

Kinetic studies of Acid blue 110 dye removal using activated carbon prepared from ripened *Bauheniaracemosa* seed pod

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Abstract

In the present work adsorption studies of Acid blue 110 dye onto *Bauhenia Racemosa* seed pod carbon has been studied in a batch system. The effect of concentration of the dye solution, adsorbent dosage, contact time, pH and temperature on the adsorption process was examined and the optimum experimental conditions were identified. The maximum removal of dye was obtained at pH 2. The percentage removal of the dye decreased with an increase in initial concentration. Though the R^2 values of pseudo first and second order rate equations are very nearer to each other the q_e values are in close agreement with second order reaction.

Key words: *Bauhenia Racemosa* seed pod (BRSP), Acid blue 110 (AB110), Kinetic study.

Introduction

Textile processing industries consume huge amount of water during dyeing and finishing processes. The presence of dyes in textile waste water inhibits photosynthetic process in water bodies and also generates toxicity to aquatic organisms and humans. There

are numerous treatment methods available for dye removal which includes Membrane filtration, Ion exchange method, Chemical oxidation, Electrolysis, Adsorption, chemical coagulation and Photo catalysis¹⁻⁴. Adsorption has been found to be superior to other techniques in terms of initial cost, simplicity of design and ease of operation. The most

commonly used adsorbent for colour removal is commercially available activated carbon. Due to its high adsorption capacity, high surface area and micro porous structure activated carbon efficiently adsorb a wide range of various types of dyes. But because of the high cost of activated carbon attempts have been made by the researchers to investigate low cost materials as alternative adsorbent materials.

In the literature several non conventional adsorbent materials like pea, red mud, Coir pith, neem leaf, activated sludge, waste organic peel, saw dust and rice husk, pine wood and number of other products have been investigated⁵⁻⁸. Hence removal of AB15 dye from aqueous solution.

Acid blue 110 is a triphenyl methane dye, (C.I 42750) used for dyeing and printing wool, silk, wool blended fabrics, nylon and leather. They are highly soluble in hot water and gives bright blue colour to the fabric. Since these dyes are highly aromatic its rate of degradation is very poor and is toxic in nature. Thus the objective of the present study is to investigate the adsorptive removal of acid blue 110 dye from aqueous solution by the adsorbent prepared from ripened *Bauheniaracemosa* seed pod carbon

Materials and Methods

The activated carbon was prepared from the ripened seed pods of *Bauhenia Racemosa* by treatment with conc. sulphuric acid. The *Bauhenia Racemosa* belonging to the family *Caesalpinaceae* and is abundantly found in Tamil Nadu, Kerala and Karnataka.

Preparation of the adsorbent :

The ripened *Bauhenia Racemosa* seeds pods were collected and cut into small pieces, dried in sunlight for 10 days and further dried in hot air oven at 60°C for 24 hours. The completely dried material was powdered well and chemically activated by treating it with concentrated sulphuric acid with constant stirring and kept for 24 hours. It is then activated at 110°C in the hot air oven for 12 hours. The carbonised material the present study is aimed at utilising a low-cost, eco-friendly adsorbent *Bauhenia Racemosa* seed pod carbon for the thus obtained was washed well with plenty of distilled water several times to remove the excess acid present and then dried at 100°C to 120°C in a hot air oven for 24 hours. The adsorbent thus obtained was ground well and sieved through a 125-250 mesh and kept in air tight containers for further use.

Preparation of adsorbate :

Stock solution (1000 mg/L) of acid blue 110 dye was prepared by dissolving 1g of AB110 dye in 1000 ml of double distilled water. All the test solutions were prepared by diluting the stock solution with double distilled water.

Equipments :

- Elico pH meter was used to measure pH
- Digital Systronic model 104 Spectrophotometer was used for measuring the concentration of the dye solution.
- Lab line mechanical shaker with temperature control was used for shaking the solution containing adsorbent and adsorbate.

Adsorption studies :

Batch mode experiments were perfo-

med to study the effect of contact time, concentration of the adsorbate, pH, adsorbent dose and temperature influence the adsorptive removal of AB110 dye. In the adsorption experiments 50 ml of the dye solutions of the desired concentration and pH were taken in Pyrex bottles containing pre-determined weighed amounts of adsorbents. The pyrex bottles containing adsorbent and adsorbate were equilibrated by shaking the contents at room temperature using thermostated rotary shaker (200 rpm) for different time intervals (10,20,30,40,50,60,80,100,120,140,160 and 180 minutes). Then the solutions were filtered using Whatmann 40 filter paper and the filtrates were analysed for the residual AB110 dye concentration spectrophotometrically at a wavelength of 603 nm against a reagent blank.

$$\text{Removal of CV dye in \%} = \frac{C_o - C_e}{C_o} \times 100$$

Where C_o and C_e (mg/L) are the initial and equilibrium concentration of AB110 dye respectively. The amount of dye adsorbed at equilibrium (q_e) was calculated from the following equation.

$$q_e = \frac{(C_o - C_e) V}{M}$$

Where q_e is the amount of dye adsorbed at equilibrium (mg/g). C_o and C_e (mg/L) are the initial and equilibrium concentration of AB110 dye respectively. V is the volume of the solution (L) and M is the mass of the adsorbent used (g).

Result and Discussion

Effect of initial dye concentration of AB110

dye solution on Acid blue110 dye removal:

The initial concentration of AB110 dye solution was varied (20,30,40,50 and 100 mg/L) and batch experiments were carried out by taking 50 mL of the AB110 dye solution with fixed adsorbent dosage of 100 mg of the adsorbent. The system was equilibrated by shaking the contents of the flask at 32°C. The results (Fig. 1) reveal that the percentage removal of AB110 dye decreases with increase in initial dye concentration and this may be due to the saturation of adsorption sites on the adsorbent surface^{9,10}. The amount of dye adsorption q_e (mg/g) increases with increase in contact time at all initial dye concentrations used in this study is on par with the results by various researchers^{11,12}. This is so because the initial dye concentration provides the driving force to overcome the resistance to the mass transfer of dye between the aqueous and the solid phase.

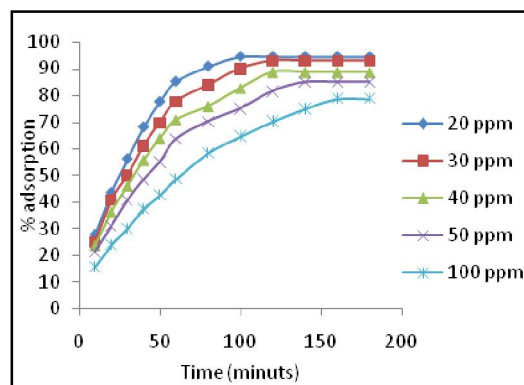


Fig: 1 Effect of initial dye concentration on AB110 dye removal

Adsorption Kinetics :

Lagergren pseudo first order, pseudo

second order and intra particle diffusion models were applied to the experimental data obtained in this study.

Lagergren's first order rate equation is given as follows¹³.

$$\text{Log}(q_e - q_t) = \log q_e k_1 t / 2.303$$

Where q_e and q_t (mg/g) are the amount of dye

adsorbed at equilibrium and at time t and k_1 (1/min) is the rate constant of the pseudo first order adsorption (Table 1). The plot of values of $\log(q_e - q_t)$ Vs. t gives a linear relationship (Figure 2). The values of k_1 and q_e were calculated from the slope and intercept of the plots respectively.

Table 1. Kinetic modeling for AB110 adsorption using Lagergren's pseudo first order equation

Condition: Adsorbent dose:100mg, pH:4.0 Temperature:32°C

Time(min)	$\log(q_e - q_t)$				
	20ppm	30 ppm	40 ppm	50 ppm	100ppm
10	0.82	1.01	1.11	1.2	1.5
20	0.71	0.89	1.02	1.13	1.44
30	0.58	0.81	0.93	1.00	1.38
40	0.42	0.68	0.82	0.96	1.31
50	0.22	0.54	0.69	0.87	1.25
60	-0.03	0.36	0.55	0.72	1.18
80	-0.44	0.13	0.41	0.56	1.01
100	-	-0.36	0.08	0.39	0.85
120	-	-	-	-0.07	0.63
140	-	-	-	-	0.28
Slope	0.0183	0.01472	0.01125	0.01072	-0.0088
Intercept	1.086	1.2253	1.2497	1.3588	1.6574
R ²	0.9915	0.989	0.9953	0.9839	0.9852

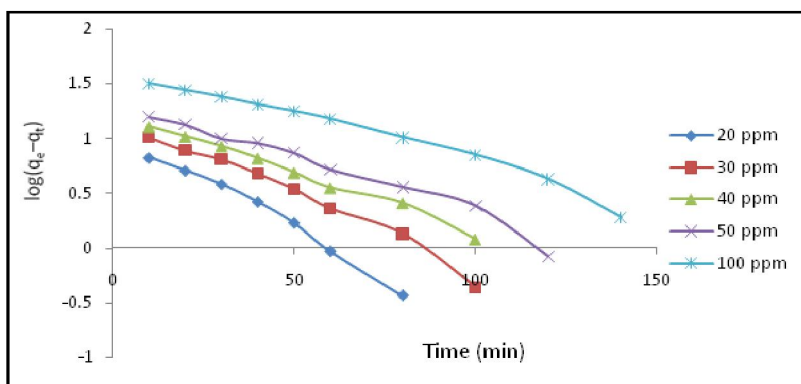


Figure 2. Lagergren's plots for AB110 adsorption

The second order Lagergren's equation was pseudo second order adsorption. given¹³ as follows

$$t/q_t = 1/K_2 q_e^2 + t/q_e(4)$$

From table 2 and Figure.3 (t/q_e Vs. t), q_e and K_2 were calculated from the slope and intercept of the plot respectively.

Where $K_2(\text{g mg}^{-1} \text{ min}^{-1})$ is the rate constant of

Table 2. Kinetic modeling for AB110 adsorption using pseudo second order equation

Condition: Adsorbent dose:100mg, pH:4.0 Temperature:32°C

t(min)	t/q _t				
	20 ppm	30 ppm	40 ppm	50 ppm	100 ppm
10	3.6	2.64	2.09	1.86	1.28
20	4.6	3.28	2.75	2.57	1.68
30	5.34	3.99	3.24	2.94	1.99
40	5.87	4.36	3.58	3.3	2.14
50	6.44	4.77	3.91	3.63	2.35
60	7.04	5.15	4.23	3.77	2.48
80	8.81	6.36	5.26	4.56	2.74
100	10.58	7.41	6.04	5.33	3.1
120	12.7	8.61	6.76	5.89	3.42
140	14.81	10.05	7.88	6.59	3.74
160	16.93	11.48	9.01	7.54	4.07
180	19.05	12.92	10.14	8.48	4.58
Slope	0.0897	0.0587	0.04516	0.0363	0.0175
Intercept	2.2452	1.9114	1.6811	1.7113	1.353
R ²	0.9956	0.9967	0.9974	0.9973	0.9945

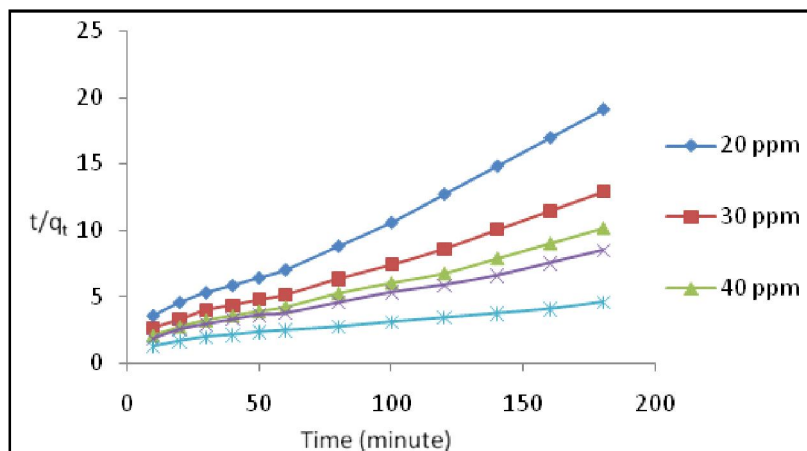


Figure. 3. Pseudo second order plots for AB110 adsorption

The first and second order adsorption rate constants with experimental and calculated q_e values for different initial AB110 dye solution concentrations are tabulated in Table 3. The values of R^2 are close to unity in pseudo second order (0.997) than that of pseudo first order. The values of q_e calculated from pseudo second order are in good agreement with q_e experimental values. This indicates that AB110 adsorption system obeys the pseudo second order kinetic rate equation.

Intraparticle diffusion :

The intraparticle diffusion rate equation is expressed as¹⁴

$$q_t = K_p t^{0.5} + C$$

Where C is the intercept and K_p is the intraparticle diffusion rate constant ($\text{mg g}^{-1} \text{min}^{0.5}$) which can be calculated from the slope of the linear plot of q_t Vs. $t^{1/2}$ given in table 4. Figure 4 shows the plot of intraparticle diffusion of AB110 onto BRSPC. The experimental data

showed a multi linear plot which indicates that two or more steps influence the adsorption process. The first linear portion is due to the diffusion of adsorbate through the solution to the external surface or boundary layer diffusion of solute molecules. The second linear portion showed the gradual reach of equilibrium stage and the third linear portion is due to low adsorbate concentration left in the solution¹⁰.

The slope of the first linear plot gives the intraparticle rate constant (k_p) and intercept of this portion is proportional to the thickness of the boundary layer¹⁵. The lines obtained by plotting q Vs $t^{1/2}$ are not passing through the origin and therefore the intraparticle diffusion alone is not the rate determining step and boundary layer control may also be involved in the process. From Table 4, it was observed that the values of C increased with increase in concentration of AB110 dye solution which showed an increase in the thickness and the effect of boundary thickness.

Table 3. Comparison of pseudo first and second order adsorption rate constants and calculated and experimental q_e values for different initial dye concentration

Dye	First order kinetic model				Second order kinetic model		
Conc	q_e (exp)	$k_1 \times 10^{-2}$	q_e (cal)	R^2	$k_2 \times 10^{-3}$	q_e (cal)	R^2
(mg/L)	(mg/g)	(1/min)	(mg/g)		(g/mg/min)	(mg/g)	
20	9.45	4.214	12.19	0.9915	3.580	11.15	0.9945
30	13.93	3.385	16.80	0.9890	1.879	16.69	0.9973
40	17.75	2.579	17.77	0.9953	1.481	20.04	0.9974
50	21.22	2.464	22.84	0.9839	1.007	24.09	0.9967
100	39.3	2.026	45.43	0.9852	0.500	38.46	0.9956

Table 4. Intra particle diffusion rate equation for adsorption of AB110 dye

$t^{1/2}(\text{min})$	$q(\text{mg/g})$				
	20 ppm	30 ppm	40 ppm	50 ppm	100ppm
3.1623	2.78	3.78	4.78	5.38	7.82
4.4721	4.35	6.12	7.28	7.77	11.90
5.4772	5.62	7.51	9.24	10.19	15.05
6.3245	6.81	9.16	11.16	12.13	18.65
7.0711	7.76	10.48	12.78	13.76	21.25
7.7459	8.52	11.65	14.17	15.90	24.20
8.9442	9.08	12.58	15.20	17.55	29.15
10.000	9.45	13.5	16.55	18.75	32.25
10.954	9.45	13.93	17.75	20.39	35.05
11.832	9.45	13.93	17.75	21.22	37.40
12.649	9.45	13.93	17.75	21.22	39.29
13.416	9.45	13.93	17.75	21.22	39.30
Slope (K_p)	0.6263	0.9903	1.2978	1.6325	3.2955
Intercept	2.3548	2.4531	2.4762	1.5377	-2.0833
R^2	0.9055	0.9417	0.959	0.9761	0.9938

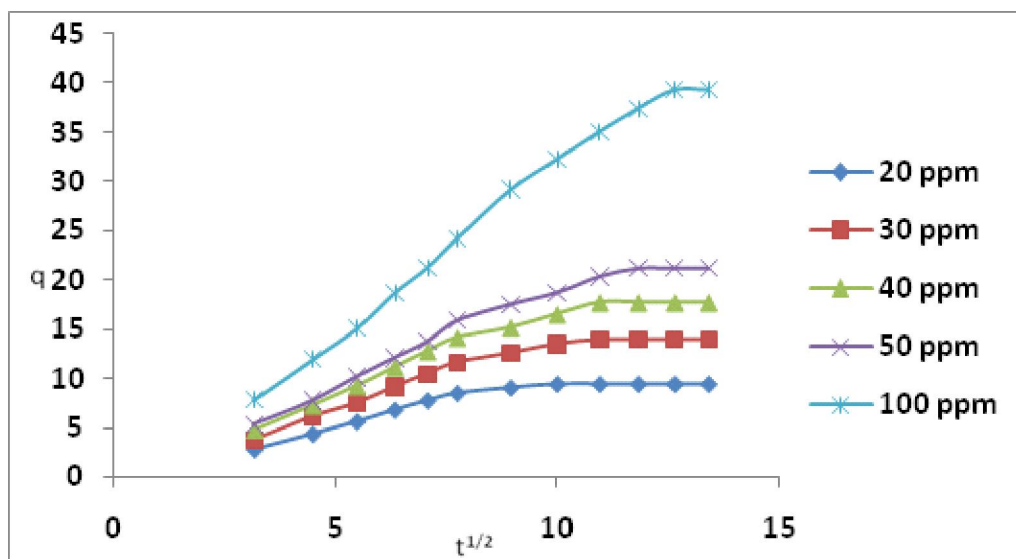


Figure 4. Intra particle diffusion plots for AB110 dye adsorption

Table 5. Intra particle diffusion for the adsorption of AB110 by BRSPC

Dye concentration(mg/l)	K _{id} mg/g/min	C	R ²
20	0.6263	2.3548	0.9055
30	0.9903	2.4531	0.9417
40	1.2978	2.4762	0.9590
50	1.6325	1.5733	0.9761
100	3.2955	-2.0833	0.9938

Conclusion

In this study a biosorbent was prepared from ripened Bauheniaracemosa seed pod by sulphuric acid activation process and the suitability of the adsorbent for adsorption of AB110 dye from aqueous solution was investigated. The results indicated that the pH, biosorbent dose, time, initial dye concentration and temperature affected the adsorption process. The optimum pH for the efficient adsorption of AB110 dye is 2. Though the R² values of pseudo first and second order rate equations are very nearer to each other the q_e values are in close agreement with second order reaction. Based on the results it can be concluded that the low cost eco friendly adsorbent prepared from the ripened seed pods of Bauheniarecemosa may be used for the AB110 dye removal from industrial effluents.

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