REMOVAL OF AZO DYE ORANGE II FROM AQUEOUS SOLUTION USING ACID ACTIVATED CASHEW LEAF POWDER: EQUILIBRIUM, KINETIC AND THERMODYNAMIC STUDIES

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ABSTRACT

This paper presents equilibrium, kinetic and thermodynamic studies on removal of Azo dye orange II from aqueous solution using acid activated cashew leaf powder (ACLP) as low cost adsorbent. The batch adsorption studies were carried out at different adsorbent dose, contact time, dye initial concentration, solution pH and temperature. The efficiency of dye removal was 78% in 60 minutes with solution pH8.0 ,1.2 g dose,10 mgL^{-1} orange II dye concentration at 30 ^0C temperature. The equilibrium data were best fitted with Langmuir isotherm model. The adsorption of orange II dye on ACLP followed pseudo first order kinetics. The values of thermodynamic parameters such as free energy change $(\Delta G)^o$, enthalpy change $(\Delta H)^o$ and entropy change $(\Delta S)^o$ indicated the removal of orange II dye on ACLP is spontaneous , exothermic and favourable. The results indicate that acid activated cashew leaf powder is found to be good adsorbent for the removal of orange II dye from waste water

Keywords: Cashew leaf powder, orange II, adsorption, kinetics, Langmuir isotherm

INTRODUCTION

Azo dyes are compounds containing one or more azo (N=N) groups attached to substituted aromatic molecules to make them stable and non-biodegradable. they are synthetic in nature. Today, more than 10000 dyes are produced commercially every year[1]. They are widely used in textile, leather, paper, cosmetic, food and pharmaceutical industries[2-3] During dying, nearly 10 to 35 % of dyes are released into water[3]. Many of these dyes are hazards or mutagenic and carcinogenic may cause adverse effect on human being such as skin, lungs and other respiratory disorders[4-5] Their disposal without further process can create environmental pollution and affect aquatic life [6-7] Therefore removal of these dyes from water sources becomes one of the major environmental concerns in developing countries like India.

There are various conventional methods to remove dyes from aqueous solution such as coagulation, photo degradation, ion exchange, reverse osmosis and adsorption are very expensive and less effective.[8] except adsorption, which is found to be an effective and alternative process for the removal of dyes and metals from waste water. Many adsorbents have been used by researchers for the removal of dyes from wastewater such as Banana pith[9], Cassava peel[10], Charcoal[11], Teakwood leaves[12], Rice husk[13-14], coconut shell[15], Sunflower stalk[16]

In this study, acid activated powder of cashew leaves has been evaluated for the removal of orange II dye from aqueous solution.

MATERIALS AND METHODS

Preparation of acid activated Cashew leaf powder (ACLP)

Mature Cashew leaves were from Sindhudurg district of Maharashtra, India. The leaves were washed with water and dried in shadow. the dried leaves were crushed and boiled in distilled water for one hour to remove colour and suspended dust .it was filtered and residue was treated with formaldehyde and dilute Sulphuric acid for about 30 minutes. the residue was washed with distilled water to remove free acid and dried at 100-110 ^0C for 8 h powdered and sieved to desired particle size and used for the study.

Preparation of orange II dye solution

The orange II dye solution of desired concentration (10 to 50 mg/L) were prepared by diluting the stock solution (1000 mg/L) in distilled water. The pH adjustment was done by using 0.1 N HCl or 0.1 N NaOH solution

Batch adsorption Studies

The equilibrium adsorption of orange II dye onto ACLP was carried out by agitating 50 mL of 50 mg/L stock solution treated with 1.2 g of adsorbent. The effect agitation time, solution pH, adsorbent dose, initial dye concentration and temperature were evaluated. After desired time interval, dye solutions were filtered and equilibrium dye concentration was determined by using UV/VIS Spectrophotometer (Elico SL-150) at a λ_{max} = 485 nm. For equilibrium isotherm studies 1.2 mg/L of adsorbent was mixed with different concentrations of dye solutions (10 to 50 mg/L) were agitated at equilibrium contact time (60 min.) at 30^0C at pH 8. The adsorption kinetics experiment were carried out using 1.2 mg/L of adsorbent with dye concentration of 10 mg/L at pH 8. The solution was mixed at different intervals of time in the temperature range 30 to 50 ^{0}C.the dye concentration left in solution is determined by spectroscopic technique.

RESULTS AND DISCUSSION

Effect of agitation time

The adsorption experiment was carried with 50 mg/L of orange II dye solution with 1.2 mg/L ACLP for 10 to 120 minutes at pH 8. the change in dye removal % with agitation time has been given in Figure 1 indicated that dye removal% was increased from 27.98 to 52.96 % with increased agitation time and equilibrium was attained in 60 minutes. similar observation were reported by other researchers[17]

Effect of dye solution pH

The effect of pH on dye removal capacity of AJLP was studied in the pH range of 2 to 10 with 50 mL dye solution of 50 mg/L , adsorbent dose 1.2 g , 60 minute equilibrium agitation time at 30^0C temperature Figure 2 revealed that 84.15% orange II dye was removed at 2 pH whereas at 8 pH it was found to be 70.21 % and. equilibrium was attained at 8 pH .Similar results were observed by other workers [18]

Effect of adsorbent dose

The effect of varying ACLP dose (0.2 to 1.2 g.) on removal capacity of orange II dye from aqueous solution. Experiment were carried out by taking 50 mL of 50 mg/L dye solutions is shown in Figure 3. The removal capacity increased from 23.78 % to 63.37 %. The increase in dye removal% may be due to increased surface area and active sites with increased adsorbent dose[19] .The maximum dye removal occurred at 1.2 g/ L dose

Effect of dye initial concentration

The effect of initial dye concentration of orange II (10 to 50 mg/L) on % removal was studied with 50 mL volume, pH 8, adsorbent dost 1.2 g/L at 30 ^{0}C temperature. It was observed Figure.4 that with increased initial orange II dye concentration % removal increased from 34.20 % to 60.88 %. The increased dye adsorption % onto ACLP may be due to surface activity and formation of molecule aggregates in the given range of dye concentration, similar observations were reported by other workers [20].

Effect of temperature

The effect of temperature on removal of dyes, the batch mode experiment was carried out at temperature varying from 30 to 50^o C. It was observed from Figure 5 that, dye removal % decreased from 58.78% to 18.09 % with increased temperature.

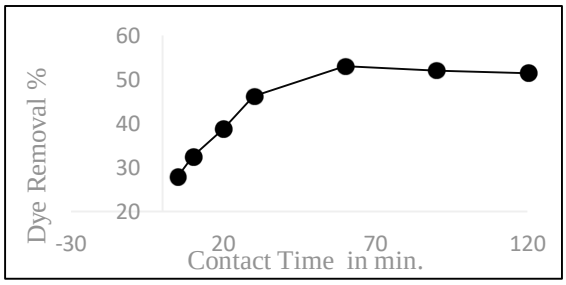

Fig. 1 Effect of agitation time on adsorption of orange II onto ACLP

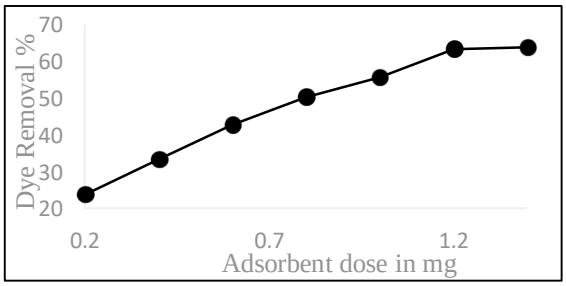

Fig. 2 Effect of Adsorbent dose on adsorption of orange II dye onto ACLP

C_o= 50 mg/L, contact time 60 minutes pH =8.0

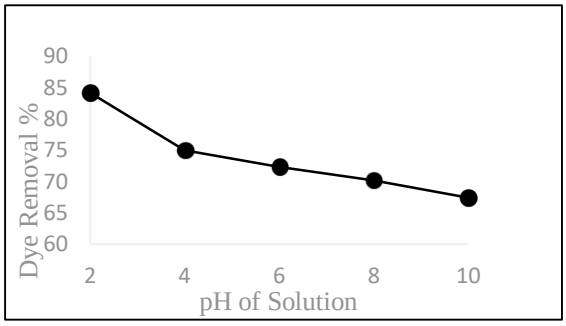

Fig.3 Effect of Dye solution pH on adsorption of orange II dye onto ACLP
C_o= 50 mg/L, contact time 60 minutes

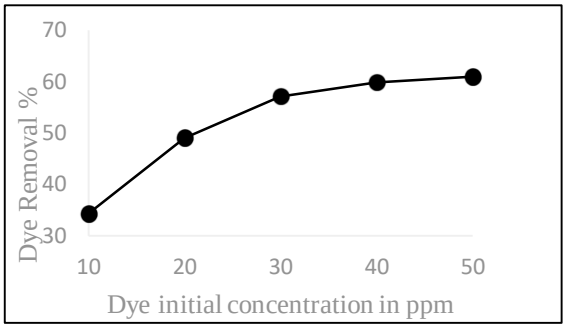

Fig. 4 Effect of Dye initial concentration on adsorption of orange II onto ACLP
Dose= 1.2 g, contact time 60 minutes pH= 8

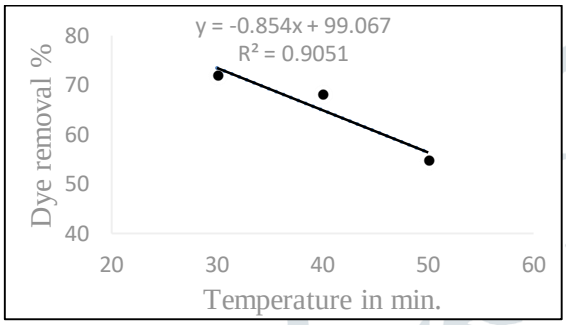

Fig 5 Effect of temperature on adsorption of orange II onto ACLP

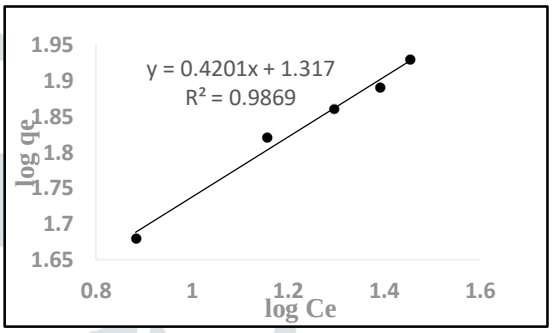

Fig.6 Freundlich isotherm for adsorption of orange II dye onto ACLP

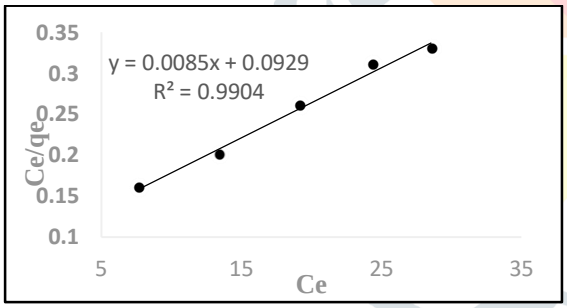

Fig.7 Langmuir isotherm for adsorption of orange II dye onto ACLP

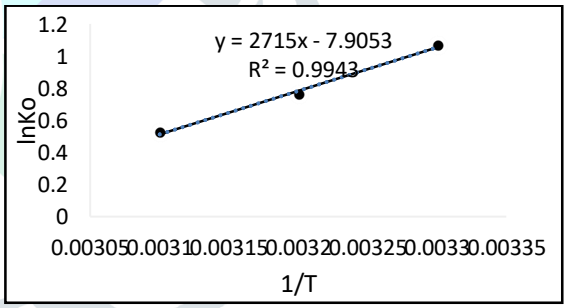

Fig. 8 Plot of $\ln K_o$ vs 1/T for adsorption of orange II onto ACLP Co= 10 mg/L, dose 1.2 g, Contact time 60 min., pH=8.0

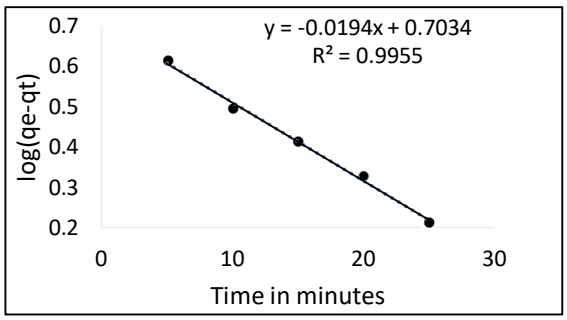

Fig. 9 Pseudo first order kinetic equation for adsorption of orange II onto ACLP

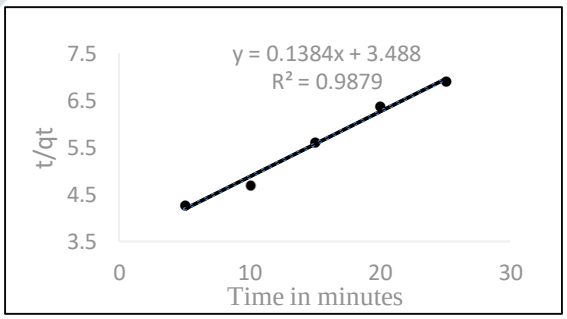

Fig. 10 Pseudo second order kinetic equation for adsorption of orange II onto ACLP

Adsorption isotherms

The adsorption isotherm is the measure of interaction of adsorbate- adsorbent system. The isotherm data were analyzed by fitting into Langmuir and Freundlich isotherms model to evaluate best fitting model

Langmuir isotherm

The linerised form of Langmuir isotherm equation was use to find out maximum monolayer adsorption capacity of orange II dye onto ACLP adsorbent[21].

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

Where C_e is equilibrium concentration of dyes (mg/L), q_e is amount of dye adsorbed (mg/g) and b is adsorption equilibrium constant related to adsorption energy and q_m maximum adsorption capacity to form monolayer on adsorbent surface. The plot of C_e/q_e vs C_e for adsorption of orange II dye onto ACLP is given in Figure 7 q_m and b, the Langmuir constants were evaluated from slop and intercept of the plot with regression correlation coefficient are shown in Table 1. The higher regression coefficient R^2 value indicate that adsorption follows Langmuir isotherm model. The separation factor $R_L = 1 / (1+ b C_i)$ is a measure of ease with which adsorption occur[22]. The R_L values (Table 1) between 0 and 1 shows feasibility of adsorption

Freundlich isotherm

The linerized form of Freundlich isotherm is given by

$$log\ q_e = logK_f + \frac{1}{n} log\ C_e \quad (2)$$

Where q_e is the amount of dye adsorbed (mg/g), C_e is equilibrium concentration of dyes (mg/L), K_f and n are Freundlich constants given in (table 1) related to relative adsorption capacity and adsorption intensity respectively[23]. A linear plots of log q_e against log C_e (Fig.6) indicate that adsorption of orange II follows Freundlich isotherm. The Freundlich constants are given in Table 1. The value of n (2.38) indicate that adsorption is favourable. The R^2 value from Table 1 shows that a Langmuir model ($R^2 = 0.99$) is better fit than the Freundlich model ($R^2 = 0.98$)

Table: 1 Langmuir and Freundlich constants for adsorption of orange II dye on ACLP

Langmuir Constants				Freundlich Constants		
q_m (mg/g)	b (L/mg)	R_L	R^2	K_f	n	R^2
10.26	11.49	0.0086	0.99	20.75	2.38	0.98

Adsorption of Kinetics

The batch mode kinetic experiments were carried out by taking 1.2 g of ACLP in 50 mL solution of orange II dye at pH 8 in conical flasks and shaken for different agitation times in orbital shaker. The residual dye concentration is determined using UV/VIS Spectrophotometer at λ_{max}.= 485 nm. The rate constants for adsorption of dye on given adsorbent were studied using pseudo first order and pseudo second order kinetic models. The linear form of Lagergren pseudo first order kinetic equation is expressed as follows

$$log\ (q_e - q_t) = log\ q_e - (\frac{K_{1p}}{2.302})t \quad (3)$$

Where q_e and q_t are amount of orange II adsorbed (mg/g) at equilibrium time t K_{1p} is pseudo first order rate constant. The values of rate constant K_{1p} and q_e has been evaluated from slop and intercept of linear plot of log (q_e - q_t) vs t Figure 9 and are given in table 3

The pseudo second order kinetic equation is expressed by[24]

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

Where q_t is the amount of orange II adsorbed at time t (mg/g), q_e is equilibrium amount absorbed (mg/g) and K_{2p} (g/mg/min) The plot of $\frac{t}{q_t}$ vs t as shown in Figure 10 the values of K_{2p} and q_e and regression correlation coefficient R^2 are given in Table 2. The correlation coefficient and similarities between q_e calculated and q_e experimental values for pseudo first order model showed that the adsorption of orange II onto ACLP follows pseudo first order rate kinetics

Table: 2 Kinetic parameters for the removal of orange II dye onto ACLP at 30 ^{0}C

Initial conc. of orange II (mg/L)	$q_{e\ exp.}$	Pseudo first order model			Pseudo second order model		
		$q_{e\ cal}$	K_{1p}	R^2	$q_{e\ cal}$	K_{2p}	R^2
10	5.27	5.05	0.045	0.995	7.22	0.0055	0.987

Table: 3 Thermodynamic parameters for adsorption of orange II dye on ACLP

ΔG^o kJ mol^{-1}			ΔH^o $kJmol^{-1}$	ΔS^o $kJmol^{-1}$	R^2
303 K	313 K	323 K			
- 2.68	- 1.97	- 1.40	--22.57	0.065	0.994

Thermodynamic Studies

Thermodynamic parameters such as change in standard free energy (ΔG^o), enthalpy (ΔH^o) and entropy (ΔS^o) were calculated by following equations[25] at different temperatures (30℃ to 50℃). $\Delta G^o = -RT \ln K_o$ (5)

$$\ln K_0 = \frac{\Delta S_0}{R} - \frac{\Delta H_0}{RT} \quad (6)$$

The negative ΔG^o values obtained from equation (5) shows spontaneous adsorption process while ΔH^0 and ΔS^0 obtained from slope and intercept of a plot of $\ln k_0$ versus 1/T Fig.8 represented in Table 3. indicate that adsorption is exothermic. The positive ΔS shows affinity between adsorbent and orange II dye.

CONCLUSIONS

In present study, the kinetic and thermodynamics of orange II dye removal by ACLP were investigated. adsorption data was best fitted with Langmuir isotherm with $R^2 = 0.99$ indicate dye monolayer formation at the adsorbent surface. The kinetic data showed that adsorption of orange II dye on ACLP follows pseudo first order kinetic equation. The negative ΔG^o values while negative ΔH^0 and positive ΔS^0 indicated that adsorption process is spontaneous, exothermic and favorable.The ACLP is used as good adsorbent for the removal of orange II dye from waste water

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