozone blue-peat [21] systems available in literature.

CONCLUSIONS

The use of hematite as an adsorbent for the removal of Orange G has been investigated. The influence of different experimental parameters, viz. contact time, concentration, temperature, pH etc., on removal of Orange G was evaluated. An increase in initial dye concentration, temperature and pH decreased the rate of dye adsorption. Various isotherms were tested; however, the Freundlich isotherm was found to be the most suitable isotherm based on the experimental data of the present study. Mass transfer phenomenon showed the applicability of Mckay et al. [17] model for the present Orange G-hematite system. The result clearly shows that the hematite may be successfully used as an efficient adsorbent for the removal of Orange G from aqueous solution.

ACKNOWLEDGEMENT

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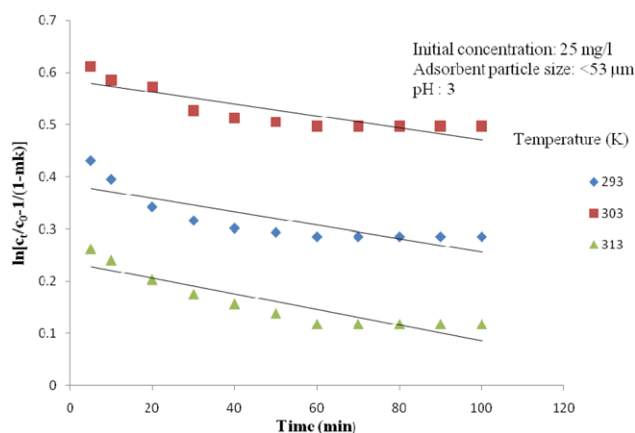
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