REMOVAL OF INDIGO CARMINE DYE FROM AQUEOUS SOLUTION USING LOW COST ADSORBENT: KINETIC AND THERMODYNAMIC STUDY

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ABSTRACT*:* The batch adsorption experiments were carried out to investigate the adsorptive removal of Indigo Carmine dye from aqueous solution using kokum (*Garcinia Indica*) leaf powder. The effect of various process parameters such as contact time, adsorbent dose, pH, initial concentration and temperature on removal of Indigo Carmine were studied. The equilibrium adsorption data were best represented by Langmuir and Freundlich isotherm models. From the experimental data, it was found that removal of Indigo Carmine by kokum leaf powder follows pseudo second order kinetics with regression coefficient value R^2= 0.995. The value of R_L and thermodynamic parameters such as ΔG^0, ΔH^0 and ΔS^0 indicated that removal of Indigo Carmine by Kokum leaf powder is spontaneous, endothermic and favorable. Thus kokum leaf powder is found to be effective adsorbent for the adsorptive removal of dyes from waste water.

Keywords: Indigo Carmine, Kokum leaf powder, Adsorption, Kinetics, Langmuir isotherm.

I. INTRODUCTION

Azo dyes are the compounds that contain azo group (N=N) substituted aromatic molecules. Every year, there are more than 10^4 dyes produced worldwide (Nigam et.al..2000).These dyes are mostly used in textile, leather, cosmetic, paper, plastic and pharmaceutical industries (Gogate, P.R.; Pandit, A.B, 2004). They are synthetic, stable, non-biodegradable and carcinogenic in nature and have adverse effect on human beings (G., McKay 1982, McKay., S., J. et.al.1981). The discharge of these dyes into natural water sources without proper treatment causes environmental pollution and affect aquatic life (Kadirwelu.k. et.al 2003, Wang Y. et.al. 2004). Therefore their removal from waste water becomes matter of environmental concern. In the past, various dye removal methods have been used by different researchers like adsorption, coagulation, electro osmosis, ion exchange, membrane filtration etc. but in these methods, adsorption in the found to be effective and most widely used method. A large number of low cost adsorbents such as Almond tree bark, Azardichta indica leaf (Bhattacharya, Sharma), Teak tree bark (Satish Patil et.al. 2012) sunflower stalk (Sun G., Xu X 1997), rice husk (Singh D.K., Srivastava N. 2001) have been used for the removal of dyes from wastewater.

In present study, the adsorption of Indigo carmine by Kokum leaf powder (KLP) as the low cost adsorbent has been evaluated

II.MATERIALS AND METHODS

2.1Preparation of kokum leaf powder as adsorbent (KLP)

Kokum plant leaves were dried in shadow, crushed and boiled in distilled water to remove colour and suspended dust.it was filtered and residue was treated with 20% formaldehyde and dilute sulphuric acid for 30 minutes. The residue was further washed with distilled water to remove free acid and dried at 100-120 ^{0}C for 8 hours, powdered and sieved to desired size and used for the study.

2.2Preparation of Indigo Carmine dye solution

The Indigo Carmine dyes solution of desired concentrations were prepared in distilled water using 1000 mg/L stock solution. The pH of solution was adjusted by using 0.1 N HCl or 0.1 N NaOH solutions

2.3Batch adsorption experiment

Batch adsorption experiments were carried by contacting 50 mL of 50 mg/L stock solution of indigo carmine and treated with 1.2g of KLP adsorbent. The effect of contact time, solution pH, adsorbent dose, initial dye concentration and temperature were evaluated. After desired time interval, sample solutions were filtered and residual dye concentration was determined using UV/VIS Spectrophotometer (Elico -1245) at 610 nm as $\lambda_{max.}$ .The equilibrium isotherm study was carried by mixing of 1.2 g adsorbent dose with various dye concentration of 10-50 mg/L for 60 minutes as equilibrium time at pH 6 .The adsorption kinetics experiment was carried out using 1.2 g /L of adsorbent with dye concentration of 50 mg/L at pH 6 .the dye solution was mixed at different time interval in the temperature range of 30 to 60 ^{0}C and residual dye concentration is determined by spectroscopic technique.

III.RESULTS AND DISCUSSION

3.1 Effect of contact time

The adsorption experiment was carried out with 50 mg/L of Indigo carmine dye solutions was treated with 1.2 g of kokum leaf powder for 5 to 90 minutes at solution pH 6. The change in dye % removal with contact time has been shown in Figure 1 indicated that % dye removal was increased from 37.18 to 85.49 with increased contact time. The equilibrium was reached at 60 minutes .Similar observations were reported by other researchers (Khatri S.D., Singh M.K.2000).

3.2 Effect of dye solution pH

The effect of solution pH on dye removal capacity of KLP was evaluated in the pH range of 2 to 10 with 50 ml dye solution for 50 mg/L concentration, 1.2 g adsorbent dose, 60 minutes contact time and 30 ^{0}C temperature. Figure 2 showed that 92.26 % of indigo carmine dye was removed at 2 pH and at pH 6, it was found to be 85.49 % and equilibrium was attained at pH 6. Similar results were reported by other workers (P. Bahadur et.al.1997)

3.3 Effect of dye initial concentration

The effect of initial dye concentration of indigo carmine (10 to 50 mg/L) on adsorption was studied with 50 mL volume, adsorbent dose 1.2 g /L, pH 6. From figure 3, it was observed that % removal of dye was decreased from 92.06 to 85.49 % whereas the amount of dye adsorbed increased with increase in concentration. It may be due to surface activity and monolayer formation in the given range of concentration. Similar results were reported by other researchers (Stephen J A, McKay G., and Kedar K. Y. 1989)

3.4 Effect of adsorbent dose

The effect of adsorbent dose was studied by the experiment carried out by taking 50 mL of 50 mg/L dye solutions and adsorbent dose was varied from 0.2 to 1.4 g. the removal of Indigo carmine was 36.23 to 85.49 % when treated with different doses of KLP as shown in Figure 4. The increase in dye removal % with increased dose is due to presence of more active sites on adsorbent surface (Namasivayam C., Yamuna R.T). The maximum removal of dye was found at 1.2 g dose

3.5 Effect of temperature

To study the effect of temperature on removal of indigo carmine batch mode experiment was carried at the temperature ranging from 30 to 60 ºC Figure 5, it was observed that, dye removal % increased from 86.02 to 90.57 % with increased temperature (Pandey K.K et.al.1988).

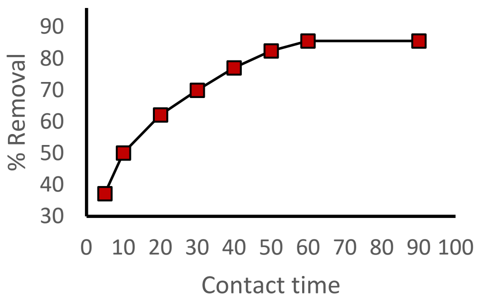

Fig. 1 Effect of contact time on adsorption of indigo carmine by KLP

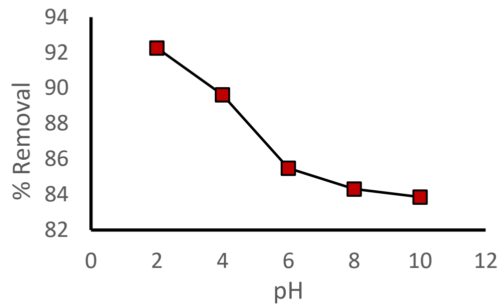

Fig. 2 Effect of pH on adsorption of indigo carmine by KLP

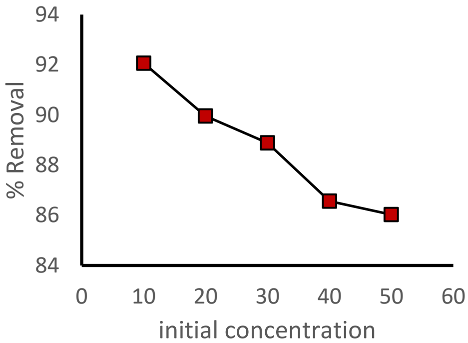

Fig. 3 Effect of initial concentration on removal of indigo carmine by KLP

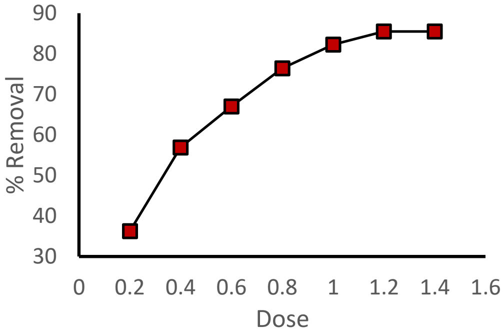

Fig. 4 Effect of adsorbent dose on removal of indigo carmine by KLP

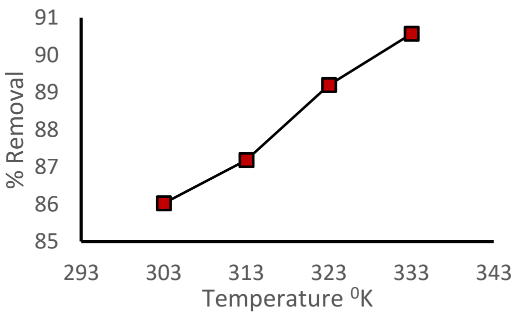

Fig. 5 Effect of temperature on removal of indigo carmine by KLP

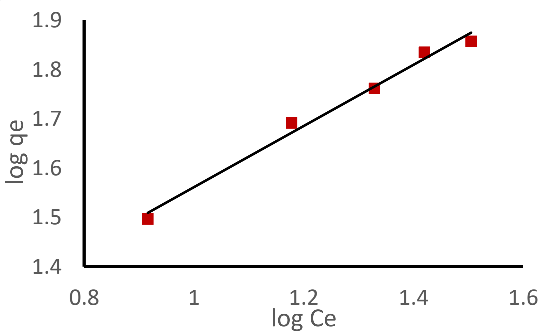

Fig. 6 Freundlich isotherm for removal of indigo carmine by KLP

3.6

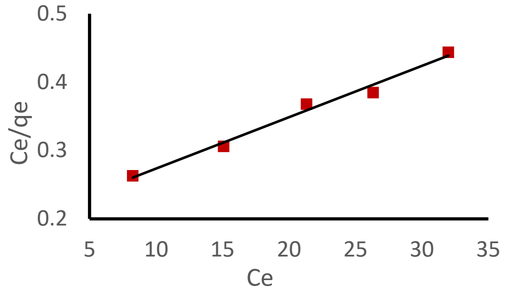

Fig. 7 Langmuir isotherm for removal of indigo carmine by KLP

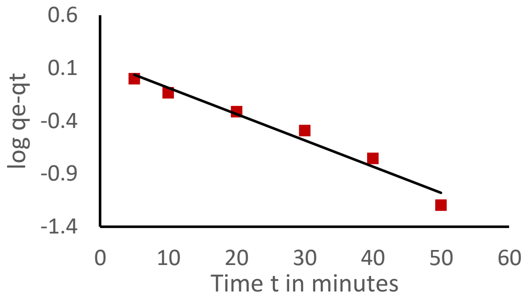

Fig. 8 Pseudo first order kinetics equation for removal of indigo carmine by KLP

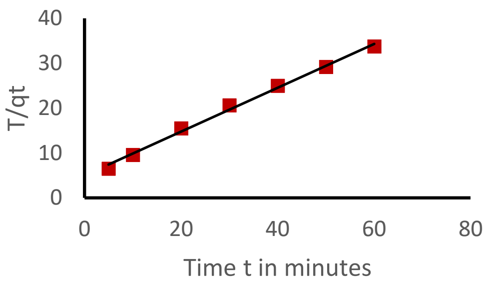

Fig. 9 Pseudo second order kinetics equation for adsorption of indigo carmine by KLP

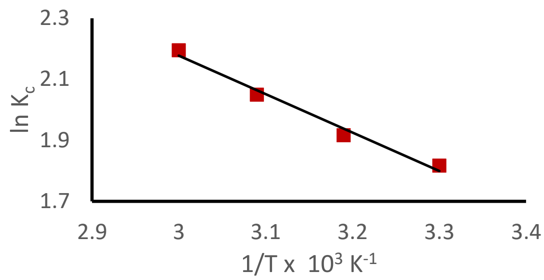

Fig. 10 Van't Hoff's plot of $ln\ K_0$ vs $\frac{1}{T}$ for adsorption of indigo carmine by KLP

Adsorption isotherms

The adsorption isotherm indicates distribution of adsorbate adsorbent molecules at equilibrium state. The adsorption isotherm study was carried out with Langmuir and Freundlich isotherm models to evaluate best fit model.

The linearized form of Freundlich isotherm can be given by (Singh A.K. 1988)

$$lnq_e = lnK_F + \frac{1}{n}\, lnC_e \quad (1)$$

Where q_e is the amount adsorbed (mg/g), C_e is dye equilibrium concentration (mg/L) K_F and n are freundlich constants of adsorption capacity and intensity respectively (Table 1) (Weber J.R.1972) .The linear plot of ln q_e vs ln C_e given in Figure 6

The linear form of Langmuir isotherm to find out maximum monolayer adsorption capacity on adsorbent (I., Langmuir 1916)

$$C_e/q_e = 1/q_m\, b + 1/q_m\, C_e \quad (2)$$

Where C_e is equilibrium dye concentration (mg/L), C_e is dye equilibrium concentration (mg/L) q_e is the amount adsorbed (mg/g), b is adsorption equilibrium constant and q_m is maximum adsorption capacity of monolayer formation on surface. The values of qm and b are evaluated from slope , intercept and correlation coefficients (Table 1) from the plot of C_e/ q_e vs C_e is given in Figure 7 the higher R^2 indicate that adsorption of indigo carmine by KLP follows Langmuir isotherm model. The dimensionless separation factor $R_L = 1/(1+bC_i)$ measure of adsorption occur (Hall K.R.1966).The R_L values between 0 to 1 indicative of the feasibility of adsorption process

3.7 Adsorption kinetics

To determine the rate controlling mechanism of adsorption process such as mass transfer and chemical reactions pseudo first and pseudo second order kinetics models were used for experimental data. The linear Lagergren pseudo first order kinetic equation is given as (Ho. Y.S. and McKay, G. 2000)

$$logq_e - q_t = logq_e - \left(\frac{K_1}{2.303}\right)t \quad (3)$$

Where q_e and q_t the amount 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 Fig.8 and Table 2

The pseudo second order kinetic equation is written as (Ho. Y.S. and McKay, G. (1999))

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \left(\frac{1}{q_e}\right) t \quad (4)$$

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 pseudo second order rate constant. The plot of $\frac{t}{q_t}$ vs t given in Fig.9 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.

3.8 Thermodynamics studies

Thermodynamic parameters such as ΔG^0, ΔH^0 and ΔS^0 were evaluated by following equations (Hossain M.A, et.al. 2013)

$$K_c = \frac{C_0 - C_e}{C_e} \quad (5)$$

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

$$ln\ K_c = \Delta S^0/R - \Delta H^0/RT \quad (7)$$

ΔG^0 values were obtained from equation (4) ΔH^0 and ΔS^0 were obtained from slope and intercept of a plot of $ln\ K_c$ versus $1/T$ Figure 10 represented in Table 3. The values of Gibbs free energy change, enthalpy change and entropy change, showed that adsorption of Indigo carmine on kokum leaf powder was spontaneous, endothermic and favorable with increased randomness during adsorption

Table: 1 Langmuir and Freundlich parameters for adsorption of Indigo Carmine on KLP

Langmuir constants			Freundlich constants		
q_m (mg/g)	b (L/mg)	R^2	K_f	n	R^2
133.33	0.0378	0.986	8.72	1.611	0.987

Table: 2 Langmuir and Freundlich parameters for adsorption of Indigo Carmine on KLP

Pseudo first order model				Pseudo Second order model			
$q_{e\,(exp.)}$ $mg\ g^{-1}$	K_1 min^{-1}	R^2	$q_{e\,(cal.)}$ $mg\ g^{-1}$	K_2 $min.^{-1}$	$q_{e\,(cal.)}$ $mg\ g^{-1}$	h mg/g.min	R^2
2.042	0.0571	0.967	1.448	0.0486	1.781	0.154	0.995

Table: 3 Thermodynamic parameters for adsorption of Indigo Carmine dye by KLP

K_c				R_L	$-\Delta G^0$	ΔH^0	ΔS^0
303^0K	313^0K	323^0K	333^0K		$kJmol^{-1}$	$kJmol^{-1}$	$Jmol^{-1}$
6.153	6.800	7.772	8.979	0.346	5.287	10.476	49.530

V. CONCLUSIONS

In this study, the equilibrium, kinetics and thermodynamics of adsorption of indigo carmine by Kokum leaf powder has been investigated. The isotherm equilibrium data were best fit with both Freundlich and Langmuir isotherm equation with R^2 = 0.986 to 0.997. The monolayer adsorption capacity q_m was found to be 133.3 mg/g. The correlation coefficient R^2 and similarities between $q_{e\ cal.}$ and $q_{e\ exp.}$ showed that Lagergren pseudo second order model best describes the kinetics of adsorption of indigo carmine by KLP. The change in Gibbs free energy, enthalpy and entropy, indicated that adsorption of Indigo carmine on kokum leaf powder was spontaneous, endothermic and favorable with increased randomness during adsorption process. Therefore Kokum leaf powder adsorbent can be better substitute for the expensive activated carbon.

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