

Studies on the Removal of Reactive Orange 4 Dye by Activated Carbon obtained from Neem Leaves (*Azadirachta indica*)

Ishtiyak Qadir*¹, R. C. Chhipa²

^{1,2}Department of Chemistry, Centre for Air and Water Modelling (CAWM),
Suresh Gyan Vihar University, Jaipur-302017, (India)

ABSTRACT

Activated carbon was prepared from the leaves of *Azadirachta indica* by H_3PO_4 impregnation method. The adsorption properties of Neem activated carbon were evaluated by Batch Mode adsorption studies. The amount of RO4 removed by NAC₂ increases from 47.48 to 107.38 mg/g while increasing the initial concentration from 25 to 100 mg/L. A maximum amount of 94.96 % dye was removed at equilibrium time & at an initial dye concentration of 25 mg/L. This treatment method also enables us to recycle the maximum possible amount of spent carbon. The adsorption studies indicate that Neem activated carbon could be used as a low cost alternative to the commercial activated carbon.

KEYWORDS: *activated carbon, adsorbent, dyes, chromophores, desorption.*

1.INTRODUCTION

Water is an important natural resource for the survival of life. More than 70% of earth's surface is covered with water. Most of the water is not suitable for human consumption due large number of contaminants. An increase in population, urbanization, growth of industries, use of chemical fertilizers & lack of environmental awareness has led to an increase in water pollution. The textile wastewaters are characterized by non-biodegradable organic and inorganic materials including metals, dyes, aerosols, phenols, surfactants, phosphates, high BOD and COD concentrations. The dyes mainly consist of heterocyclic & aromatic compounds with color imparting polar groups. Due to complicated structures, complicated and stable, the dyes are difficult to degrade¹.

The color of dyes is due to the presence of chromophore like $-N=N-$, $-NO_2$, $-NO$ groups etc. Auxochromes can intensify the color of chromophore and thereby increase the solubility of dyes and their adherence with the fibre. Some important auxochromes are $-NH_2$, $-NHR$, $-COOH$, and $-OCH_3$ groups². The conventional bio-treatment methods are not effective for the dyed textile effluents. The adsorption technique is one of the most promising and convenient treatment techniques for the removal of the dyes from dyed effluents.

II. MATERIALS AND METHODS

Activated carbon was prepared from the leaves of Neem (*Azadirachta indica*). The leaves were washed, dried and cut into small pieces of 2-3 cm size. The carbonized material was sieved into fine 300-850 μm size particles. The precursor material was impregnated with boiling solution of 10 % H_3PO_4 for nearly 2 hrs and then kept for 24 hrs. At the end of 24 hrs, the supernatant was removed by decantation. The residual matter was dried and carbonized at 400 $^\circ\text{C}$ for half an hour in muffle furnace. The material was powdered and activated in muffle furnace at 800 $^\circ\text{C}$. The activated carbon obtained was finally washed with excess of water to remove any residual acid present and then dried³. The activated carbon obtained from Neem leaves by H_3PO_4 impregnation method is abbreviated as NAC_2 .

ADSORPTION STUDIES OF BR29 BY NAC_2

The dye Reactive Orange 4 (RO4) was dissolved in 1000 ml of distilled water to get a stock solution of 1000 mg/L. Appropriate concentrations of the stock solution were obtained by dilution method.

Table1: Details of selected dye (RO4) for the adsorption studies

Selected Dye	Molecular formula	Molecular weight, g/mol	λ_{max} nm
Reactive Orange 4	$\text{C}_{24}\text{H}_{13}\text{Cl}_2\text{N}_6\text{O}_{10}\text{S}_3\text{Na}_3$	781.46	479

Batch Adsorption Studies for RO4

The batch mode adsorption studies were carried out by varying the initial dye concentration, initial pH and temperature. 100 mg of adsorbent was agitated with 200 mL of aqueous dye solution. The agitation was carried out by keeping the contents of flask in a temperature controlled orbital shaker. The mixture was then withdrawn at specified time intervals and centrifuged at 5000 rpm for 10 minutes. The un-adsorbed supernatant was further analyzed for the residual dye concentrations using UV-visible spectrometer.

Batch Desorption Studies

The activated carbon loaded with dye was washed with distilled water to remove any un-adsorbed dye from it. 500 mg of dye loaded activated carbon was centrifuged with 50 mL of distilled water at 300 rpm. The supernatant liquid was removed at several pH values. The desorbed dye solution was estimated by the adsorption studies.

III. RESULTS AND DISCUSSION

Batch Mode Adsorption Studies

Effect of agitation time and initial dye concentration on adsorption of RO4 by NAC_2

The influence of dye concentration and temperature on the adsorption of RO4 dye by NAC_2 is shown in figures 1 and 2 and the relevant data are given in Tables 1.1 to 1.5 The amount of RO4 removed by NAC_2 increases

from 47.48 to 107.38 mg/g while increasing the initial concentration from 25 to 100 mg/L. At 25 mg/L of initial concentration a maximum of 94.96 % of dye removal was observed as shown in the Figure 4.3.0. In all the range of concentrations under investigation, rapid uptake was noticed in the initial 30 minutes of contact time and the adsorption rate decreases thereafter and finally reaches equilibrium at 80 minutes. The initial rapid uptake is due to the concentration gradient created by the vacant adsorbent surface between adsorbate in solution and adsorbate on the carbon. The increase in dye concentration eases the resistance and makes more contact between dye and sorbent^{5,6}.

Adsorption capacity of NAC₂ increases on increasing the initial dye concentration. This may be due to the creation of concentration gradient at a faster rate. The studies show that the adsorption reaches equilibrium at 80 minutes and thereafter, there is no change in the adsorption capacity and therefore 110 minutes was fixed as equilibration time for isotherm studies.

At higher concentrations the percentage dye removal is low due to saturation of the adsorption sites on the surface of the adsorbent^{7,8}. The smooth adsorption curves obtained suggest the possibility of monolayer coverage of dyes on the surface of the activated carbon.

Effect of temperature on the adsorption of Basic Red 29 by NAC₂

The adsorption of BR29 on NAC₂ at temperatures of 30, 40 and 50°C with a fixed initial dye concentration of 50 mg/l is represented in Figure 2. The percentage of BR29 adsorption by NAC₂ increased from 84.76 to 89.54 % as the temperature was increased from 30 to 50°C. This increase in uptake with increase in temperature indicates that adsorption of BR29 by NAC₂ is endothermic in nature. The increase in temperature may increase the ionic mobility of large sized dye cation. Further, the increase in temperature may cause a swelling effect in the internal structure of the carbon which makes the large dye to penetrate more⁹.

Table 1.1: Effect of agitation time & initial dye concentration on adsorption of BR29 dye

Time (min)	Final Concentration, C _t (mg/L)	Dye adsorbed (%)	Amount of dye adsorbed q _t , mg/g
0	25.0	0.0	0.0
5	17.32	30.8	15.36
10	12.61	49.56	24.78
15	9.72	61.12	30.56
20	8.25	67.00	33.50
30	7.61	69.56	34.78
40	6.26	74.96	37.48
50	5.71	77.16	38.58
60	3.76	84.96	42.48

70	2.98	88.08	44.04
80	1.26	94.96	47.48
90	1.26	94.96	47.48
100	1.26	94.96	47.48
110	1.26	94.96	47.48

Initial concentration of dye= 25 mg/L pH=8.58 Temperature= 30 °C

Table 1.2: Effect of agitation time & initial dye concentration on adsorption of dye

Time (min)	Final Concentration, C_t (mg/L)	Dye adsorbed (%)	Amount of dye adsorbed q_t , mg/g
0	50.0	0.00	0.0
5	36.25	27.5	27.5
10	32.13	35.74	35.74
15	30.52	38.96	38.96
20	28.76	42.48	42.48
30	26.41	47.18	47.18
40	24.15	51.70	51.70
50	22.62	54.76	54.76
60	19.26	61.48	61.48
70	16.02	67.96	67.96
80	14.41	71.18	71.18
90	13.23	73.54	73.54
100	13.23	73.54	73.54
110	13.23	73.54	73.54

Initial concentration of dye= 50 mg/L pH=8.54 Temperature= 30 °C

Table 1.3: Effect of agitation time & initial dye concentration on adsorption of dye

Time (min)	Final Concentration, C_t (mg/L)	Dye adsorbed (%)	Amount of dye adsorbed q_t , mg/g
0	75.0	0.0	0.0
5	57.49	23.34	47.02
10	51.25	31.66	52.50
15	48.92	34.77	54.16
20	47.63	36.49	63.74
30	43.01	42.65	69.98

40	40.21	46.38	81.58
50	34.36	54.18	88.28
60	30.62	59.17	94.76
70	27.92	62.77	99.16
80	25.24	66.34	99.52
90	25.21	66.38	99.58
100	25.21	66.38	99.58
110	25.21	66.38	99.58

Initial concentration of dye= 75 mg/L pH=8.54 Temperature= 30 °C

Table 1.4: Effect of agitation time & initial dye concentration on adsorption of BR29 dye

Time (min)	Final Concentration, C_t (mg/L)	Dye adsorbed (%)	Amount of dye adsorbed q_t , mg/g
0	100.0	0.0	0.00
5	85.86	14.44	28.88
10	78.26	21.74	43.48
15	73.61	26.39	52.78
20	68.42	31.58	63.16
30	63.76	36.24	72.48
40	60.62	39.38	78.76
50	58.46	41.54	83.08
60	55.27	44.73	89.46
70	52.01	47.99	95.98
80	48.53	51.47	102.94
90	46.31	53.69	107.38
100	46.31	53.69	107.38
110	46.31	53.69	107.38

Initial concentration of dye= 100 mg/L pH=8.54 Temperature= 30 °C

Table 1.5: Effect of agitation time & temperature on adsorption of BR29 dye

Time (min)	Final Concentration, C_t (mg/L)	Dye adsorbed (%) 30°C	Dye adsorbed (%) 40°C	Dye adsorbed (%) 50°C
0	50.0	0.00	0.00	0.0
5	36.25	27.5	30.94	32.56

10	32.13	35.74	42.78	44.78
15	30.52	38.96	49.58	50.92
20	28.76	42.48	53.28	55.26
30	26.41	47.18	55.44	58.76
40	24.15	51.70	56.54	62.18
50	22.62	54.76	60.60	64.54
60	19.26	61.48	63.94	71.48
70	16.02	67.96	69.16	74.72
80	14.41	71.18	73.10	77.46
90	13.23	73.54	75.38	81.52
100	5.23	73.54	75.38	81.52
110	5.23	73.54	75.38	81.52

Initial concentration of dye= 50 mg/L

pH=8.54

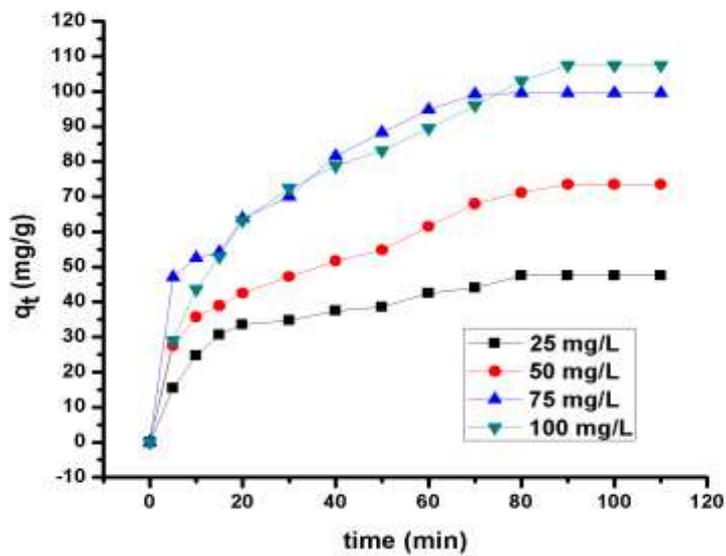


Fig 1: Amount of dye (RO4) adsorbed versus time at different initial concentrations.

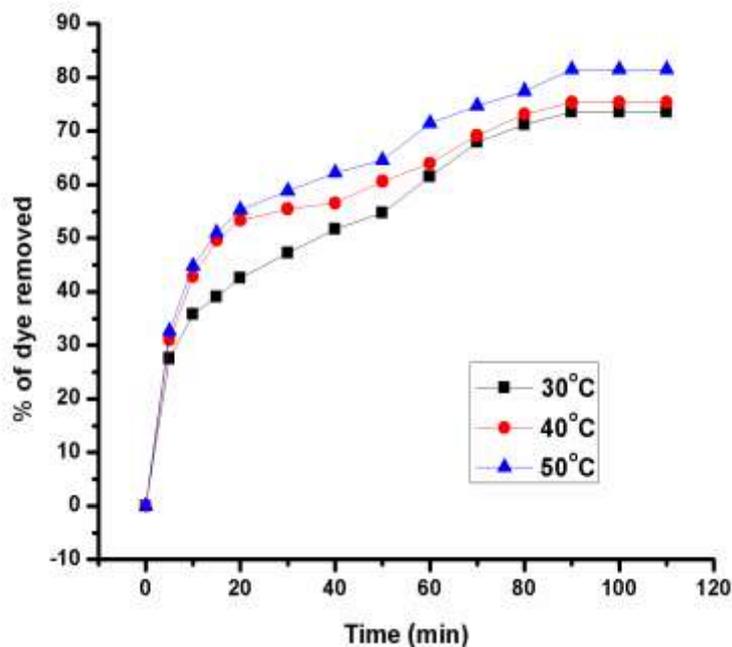


Fig 2: Amount of dye (RO4) adsorbed versus time at different temperatures.

Desorption studies of Activated Carbon

Major amount of dye could be recycled from the dye loaded carbon due to physisorption of dye¹⁰. Desorption of RO4 from NAC₂ surface increased with increase in pH from 2 to 9 and there is no considerable change in desorption of dye above pH 9. The maximum desorption of 26.13 % was observed at pH 8. The poor desorption may be due to the strong binding of the bulky dye molecules inside the micro and mesopore.

IV.CONCLUSION

The batch mode adsorption studies of Neem activated carbon (NAC₂) prepared by H₃PO₄ on Reactive Orange 4 (RO4) indicated that Neem Activated Carbon (NAC₂) could be effectively used as a low cost adsorbent and alternative to the commercial activated carbon. The dyed industrial effluents of effectively be treated by Neem Activated Carbon and thus the pollution problem arising due to color could be solved effectively. Also, sufficient amount of activated carbon could be to recycled for further use.

REFERENCES

- [1.] Correia VM, Stephenson T, Judd SJ. “Characterization of textile wastewaters a review”. *Environ Technol.*, 1994;15:917-929.
- [2.] Srivastava, R. and Rupainwar, D.C. “A comparative evaluation for adsorption of dye on neem and mango bark powder”, *Indian J. Chem. Technol.*, 2011; Vol. 18, pp. 67-75.
- [3.] APHA.; Standard methods for the examination of water and wastewater., 1998; 20th edn. DC, New York.
- [4.] Monika, Drivjot and Amita “Adsorption of dyes from Aqueous solution using Ormangel Peels: Kinetics and Equilibrium Studies”, *J. Adv. Lab. Res. Bio.*, 2012; 3, 1-10.
- [5.] Eren, Z. and Acar, F.N. “Adsorption of Reactive Black 5 from an aqueous solution: Equilibrium and kinetic studies”, *Desalination.*, 2006; Vol. 194, pp. 1-10.
- [6.] Aksu, Z. and Kabaskal, E. “Batch adsorption of 2,4-dichlorophenoxyacetic acid (2,4-D) from aqueous solution by granular activated carbon”, *Separ. Purif. Technol.*, 2004; Vol. 35, pp. 223-240.
- [7.] Gupta, V.K. and Suhas. “Application of low-cost adsorbents for dye removal –A review”, *J. Environ. Manage.*, 2009; 90, 2313-2342.
- [8.] Andre dos BS, Francisco JC, Jules van BL. Review paper on current technologies for decolourisation of textile wastewaters: Perspectives for anaerobic biotechnology. *Bioresource Technology.*, 2007; 98:2369-2385.
- [9.] Forgacs E, Cserhati T, Oros G. Removal of synthetic dyes from waste waters: A Review. *Environment International.*, 2004; 30(7):953-971.
- [10.] Abassi, M., & Nima, R.A. (2009). Removal of hazardous reactive blue19 dye from aqueous solutions by agricultural waste. *J. Iran. Chem. Res.*, 2009; 2, 221-230.