Removal of Direct Yellow-12 Dye from Water by Adsorption on Activated Carbon Prepared from *Ficus Racemosa* L.

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Abstract: The adsorption of direct yellow-12 dye (DY-12) by Atti leaf (*Ficus racemosa*) powder carbon (ATC) was carried out by varying the parameters such as agitation time, dye concentration, adsorbent dose, pH and temperature. Equilibrium adsorption data followed both Langmuir and Freundlich isotherms. Adsorption followed second-order kinetics. The adsorption capacity was found to be 6.7 mg dye per gram of the adsorbent. Acidic pH was favorable for the adsorption of DY-12. Desorption studies suggest that chemisorptions might be the major mode of adsorption.

Keywords: Direct yellow-12 dye, Adsorption, Atti tree leaf powder carbon, Isotherms, pH effect, Desorption studies

Introduction

In developing countries like India, industries cannot afford to use conventional wastewater treatment chemicals like alum, ferric chloride, polymer flocculants and coal based activated carbon because they are not cost-effective. An inexpensive and more easily available adsorbent would make the removal of pollutants an economically viable alternative. As such, there has been a great deal of research in finding cost-effective methods for the removal of contaminants from wastewater. Interest in this area is exemplified by publication of several reviews worldwide¹⁻⁷.

An economic sorbent is defined as one which is abundant in nature or is a by-product or waste from industry and requires little processing⁸. In recent past, considerable attention has been devoted to the study of removal of dyes from wastewater by adsorption using agricultural products and by-products⁹⁻¹¹. Natural materials that are available in large quantities from agricultural operations may have potential to be used as low cost adsorbents, widely available and are environmental friendly¹². The present study deals with the adsorption efficiency of Atti tree leaf powder carbon (ATC) for the removal of direct yellow-12 (DY-12) dye from aqueous solution. DY-12 is commonly used in textile and leather industries.

The Atti tree is a plant belonging to the family Moraceae (*Ficus racemosa* L.). It is an evergreen plant, which is extensively grown in India. The Atti tree leaves are agricultural waste which is arbitrarily discarded or set on fire.

The dye selected as sorbate was direct yellow-12 (DY-12) ($\lambda_{\text{max}} = 389$). The effects of various operating parameters on adsorption such as sorbent dosage, particle size, contact time, initial dye concentration and pH were monitored and optimal experimental conditions were decided.

The properties of adsorbate and adsorbents are quite specific and depend upon their constituents. The constituents of adsorbents are mainly responsible for the removal of any particular pollutants from wastewater¹³.

Experimental

The dried Atti leaf (2.0 kg) was added in small portions to sulphuric acid (98%, 2.5 L) for 2 h followed by boiling for 3 h in a fume hood. It was cooled in an ice bath and the reaction mixture was poured onto cold water (8 L) and filtered. The obtained carbon was dried in an open oven at 180 °C for 2 h followed by immersed in 5% sodium bicarbonate (5.0 L) to remove any remaining acid and then filtered. The obtained carbon was then washed with distilled water until the pH of the activated carbon reached 6; it was dried at 150 °C for 3 h and sieved to the particle size ≤ 0.200 mm and kept in a glass bottle until used.

Preparation of dye solution

The dye direct yellow-12 (DY-12); 98% purity; molecular formula is $\text{C}_{30}\text{H}_{26}\text{N}_4\text{Na}_2\text{O}_8\text{S}_2$, C.I. No. 24895; molecular weight 680.66, (obtained from Sigma-Aldrich, Bangalore, India), in commercial purity, was used without further purification. The dye stock solutions were prepared by dissolving accurately weighed dye in distilled water to the concentration of 1000 mg/L. The experimental solutions were obtained by diluting the stock solution in accurate proportions to different initial concentrations.

Methods and measurements

Adsorption experiments were carried out in a rotary shaker at 150 rpm at 27 °C using 250 mL shaking flasks containing 100 mL different concentrations and initial pH values of dye solutions. The initial pH values of the solutions were previously adjusted with 0.1M HNO_3 or NaOH using pH meter. Different doses of sorbent were added to each flask. After shaking the flasks for predetermined time intervals, the samples were withdrawn from the flasks and the dye solutions were separated from the sorbent by filtration then centrifugation. Dye concentrations in the supernatant solutions were estimated by measuring absorbance at maximum wavelengths of dyes with a 752W Grating Spectrophotometer (Avatar, India) and computing from the calibration curves. The experiments were conducted in duplicate and the negative controls (with no sorbent) were simultaneously carried out to ensure that adsorption was by Atti leaves powder carbon (ATC) and not by the container.

Results and Discussion

Effect of sorbent dose

The effects of sorbent dose on the removal ratios of dyes were shown in Figure 1 and Table 1. The percentages of dyes sorbed increased as the sorbent dose was increased over the range 0.1–1.5 g/L.

Table 1. Effect of carbon dose (Concentration of dye: 100 ppm; particle size: 400 μ ; contact time: 5 h; pH 7.0)

S.No.	Carbon dose, g	Percentage removal of dye
1	0.1	23.21
2	0.2	35.00
3	0.3	41.43
4	0.4	53.24
5	0.5	61.56
6	0.6	69.22
7	0.7	76.16
8	0.8	84.42
9	0.9	86.38
10	1.0	94.11

The adsorption ratios of dyes increased from 23.21 to 94.11% DY-12 dye. Above 1.0 g/L of sorbent dose, the adsorption equilibrium of dye was reached and the removal ratio of dye has almost no variation. So, the ATC of 1.0 g/L was chosen for subsequent experiments.

Figure 1. Effect of sorbent dose on adsorption of DY-12

Effect of equilibration period

The graphical representation of the dependence of the retained amount of dye *versus* time is given by single and continuous curves, which proves the formation of a monolayer at the external surface of the sorbent (Table 2 & Figure 2). For DY-12 the equilibrium is attained in 120–210 min. It was observed that depending on equilibration period, the dye is retained after various time of contact with the sorbent.

Effect of initial pH

An important influencing factor for dye biosorption on agricultural by-products has been referred to pH as in most studies published in the literature¹⁴. The effects of initial pH on adsorption percentages of dyes were studied over a range of pH values from 2 to 10.

As elucidated in Table 3 & Figure 3, for the dye DY-12, the dye removal ratio was high at the initial pH 2. The ratio of dye sorbed increased as the initial pH was increased from 2 to 7, then the dye removal ratios were not significantly altered beyond pH 8. From the Figure 3, it was observed that in the pH range of 7-8, the activated carbon adsorbs to the extent of 94.45 % of the colouring matter. Hence in all the studies an optimum pH of 7.0 was used.

Table 2. Effect of equilibration period (Carbon dose: 1.0 g; particle size: 400 μ ; contact time: 5 h; pH 7.0)

S.No.	Contact time, min	% of dye removal
1	10	42.11
2	20	45.12
3	30	47.01
4	60	51.11
5	90	53.01
6	120	59.54
7	150	60.84
8	180	69.50
9	210	71.52
10	240	67.77
11	270	64.12
12	300	61.02

Figure 2. Effect of equilibration period

Table 3. Effect of pH on adsorption (Dye concentration: 100 mg/L; sorbent dose: 1 g/L; particle size: 400 μ ; contact time: 5 h; temperature: 300 K)

S.No.	pH	% of dye removal
1	2	58.45
2	3	62.32
3	4	74.35
4	5	86.42
5	6	89.99
6	7	91.25
7	8	94.45
8	9	92.40

Figure 3. Effect of pH on adsorption of DY-12 dye

Adsorption isotherm

Adsorption isotherms are prerequisites to understand the nature of the interaction between adsorbate and the adsorbent used for the removal of organic pollutants¹⁵. In the present study, the adsorption of DY-12 dye on ATC (Table 4 & Figure 4) shows that the adsorption of the dye increases with increase in dye concentration and tends to attain almost saturation at higher concentrations.

Table 4. Adsorption isotherm data (carbon size: 400 micron; contact time: 120 min)

S.No	Initial dye concentration mg/L	Weight of carbon (m) mg	Initial OD	Final OD	Equilibrium dye concentration (Ce) mg/L	Amount of dye adsorbed (x) mg/L	x/m	Ce/x/m	log x/m	log Ce/x/m
1	20	50	0.103	0.66	4.29	12.10	0.242	17.72	0.6324	-0.6161
2	40	100	0.283	0.188	5.83	26.21	0.262	22.25	0.7656	-0.5816
3	60	150	0.362	0.264	7.29	47.14	0.316	23.06	0.8627	-0.5003
4	80	200	0.469	0.325	8.02	68.78	0.343	23.38	0.9041	-0.4647
5	100	250	0.652	0.434	8.92	87.83	0.351	25.41	0.9503	-0.4546

Figure 4. Equilibrium adsorption of DY-12

The experimental data have also been analyzed by two well-known adsorption isotherm models Langmuir (Eq 1) and Freundlich (Eq 2).

$$C_e/q_e = (1/K_L) + (a_L C_e/K_L) \quad (1)$$

Where C_e and q_e are the equilibrium dye concentration in the solution (mg/L) and on sorbent (mg/g), respectively, a_L and K_L are Langmuir constants.

Figure 5 shows that adsorption of ATC fits well to the Langmuir isotherm model with a correlation coefficient of 0.998, supporting monolayer coverage of the adsorbate on the surface of adsorbent. The theoretical monolayer saturation capacities of ATC have been calculated to be 33.7 mg/g (0.051 mmol/g). This value is higher to that of other biosorbents such as GAC¹⁶, coir pith¹⁷, PAC¹⁶, banana peel and orange peel¹⁸. However, adsorption capacity of neem leaf powder^{19,20} and waste coir pith²¹ respectively towards DY-12 is higher to a small extent.

Figure 5. Langmuir plots for the adsorption of DY-12

Langmuir equation can also be used to obtain, R_L , the dimensionless equilibrium parameter or the separation factor from the expression:

$$R_L = 1 / (1 + a_L C_0)$$

Where C_0 is the initial concentration of the adsorbate and a_L is the Langmuir coefficient as described above. The value of R_L has been determined to be 0.050 for DY-12, for an initial dye concentration of 250 mg/L indicating that the adsorption process is favourable.

Figure 6. Freundlich plot for the adsorption of DY-12

The data was also analyzed by the linearized form of Freundlich isotherm model

$$\log q_e = \log K_F + (1/n) \log C_e \quad (2)$$

Where, C_e and q_e are the equilibrium concentration of dyes in the solution (mg/L) and on ATC (mg/g), respectively. K_F is the Freundlich constant and $1/n$ is the heterogeneity factor. Figure 6 shows that Freundlich model also fits for DY-12 dye (correlation coefficient 0.997) adsorption process.

Adsorption kinetics

The rate as well as mechanism of adsorption process can be elucidated on the basis of kinetic study.

Influence of initial dye concentration

The initial concentration provides an important driving force to overcome all mass transfer resistance of dye anions between the aqueous and solid phases. In addition, increasing initial dye concentration increases the number of interactions between dye anions and sorbent, which enhances the sorption process. Hence a higher initial concentration of DY-12 dye will increase the biosorption rate. The effect of initial dye concentration on the dye sorption capacity of dried ATC was investigated between 30 and 60 mgL⁻¹ (Table 5-8 and Figure 7-9). When the dye concentration was increased from 50 to 500 mg/L, the percentage of dye sorbed decreased. The sorption is very fast initially. It was observed that depending on concentration, the dye is retained after 20 min. time of contact with the sorbent.

Table 5. Kinetic data (Initial dye concentration (q_0) = 30 ppm; O.D. for initial dye concentration = 0.214; equilibration dye concentration (q_e) = 0.007; $q_0 - q_e = 30.00 - 0.007 = 29.993$)

Contact time, min (t)	Final O.D.	q_t	$q_0 - q_t$	$\log q_0 - q_t$	t/q_t	$\log t$
20	0.062	6.20	23.80	1.376	3.225	1.3010
40	0.057	11.52	18.48	1.266	3.472	1.6021
60	0.052	16.66	13.34	1.125	3.601	1.7780
80	0.049	19.60	10.40	1.017	4.081	1.9031
100	0.044	22.37	7.63	0.882	4.470	2.0000
120	0.042	24.52	5.48	0.738	4.893	2.0791

Table 6. Kinetic data (Initial dye concentration (q_0) = 40 ppm; O.D. for initial dye concentration = 0.227; equilibration dye concentration (q_e) = 0.008; $q_0 - q_e = 40.00 - 0.008 = 39.992$)

Contact time, min (t)	Final O.D.	q_t	$q_0 - q_t$	$\log q_0 - q_t$	t/q_t	$\log t$
20	0.072	5.42	34.58	1.538	3.690	1.3010
40	0.066	10.21	29.79	1.474	3.917	1.6021
60	0.064	14.86	25.14	1.400	4.037	1.7780
80	0.060	17.82	22.18	1.345	4.489	1.9031
100	0.056	20.28	19.72	1.294	4.930	2.0000
120	0.052	22.64	17.36	1.239	5.300	2.0791

Table 7. Kinetic data (Initial dye concentration (q_0) = 50 ppm; O.D. for initial dye concentration = 0.312; equilibration dye concentration (q_e) = 0.010; $q_0 - q_e = 50.00 - 0.010 = 49.990$)

Contact time, min (t)	Final O.D.	q_t	$q_0 - q_t$	$\log q_0 - q_t$	t/q_t	$\log t$
20	0.101	6.78	43.22	1.635	2.949	1.3010
40	0.098	12.68	37.32	1.571	3.155	1.6021
60	0.092	17.42	32.58	1.512	3.444	1.7780
80	0.082	20.49	29.51	1.469	3.904	1.9031
100	0.079	23.64	26.36	1.420	4.230	2.0000
120	0.068	25.98	24.02	1.380	4.618	2.0791

Table 8. Kinetic data (Initial dye concentration (q_0) = 60 ppm; O.D. for initial dye concentration = 0.384; equilibration dye concentration (q_e) = 0.011; $q_0 - q_e = 60.00 - 0.011 = 59.989$)

Contact time, min	Final O.D.	q_t	$q_0 - q_t$	$\log q_0 - q_t$	t/q_t	$\log t$
20	0.121	6.82	53.18	1.725	2.933	1.3010
40	0.096	10.48	49.52	1.694	3.816	1.6021
60	0.090	14.60	45.40	1.657	4.109	1.7780
80	0.084	17.76	42.24	1.625	4.504	1.9031
100	0.078	20.71	39.29	1.594	4.828	2.0000
120	0.072	22.62	37.38	1.572	5.305	2.0791

Dye adsorption on solid surface may be explained by two distinct mechanisms; (i) an initial rapid binding of dye molecules on the adsorbent surface followed by (ii) relatively slow intra-particle diffusion.

Progress of the adsorption of dye by sorbent with agitation time (Table 6-8 & Figure 7) shows that the rate of adsorption of the dye molecules was initially very fast and then gradually slows down to reach equilibrium within 1 h.

Figure 7. Elovich plot - Effect of contact time on DY-12 dye

To determine the rate controlling and mass transfer mechanism, experimental kinetic data were correlated to linear form of the pseudo first order (Eq. 3) and second-order (Eq. 4) rate models.

$$\log (q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

Where, q_e is the equilibrium concentration, t is the time, k_1 and k_2 are the first- and second-order rate constants, respectively; q_t is the uptake per gram of ATC activated carbon at time t .

On the other hand, linearity (Figure 8 & 9) with high correlation coefficients (0.999) indicates that the present sorption process follows second-order rate model. Transportation of the dyes from the solution phase into the pores of the adsorbent may also be considered as the rate controlling stage in batch experiments under rapid stirring condition

Figure 8. Pseudo first order plot at different initial concentration of DY-12 dye

Fig.9. Pseudo-second order plot at different initial concentration of DY-12 dye

Conclusion

This study showed that Atti tree leaf powder carbon particle (ATC) could effectively remove DY-12 dye from aqueous solution. The optimal pH for favorable adsorption of dyes was 7 and above. The percentages of dyes sorbed increased then reached maximum values as

the sorbent dose was increased. The adsorption equilibrium was reached at about 12 h. The isothermal data fitted the Langmuir model and Freundlich model. The adsorption processes followed the pseudo-first-order rate kinetics.

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