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Kinetic & Thermodynamic Studies of Adsorption of Congo Red Dye by using Polyalthia longifolia Seeds as a Natural Adsorbent

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Abstract : The mechanism of adsorption depends on physical and chemical characteristics of the adsorbent as well as the mass transfer process. In order to determine the mechanism and rate constants of dye adsorbed on the biosorbents adsorption kinetic models are employed. The rate constant k, for a reaction is simply a numerical measure of how fast a reaction can occur if reactants are brought together at unit concentration. Adsorption Study of removal of Congo red from aqueous solution at 500 nm wavelength has been investigated through a batch study. Solutions of Congo red having concentrations 10, 20, 30 & 40 ppm were used. Maximum removal of dye was found to be 91%. Kinetic and Thermodynamic study of Congo red dye was carried out for 50 ml volume of dye solution for time period 120 min with amount of adsorbent 200 mg/50 ml. The adsorption followed Lagergren pseudo-first order kinetics. The values of free energy change (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°) indicated the process to be spontaneous. The diffusion studies indicated that adsorption initially takes place by external mass transfer and later by intraparticle diffusion. Result suggests that it is a non conventional and efficient biosorbent for the removal of Congo red from aqueous solution and can be used for the development of clean and cheap technology for effluent treatment.

Keywords : Congo red, Polyalthia Longifolia, Lagergren 1st order, Pseudo 2nd order, Kinetic and thermodynamic, Clean & Cheap, Biosorbent.

Introduction

Dyes contamination exist in aqueous waste streams from many industries, interest not only in textile but polymer, paint, printing, cosmetics, food and many others. There are over 100,000, commercially available dyes and more than 7x10 tonnes annually[19].An adsorbent such as activated carbon has been widely investigated for the adsorption of dyes[20] but drawback such as its high cost limits its large scale application. There are thus extensive research towards finding inexpensive and effective alternatives to carbon. These materials include rice husk chitin, saw dust, egg shells, barley husk, corn cobs, coconut shells, lemon peel and date palm are not expensive and readily available [21-24]. During the last few decades the mobility and distribution of dyes in water have been studied extensively due to their toxic effects to humans, animals, plants and the aquatic organisms. Colour causing compounds can react with metal ions to form substances which are very toxic to aquatic flora and fauna and cause many water borne diseases. The thermodynamic parameters were also evaluated from the adsorption measurements. Adsorption kinetics involves the study of the rate at which pollutants are removed from aqueous solution onto adsorbent surface, which in turn controls the residence time of the adsorbate uptake

at the solid – solution interface . Several kinetic models are available to describe reaction order of adsorption processes, pseudo-first order and pseudo-second order.

Materials and Methods

A. R. Grade chemicals were used to study the adsorption of Congo red dye. The instruments which are used, Digital colorimeter (Make: Equiptronics) Model EQ-650-A and Digital pH Meter (Make: Equiptronics) Model EQ-610 were used.

Preparation of Carbonized Powder of Polyalthia Longifolia Seeds (CPPL)

Raw material i.e. Seeds of polyalthia Longifolia were collected from the local areas Hadapsar Pune district, India. First seeds were washed with distilled water and dried in the oven at 110 to 120^{o} C. Then they are crushed into small pieces & carbonized in the muffle furnace at temperature 600^{o}C in presence of inert medium of nitrogen gas for 6-7 hrs. Carbonized material was grinded into fine powder with the help of mortar and pestle. Then it was passed through a 63 mesh sieve to get particles of uniform size and stored in air tight container.

Preparation of dye solutions

Dye solutions of different concentrations. (10 to 40 ppm) were prepared by using the stock solution (1000 ppm) with distilled water. The pH adjustment was carried out using 0.1 N HCl or NaOH solutions.

Batch adsorption studies

For study of kinetic and thermodynamic parameter of Congo red dye different concentration dye solutions were used (10, 20, 30 & 40 ppm) and 200 mg of adsorbent were added in to 50 ml volume of dye solution for 120 min and at different temperature. During adsorption process stirring of solution continuously takes place on magnetic stirrer with heater. After given time interval solution was filtered through Whatman filter no. 41 and equilibrium concentration (Ce) of the dye was determined by measuring the absorbance of solution at a λmax = 500 nm.

Results and Discussion

Effect of contact time

After study of rate of adsorption of Congo red at different time interval it was observed that maximum adsorption take place at time 120 min. Adsorption is greater in the initial stage up to 25 min.

Effect of pH

Change in adsorption rate due to change in pH 3.5 to 6.5 at room temperature increases from the value of q_e increases from 1.23 to 2.13 mg/gm and percentage removal (49.18% to 85.25%) adsorption capacity 1.35 to 2.30 mg/gm and %removal also goes on increasing 54.10% to 91.80%.

Effect of Adsorbent dose

Adsorption rate of Congo red solution (10 to 40 ppm) changes as amount of adsorbent changes (25 mg to 200 mg). For 10 mg/lit solution of Congo red adsorption capacity decreases from 2.62 to 1.68 mg/gm and %adsorption increases 13.11 to 67.21%. Maximum %removal was observed for dye 10 mg/lit concentration with amount of absorbent 200 mg and therefore it is selected as optimized dose.

Effect of Initial concentrations and temperature

During the experimentation work it was observed that as the concentration of Congo red solution increases %removal decreases (44.26 to 83.61%) to (31.63 to 55.10%) at 25^{o}C, while at 40^{o}C it changes from (50.82 to 91.80%) to (37.76 to 62.24%).

Lagergren Pseudo 1st Order Kinetic Model

The pseudo first order equation which was suggested by Lagergren is as:

$Dq / dt = K1 (q_e - q_t)$
Where
qe : Amount adsorbed at equilibrium (mg/gm)
q_t : Amount adsorbed at time t (mg/gm)
K_1 : Lagergren rate constant of pseudo 1st order (min^{-1})
After integrating the equation between the limits
t = 0 to t = t and q = 0 to q = q_e
$\log (qe - qt) = \log qe - K_1 t / 2.303$ (1)
Linear plot of log(qe-qt) vs. t are obtained and the lagergren rate constant, K_1 are determined from the slope of plot.

Table 1: Lagergren Pseudo 1st Order Parameters

	10 mg/lit	20 mg/lit	30 mg/lit	40 mg/lit
m	0.002	0.002	0.001	0.001
c	0.018	0.305	0.383	0.462
qe	1.042	2.018	2.415	2.897
K_1	0.046	0.702	0.002	0.002
R^2	0.792	0.761	0.686	0.790

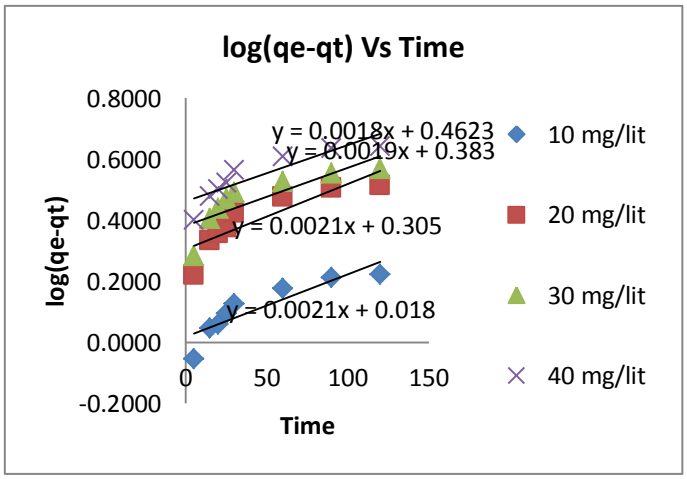

Figure 1. Lagergren 1st Order

The plot of log(qe-qt) vs t indicates that they are not linear and the correlation coefficient, R^2 Value is also very small. This clearly reveals that the pseudo first order model of Lagergren is not applicable to Congo red and CPPL adsorption system.

Pseudo 2nd Order Kinetic Model
Pseudo 2nd order kinetic equation was developed by Ho and McKay which is given as:
$dq / dt = k_2 (qe - q)^2$
After integrating the equation between the limits t = 0 to t = t and q = 0 to q = qe gives
$t / a = (1 / k_2 qe^2) + (1 / qe) * t$ (2)
Comparative value of m, c, qe and K_2 for different concentration solution is as:

Table 2: Pseudo 2nd Order Kinetic parameters

	10 mg/lit	20 mg/lit	30 mg/lit	40 mg/lit
m	2.235	1.135	1.022	0.855
c	20.69	10.67	7.813	6.784
qe	0.4474	0.8811	0.9785	1.1696
k_2	0.2414	0.1207	0.1337	0.1078
R^2	0.997	0.997	0.998	0.998

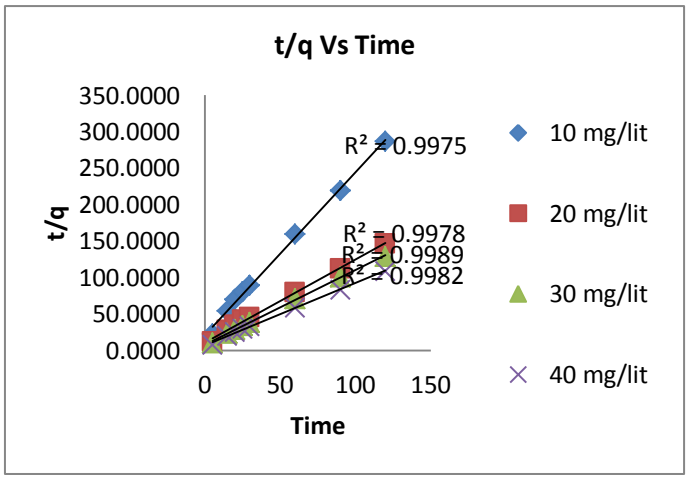

Figure 2. Pseudo 2nd Order

After plot of t / q vs t it is observed that the nature of line is straight line which gives k_2 and qe from the intercept and slope. So it follows pseudo 2nd order kinetic model.

Internal Diffusion Method (Weber and Moris)

The relation between amount adsorbed and the reaction time can be expressed as:

$$\mathbf{q = K_w t^{1/2} + C} \qquad \mathbf{(3)}$$

K_w: Intra paricle diffusion rate constant (mg/gm/min)
C : Intercept (mg/gm)
q : Amount adsorbed (mg)

In this model, due to porous nature of adsorbent, pore diffusion is expanded to be surface sorption. Therefore the rate constant of intraparticle transport, Kw was evaluated from the slopes of linear portion of the plots of q Vs $t^{1/2}$. The line is straight line but it does not passes through origin means it does not follow intraparticle diffusion

Table 3: Internal Diffusion parameters

	10 mg/lit	20 mg/lit	30 mg/lit	40 mg/lit
c	0.191	0.363	0.46	0.556
K_w	0.022	0.045	0.047	0.054

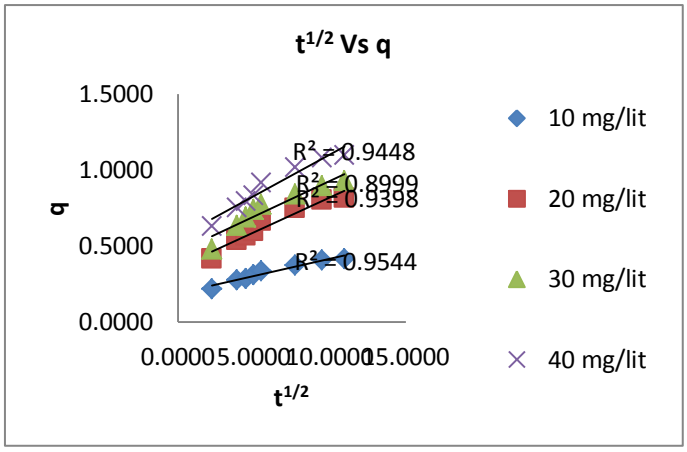

Figure 3. Internal Diffusion Method

Thermodynamic Parameters

In order to confirm the feasibility and the nature of adsorption process, thermodynamic parameters were calculated using the following equations at different temperature (25 to 40°C): Thermodynamic parameters are evaluated using equation

$\Delta G = -2.303\ RT \log Kc$ (4)

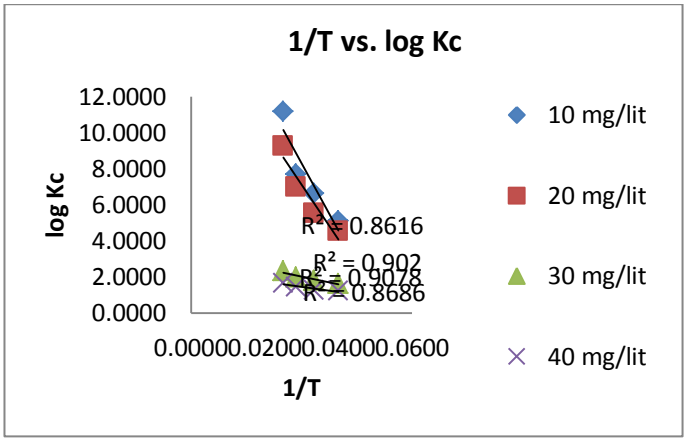

Figure 4. Study of thermodynamic parameters

Table 4: Thermodynamic Paramters for different concentration solutions of Congo red solution

		10 mg/lit	20 mg/lit	30 mg/lit	40 mg/lit	
25°C	**Kc**	5.1	4.5384	1.6363	1.2272	
	ΔG	-4037.29	-3748.22	-1220.37	-507.484	Spontaneous
30°C	**Kc**	6.625	5.5454	1.8064	1.2790	
	ΔG	-4764.18	-4316.01	-1490	-620.156	Spontaneous
35°C	**Kc**	7.7142	7	2	1.45	
	ΔG	-5232.67	-4983.81	-1775.27	-951.639	Spontaneous
40°C	**Kc**	11.2	9.2857	2.3461	1.6486	
	ΔG	-6288.02	-5800.17	-2219.57	-1301.26	Spontaneous
	ΔH	7101.675	5774.778	856.6431	523.6743	Endothermic behaviour
	ΔS	371.8375	309.41	64.4492	43.444	Favourable

Conclusions

The equilibrium, kinetics and thermodynamics for the uptake of Congo red dye by CPPL from aqueous solution were studied. The adsorption data was fitted the best in Temkin adsorption isotherm model. The kinetics data agreed well with pseudo-first order rate equation. The negative values of ΔG and positive values of ΔH and ΔS indicated adsorption process as spontaneous, endothermic and favourable. Besides, the results indicated that the CPPL adsorbent is capable for the removal of Congo red with high affinity and capacity indicating its potential use as a low cost adsorbent in near future.

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