Kinetic study of orange II removal from aqueous solution by kokum (*Garcinia Indica*) leaf powder

Pramod Jamdade[1], Sanjay Ubale[2]

1. Department of Chemistry, SRM College, Kudal - 416520 (MS), India,

2. Research Guide. Department of Chemistry, Deogiri College, Aurangabad- 431001 (MS), India.

ABSTRACT

In the present Paper, kinetics of acid activated kokum (*Garcinia Indica*) leaf powder was investigated as an adsorbent to remove orange II dye from aqueous solutions in batch mode experiment. The rate of adsorption was tested by pseudo first-order and second-order kinetics models. The pseudo second - order kinetics model was found to be the most suitable. The data of thermodynamic parameters indicated that adsorptive removal is spontaneous, endothermic and favorable with increase in disorder .The results indicated that Kokum leaf powder can be used as potential adsorbent for removal of azo dyes like orange II from aqueous solutions.

Key words: Kokum leaf powder, Orange II dye, adsorption, pseudo second order kinetics.

I. INTRODUCTION

There has been increased use of synthetic dyes by textile, cosmetics, plastic, paper, leather and pharmaceutical industries due to ease of their use, low cost of synthesis, high stability and variety of colours as compared to natural dyes.[1-2]. Most of these dyes are non-biodegradable due to their complex aromatic structure and synthetic origin[3].The discharge of these dyes by industrial activities into water sources as effluent causes low light penetration and thereby reducing photosynthetic activities[4]. These dyes are not only aesthetic but carcinogenic in nature and can have adverse effects on human beings and aquatic life[5-6.] The conventional dye removal technologies are not effective because of the presence of different organics in these dye molecules.[7-8] hence there is a need of other efficient technologies. Adsorption by activated carbon is found to be the most effective and widely used technology for wastewater treatment but high cost of activated carbon and difficulties in regeneration led investigators to search for new low cost adsorbents such as Neem leaf powder[9-10], Gulmohor leaf powder[11], orange peel[12], Coconut shell[13], guava leaf powder[14], rice husk[15-16 ,] saw dust[17] teak leaves for the removal of dyes from waste water.

In present study, the adsorption properties of Kokum (*Garcinia Indica*) leaf powder for the removal of orange II dye from waste water has been evaluated

II. MATERIALS AND METHODS

2.1 Preparation of adsorbent

Kokum Tree leaves were collected from nearby area and dried in shadow, crushed and boiled in distilled water to remove colour and suspended particles. Then it was filtered, residue was treated with formaldehyde and then by dilute sulphuric acid for 30 minutes. The residue left was further washed with distilled water to remove free acid and dried at 100-120 ^{0}C for 8 hours, powdered, sieved and used for further study.

2.2 Preparation of adsorbate solution

The orange II dye was used to prepare solutions of 10 to 50 mg/L concentration in distilled water using 1000 mg/L stock solution. The pH of solution was adjusted with 0.1 N HCl or 0.1 N NaOH solutions

2.3 Batch adsorption experiment

The batch adsorption experiments were carried by mixing 50 mL of 50 mg/L dye solution with 1.2 g of KLP adsorbent. The effect of contact time, solution pH, adsorbent dose, initial dye concentration and temperature were evaluated. The dye kinetic experiment was carried by taking 1.2 g adsorbent dose in 50 mL of 50 mg/L dye solution at pH 8 and equilibrated for different time intervals in mechanical shaker. The residual dye concentration was determined by using UV/VIS Spectrophotometer (Elico -1245) at 485 nm. Wavelength

IV. RESULTS AND DISCUSSION

4.1 Effect of contact time

The effect of contact time on adsorption was studied by taking 50 mg/L of orange II dye solutions treated with 1.2 g of kokum leaf powder for 5 to 90 minutes at solution pH 8. The dye % removal with contact time has been shown in Figure 1 indicated that % dye removal was increased from 39.51 to 86.46 with increased contact time. The equilibrium was attained at 60 minutes .Similar results were reported by other researchers [18].

4.2 Effect of dye solution pH

The effect of solution pH was evaluated in the pH range of 2 to 10 with 50 ml orange II dye solution of 50 mg/L concentration, 1.2 g adsorbent dose, 60 minutes contact time and 30 ^{0}C temperature. Figure 2 showed that 93.08 % of dye was removed at 2 pH and at pH 8, it was found to be 86.46 % and equilibrium was attained at pH 8. Similar results were reported by other resrearchers[19-20]

4.3 Effect of dye initial concentration

The effect of initial dye concentration of orange II dye (10 to 50 mg/L) on adsorption was studied with 50 mL volume, adsorbent dose 1.2 g /L, pH 8. From figure 3, it was observed that % removal of dye was decreased from 90.95 to 86.46 % whereas the amount of dye adsorbed increased with increase in concentration. Due to surface activity and monolayer formation for given concentrations. Similar observations were reported by other researchers[21]

4.4 Effect of adsorbent dose

The effect of adsorbent dose was studied by taking 50 mL of 50 mg/L orange II dye solutions and varying adsorbent dosages from 0.2 to 1.4 g. The removal of orange II dye was 44.46 to 88.13 when treated with different doses of KLP as shown in Figure 4. The increase in dye removal % with increased dose may be due to presence of more active sites on adsorbent surface[22]. The maximum dye removal was found at 1.2 g of adsorbent dose

4.5 Effect of temperature

The effect of temperature on removal of orange II dye, batch mode experiment was carried out from 30 to 60 ºC Figure 5, showed that, dye removal % increased from 86.02 to 90.57 % with increase in temperature[23]

.

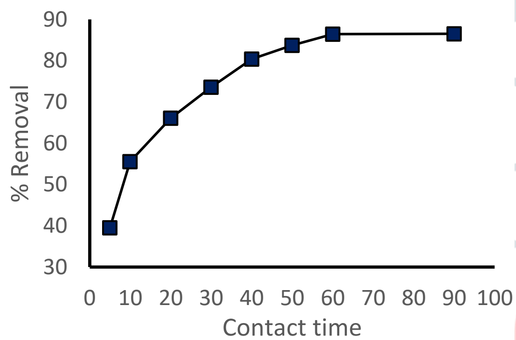

Figure- 1 Effect of contact time on adsorption of orange II by KLP

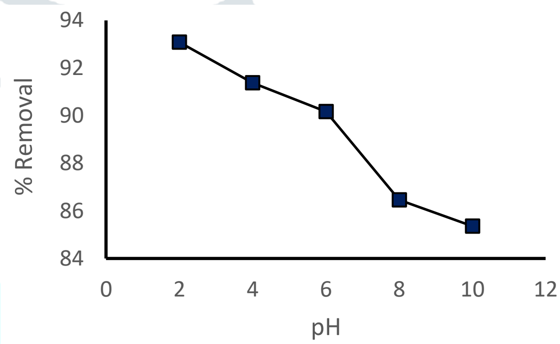

Figure- 2 Effect of pH on adsorption of orange II by KLP

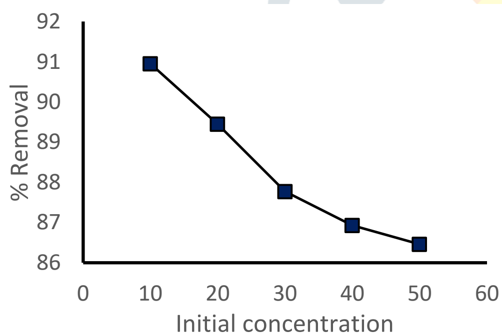

Figure -3 Effect of initial concentration on adsorption of orange II by KLP

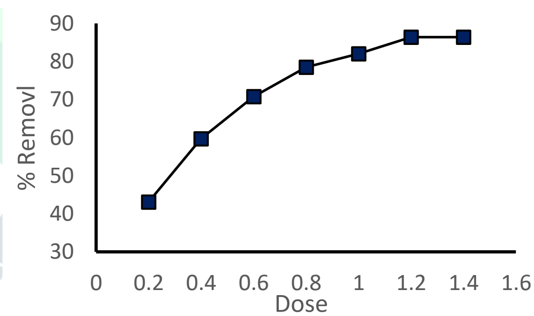

Figure -4 Effect of adsorbent dose on adsorption of orange II by KLP

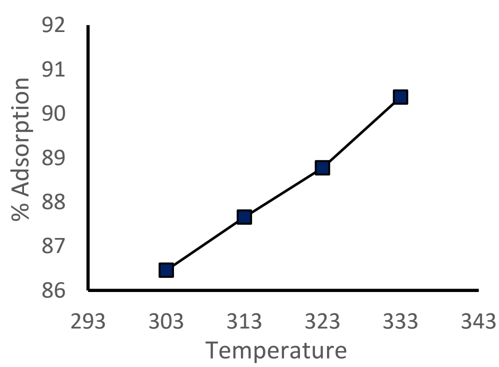

Figure- 5 Effect of temperature on adsorption of orange II by KLP

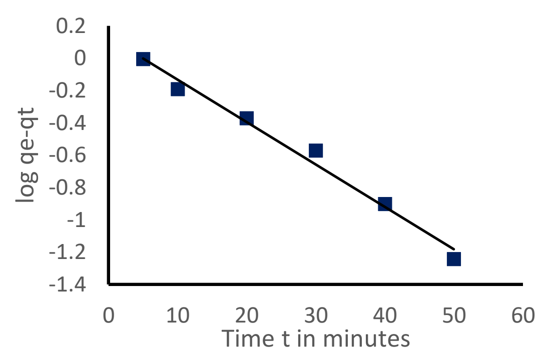

Figure- 6 Pseudo first order kinetics for adsorption of orange II by KLP

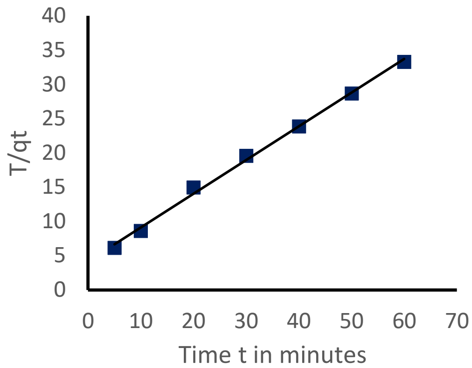

Figure -7 Pseudo second order equation for adsorption of orange II by KLP

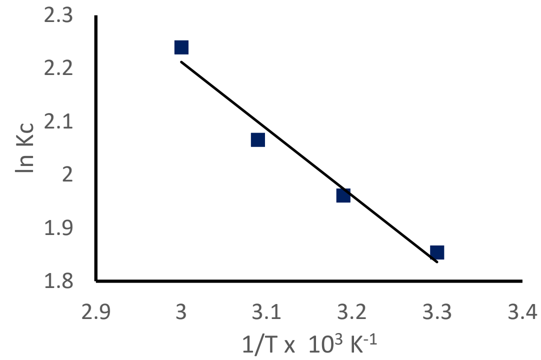

Figure -8 Van't Hoff's plot of $ln\ K_0$ vs $\frac{1}{T}$ for adsorption of orange II by KLP

4.6 Kinetics of Adsorption

To determine the rate controlling mechanism pseudo first and pseudo second order kinetics models were used for adsorption data. The linear form of Lagergren pseudo first order rate equation is given as[20]

$$log q_e - q_t = log q_e - (\frac{K_1}{2.303})t \quad (1)$$

Where q_e and q_t the amount of dye adsorbed (mg/g) at equilibrium and at time t, K_1 is pseudo first order rate constant. The values of K_1 and can be evaluated from slop and intercept of plot of $\log(q_e - q_t)$ vs t given in Figure 6 and Table 2

The pseudo second order rate equation is written as [21]

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + (\frac{1}{q_e})\ t \quad (2)$$

Where q_t *is* the amount of dye adsorbed at time t (mg/g) and q_e is equilibrium amount adsorbed (mg/g), K_2 *(g/mg.min.)* is the pseudo second order rate constant. The plot of $\frac{t}{q_t}$ vs t given in Fig.7 The correlation coefficient and similarities between $q_{e\ cal.}$ and $q_{e\ exp.}$ showed that adsorption of indigo carmine by KLP follows pseudo second order rate kinetics.

4.7 Thermodynamics Studies

The change in standard free energy ΔG^0, enthalpyΔH^0 and entropy ΔS^0 (Table 2) were determined by following equations[23]

$$K_c = \frac{C_0 - C_e}{C_e} \quad (3)$$

$$\Delta G^0 = -RT\ ln\ K_c \quad (4)$$

$$ln\ K_c = \Delta S^0/R - \Delta H^0/RT \quad (5)$$

Table: 1 Kinetic parameters for adsorption of orange II dye by kokum leaf powder

Pseudo first order model				Pseudo Second order model				
$q_{e\ (exp.)}$ $mg\ g^{-1}$	K_1 min^{-1}	R^2	$q_{e\ (cal.)}$ $mg\ g^{-1}$	$q_{e\ (exp.)}$ $mg\ g^{-1}$	K_2 $min.^{-1}$	$q_{e\ (cal.)}$ $mg\ g^{-1}$	h mg/g.min	R^2
1.801	0.0603	0.986	1.347	1.801	0.0575	2.034	4.202	0.997

Table: 2 Thermodynamic parameters for adsorption of orange II dye by kokum leaf powder

K_c				$-\Delta G^0$	ΔH^0	ΔS^0
303 ^{0}K	313 ^{0}K	323 ^{0}K	333 ^{0}K	$kJmol^{-1}$	$kJmol^{-1}$	$Jmol^{-1}$
6.385	7.104	7.817	9.395	5.381	10.424	49.663

V. CONCLUSIONS

The adsorption of orange II dye by Kokum leaf powder was studied and high value of correlation coefficient (R^2=0.999) and similarities between $q_{e\ cal.}$and $q_{e\ exp.}$ indicated that Lagergren pseudo second order model best describes the kinetics of CV dye adsorption. The results of thermodynamics parameters indicated spontaneous, endothermic and favorable nature of adsorption with increasing disorder at solid -solution interface. Therefore sulphuric acid and formaldehyde activated Kokum leaf powder could be used as better alternative for dyes removal.

References

1. K.R. Ramakrishna, T. Viraraghavan, *Water Sci. Technol.,1997, 36,189*
2. Malik P K ,*Dyes* ,*Pigments* ,56 (2003) 239
3. R. Shivraj,C. Namasivayam, K. Kadirvelu,2001,*Waste Manag.*,21: pp105-110
4. C. Namasivayam, R. Radhika and S. Suba, *Waste Manag.*,21, 381
5. McKay., S.,J., Allen., I., F., Meconney., M., S., Ottrbun, *J.Colloid Interface Sci*.1981,80 (2),323
6. Rais Ahmed and Rajeev Kumar, *J.Iran Chem. Res.* , 2008, 1,85
7. S.J. Allen, Q., Gan, R. Mathew and P.A.Johnson, *Ind. Eng. Chem. Res.* , 2005, 44, 1942

8. G. McKay, J. Chem. Technol. Biotechnol.,1982,32, 759
9. Nigam P, Armour G, Banat I M, Singh D, Merchant R, *Bioresour.Technol*,72, (2000) pp 219-226
10. Y.S.Ho.,T.H.Chiang,Y.M.Hsuch,2005,*Process Biochem*., 40; pp 119-124
11. Weber W.J. 1967, Principle and application of water chemistry, edited by Faust S.D. and Hunter J.V. Wiley. New York.
12. Renmin G,, Yingzhi S., Jian C., Huijun L., Hao Y., *Dyes and Pigments*,67 : pp 179
13. D. Kavitha and C. Namasivayam, *Dyes Pigments* 74, 237, (2007)
14. Singh A.K., Singh D.P., Pandey K.K. and Singh V.N., 1988 Wollastonite as adsorbent for removal of Fe (II) from water. *J. of Chem. Techol.,42,pp39*
15. Vadivelan V., Kumar K., V., *J. Colloid. Interf. Sci.* 286, (2005) 90
16. Singh D.K.,Srivastava N. (2001).Basic dyes removal from wastewater by adsorption on rice husk carbon., *Indian Journal of Chemical Technology*, 8(2), 133-139
17. Gerg V. K., Gupta R., Yadav A.B. and Kumar R., *Biores. Technol.*, 89, (2003),121
18. Khatri S.D., Singh M.K., *Water Air &Soil Pollution ,120,(3-4),283-294(2000)*
19. P. Bahadur, M. Desai, A. Dogra,S. Vora & R.N. Ram , *Indian J. Chem.*1997, 36 A,938
20. S. V. Mohan, N.C. Rao and Karthikeyan, *J. Hazard Mater.*, 2002, 90, 189
21. R.S. Shelke, J.V. Bharad. R. Madje and M. B. Ubale, *Arch. Appl. Sci., Res.*,2010, 2(3) 260
22. Namasivayam C., Yamuna R.T.,*Amer.Dyestuff Rep. Aug.* 235-239
23. Pandey K.K, Prasad G.,Singh V.N.,*Water Air & Soil Pollution,27* ,287-292 (1988)