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Sorption Studies of Rhodamine B Dye Using Newly Prepared Kaza's Carbons

M. Nageswara Rao¹, B. V. Rajeswara Reddy², Ch. Suresh Babu², Ch. Chakrapani³, P. Haritha³, K. A. Emmanuel⁴ and Kaza Somasekhara Rao^{*5}

¹Dept. of Chemistry, Sri Chaitanya Mahila Kalasala, Vijayawada

²Dept. of Chemistry, ANU-Nuzvid Campus, NUZVID

³Dept. of Chemistry, Gudlavalleru Engg. College, Gudlavalleru, A.P

⁴Dept. of Chemistry, Sir C. R. Reddy College, Eluru

⁵Dept. of Chemistry, Nagaland University, LUMAMI

ABSTRACT

Activated Carbons are prepared from bio-wastes – *Phaseolus trilobus*, *Leucena leucocephala* and *Casurina*. Studies are made on the Rhodamine B dye color removal using these prepared Carbons. Percent removal of color, contact time, dose of the adsorbent and other effects are studied.

Key words: Sorption Studies, Rhodamine B, Activated Kaza' Carbons.

INTRODUCTION

Modern environmental legislation is becoming Internationally coherent and more focused on pollution through control of hazardous materials and on protection of eco-systems. The waste water originated from reactive dye processes is characterized by poor biodegradability, passing unaffected through conventional treatment systems and discharging into environment[1]. In comparison with conventional processes, adsorption has proved to be more versatile and efficient method[2]. Rhodamine B dye is a red colored true fluorescent basic dye. It is used in Dyeing cotton, wool, Coloring paper ,etc. Commercial rhodamine dyes 6G&B induce reversion mutations in salmonella typhimurium and single-strand breaks in Chinese hamster ovary cells. In the present study, with the prepared activated Kaza's carbons adsorptions studies are made

MATERIALS AND METHODS

The carbons were prepared from the three bio-materials – *Phaseolus trilobus*, *Leucena leucocephala* and *Casurina* and activated with 1N HNO₃ by following the standard procedure[3].

These newly prepared activated carbons NPTC (nitric acid activated phaseolus trilobus carbon), NLLC (nitric acid activated leucena leucocephala carbon) and NCC (nitric acid activated casuarina carbon). These are collectively Named as Kaza's carbons.

Rhodamine B (RB) is supplied by ATUL LIMITED, Colours Division, Atul 3962020, Gujarat, India. All the reagents used are of analytical reagent grade.

1g of rhodamineB is weighed accurately and transferred into 1000ml volumetric flask. The substance is dissolved in double distilled water and then the solution is diluted to 1 litre. The resultant solution contains 1000 mg l⁻¹ of RB. This solution is used as stock solution of RhodamineB((RB). From stock solution, different concentrations of dye 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10 in mg l⁻¹ are prepared. The absorbance of all these solutions are measured using the double distilled water as reference solution at a wavelength of 510 nm using Visible spectrophotometer. Photometer is set at zero absorbance with reference solution and absorbance readings of standard solutions are taken to prepare standard curve.

Batch mode adsorption studies:

Test solution of dye of 20 mg l⁻¹ concentration was prepared from fresh stock solution. All the experiments were carried out in 250 ml conical flasks with 100 ml test solution at room temperature (25±2⁰C). These flasks, along with test solution and adsorbent, were shaken in horizontal shaker at 120 rpm to study the various control parameters. At the end of desired contact time, the conical flasks were removed from shaker and allowed to stand for 2 min for settling the adsorbent. The adsorbent and dye solution were separated using filtration method[4,5].The samples were filtered using Whatman no. 42 filter paper, the first part of the filtrate was discarded to avoid the effects of adsorption on to the filter paper and the remaining filtrate was analyzed for residual dye concentration using UV-visible spectrophotometer. To correct any adsorption of dye on containers, control experiments were carried out in duplicate. Batch study was conducted to determine the optimum conditions and to study the effect of pH, adsorbent dose and contact time on test solution. The effect of pH on dye was studied by adjusting the pH of test solution using 0.1N HCl or 0.1N NaOH on fixed quantity of adsorbent, while effect of adsorbent dose and contact time were studied by varying dose and contact time, respectively. Optimum conditions were selected for further studies. The percentage removal of the dye and the amount of dye adsorbed were calculated by the following equations. All the experiments were done separately for each adsorbent NLLC, NPTC and NCC separately for rhodamineB

$$\% \text{ removal} = \frac{(C_i - C_e)}{C_i} \times 100$$

$$\text{Amount adsorbed } (q_e) = \frac{(C_i - C_e)}{m} V$$

where C_i = initial concentration of dye solution in mg l⁻¹

C_e = equilibrium concentration of dye solution in mg l⁻¹

m = mass of the adsorbent in grams (g)

V = Volume of test solution in litres (l)

The experiments were conducted on the effects of adsorption dose, contact time, initial Concentration, pH, particle size in the sorption of rhodamineB dye for the prepared Carbons.

RESULTS AND DISCUSSION

Effect of adsorbent dosage:

The study of effect of adsorbent dosage is necessary and very useful to find the optimum amount of carbon required for the removal of dye. The percentage removal of dye by adsorption onto activated carbon samples *viz.*, NLLC, NPTC and NCC in the range 0.1 to 4.0 g with 20 mg l⁻¹ initial concentration of each dye and agitation time of 45 min at pH 7 and at temperature (25±2⁰C) were studied . The results are tabulated in Table.1., The removal of dye increased from 18 to 89% for NLLC, 16 to 82.5% for NPTC and 12.5 to 77.1% for NCC. Initially the rate of removal of dye was found to increase rapidly with increase of carbon dosage and slowed down later when the dose increased from 2 to 4 g .

From the results, the optimum dose of adsorbent fixed for all carbons is 2 g. It can also found that after dosage of 2 g, there was no significant change in percentage removal of dye . Though the percentage removal increased with increased adsorbent dosage, from the Table.1, it is obvious that the adsorption capacity (q_e) relatively decreased. There are many factors, which can contribute to this adsorbent dose effect. (i) as the dosage of adsorbent is increased, the adsorption sites remain unsaturated during the adsorption reaction leading to drop in adsorption capacity; (ii) the aggregation/agglomeration of sorbent particles at higher doses, which would lead to decrease in the surface area and an increase in the diffusional path length [6] . However, the observed increase in the percentage of dye removal with adsorbent dosage could be attributed to increase in the adsorbent surface areas, augmenting the number of adsorption sites available for sorption process [7].

From the results, at the optimum dosage of adsorbents , the decreasing order of percentage removal of dye is NLLC>NPTC>NCC.

Effect of contact time:

In the adsorption system contact time plays a vital role, irrespective of the other experimental parameters affecting the adsorption kinetics. In order to study the effect of contact time which is related to kinetics of adsorption of dye by carbon adsorbent sample *viz.*, NLLC, NPTC and NCC. The time profile of adsorption of dye RB onto adsorbents is presented in Table.2 .In case of RB dye, the removal of dye increased from 53 to 85.28% for NLLC, 48 to 79.5% for NPTC and 45 to 74.25% for NCC. As contact time was increased, initially, percentage removal also increased, but after some time, it gradually approached almost constant value, denoting attainment of equilibrium. It was assumed that the equilibrium time is that at which curves appear nearly asymptotic to the time axis. The equilibrium time was at 35 min for RB dye for all the three sorbents NLLC, NPTC and NCC. The changes in the rate of removal with time might be due to the fact that initially all adsorbent sites were vacant and the solute concentration gradient was high. Later, the dye uptake rate by adsorbent had decreased significantly due to the decrease in adsorption sites. Decreased removal rate, particularly, towards the end of experiment, indicates the possible monolayer of adsorbate on the outer surface and pores of the adsorbent leading to pore diffusion onto inner surface of adsorbent particles [8].

From the results, at the optimum contact time for each MB and RB dyes, the decreasing order of percentage removal of dye is NLLC>NPTC>NCC.

Effect of initial concentration:

Initial concentration of adsorbate has its own importance in adsorption process and variation in its concentration shows significant effect. The effect of initial concentration of dye on the extent of removal of dye in terms of percent removal and amount of the dye adsorbed on prepared activated carbon adsorbents *viz.*, NLLC, NPTC and NCC has been studied by varying the initial concentration of dye (range: 1 – 60 mg l⁻¹) and keeping the other control parameters at their optimum conditions. The results of RB dye adsorption onto adsorbents are tabulated in Table.3. In case of RB dye removal, the results indicate that when NLLC is used as an adsorbent, the dye removal decreases from 93 to 54.67% while the amount adsorbed increases from 0.047 to 1.64 mg g⁻¹. For NPTC the dye removal decreases from 88 to 45% and amount adsorbed increases from 0.044 to 1.35 mg g⁻¹. In the case of other adsorbent NCC, dye removal decreases from 83 to 38.33% and the amount adsorbed increases from 0.042 to 1.15 mg g⁻¹.

It is observed that, as dye concentration increases, the percentage removal decreased but the adsorbed amount of dye increased. These results may be explained by the fact that, at low adsorbate concentration, the ratio of surface active sites to total dye is high; hence the dye ions could interact with the sorbent to occupy the active sites on the carbon surface sufficiently and can be removed from the solution [9]. But with the increase in adsorbate concentration, the number of active adsorption sites is not enough to accommodate dye ions.

The data in Tables 3. also reveal that under optimum experimental conditions, the order of adsorption capacity of the studied adsorbents is NLLC>NPTC>NCC for each dye.

3.3.6. Effect of pH:

The effect of pH of the dye solution on the amount of dye adsorbed on carbon adsorbents was studied by varying the pH from 3 to 11 for RB dye under constant process parameters. The results were presented in Table 4.

These results for dye indicate that all the selected adsorbents showed good adsorption capacity in acidic medium than in basic medium. The percentage removal of dye by adsorption on these adsorbents progressively decreased as the pH of the solution increased from 3 to 11.

This pH dependence of dye sorption onto carbon adsorbents for RB could be well explained in terms of their p*H*_{ZPC}. When p*H* < p*H*_{ZPC}, the net surface charge on solid surface of carbon adsorbents is positive due to adsorption of excess H⁺, which favours adsorption due to coulombic attraction. At p*H* > p*H*_{ZPC}, the net surface charge is negative due to desorption of H⁺ and adsorption must compete with coulombic repulsion. The low percentage of dye removal in the p*H* range 3–8, could be due to the combined effect of both chemical and electrostatic repulsions between adsorbent surfaces and positive charge on dye. The observed increase in dye adsorption above p*H* 8 may suggest that the strong negative surface charge developed may cause attraction for the available adsorption sites. Another factor is that in acidic medium, lower adsorption capacity may be due to the competition of H⁺ ions with dye cations [10]. The decrease in dye adsorption is particularly sharp below p*H* 8, as the surface charge becomes more positive. Hence,

dye ions would have to overcome electrostatic forces as there would be a higher density of positive charge very close to the surface, hence greater electrostatic repulsion.

To study the variation in pH of the solution during dye adsorption, 2 g of each carbon adsorbent is agitated with 100 ml of 20 mg l⁻¹ dye solutions (separately) at pH 7 up to their corresponding optimum contact times without controlling the pH of the solution. After this, those agitated carbon adsorbents are dried and again tested for their pH_{ZPC} values. In case of RB dye, the pH_{ZPC} values are changed from 8.6 to 5.6 for RB dye loaded NLLC, 8.1 to 6.3 for RB dye loaded NPTC and 8.65 to 6.1 for RB loaded NCC which are named as NLLC-RB, NPTC-RB and NCC-RB accordingly. This shifting of pH_{ZPC} in each case may be attributed to the fact that the active sites on sorbent surface are occupied by dye ions.

However, the percent removal of dye at pH 11 of NLLC is 89%; NPTC, 82%; and for NCC, 76.25% for RB dye. This indicates that these adsorbents have high adsorption capacity in alkaline medium and can be useful in removal of dye from bases like sodium hydroxide and industrial effluents of textile industry which generally contain bases. The adsorption capacities of these adsorbents for dye in the neutral medium, for RB dye the percent removals at pH 7 are 85, 79 and 74% for NLLC, NPTC and NCC respectively. The prepared activated carbon adsorbents showed good adsorption capacity in the neutral medium also.

Table 1. Effect of adsorbent dose on RB dye removal. pH 7.0, contact time and initial dye concentration are 45 min and 20 mg l⁻¹ respectively for all the three sorbents

S. No.	Adsorbent dose (g)	Equilibrium concentration of dye (C _e) (mg l ⁻¹)			% removal			Amount of RB dye adsorbed (q _e) (mg g ⁻¹)		
		NLLC	NPTC	NCC	NLLC	NPTC	NCC	NLLC	NPTC	NCC
1	0.1	16.40	16.80	17.50	18.00	16.00	12.50	3.600	3.200	2.500
2	0.4	12.50	13.40	14.40	37.50	33.00	28.00	1.875	1.650	1.400
3	0.8	10.40	11.00	12.20	48.00	45.00	39.00	1.200	1.125	0.975
4	1.2	7.80	9.50	10.60	61.00	52.50	47.00	1.017	0.875	0.783
5	1.6	5.40	6.80	7.50	73.00	66.00	62.50	0.913	0.825	0.781
6	2.0	2.50	3.80	4.96	87.50	81.00	75.20	0.875	0.810	0.752
7	2.4	2.44	3.70	4.92	87.80	81.50	75.40	0.732	0.679	0.628
8	2.8	2.42	3.65	4.85	87.90	81.75	75.75	0.628	0.584	0.541
9	3.2	2.42	3.62	4.82	87.90	81.90	75.90	0.549	0.512	0.474
10	3.6	2.20	3.50	4.60	89.00	82.50	77.00	0.494	0.458	0.428
11	4.0	2.20	3.50	4.58	89.00	82.50	77.10	0.445	0.413	0.386

Effect of ionic strength:

In general, reactive dyes are applied to fabric in high salt concentrations in order to lower the dye solubility[11]. In textile effluents commonly high concentrations of chloride and sulphate ions will present. So, the effect of sodium salts of these ions in the concentration range 1000 to 5000 mg l⁻¹ on RB dye adsorption was investigated separately with an initial dye concentration of 20 mg l⁻¹ by keeping other control parameter at their optimum conditions. The results are tabulated in Table 5.

Table .2 Effect of contact time on RB dye removal. pH 7.0, adsorbent dose and initial dye concentration are 2 g and 20 mg l⁻¹ respectively for all the three sorbents

S. No.	Contact time (t) (min)	Equilibrium concentration of RB dye (C _e) (mg l ⁻¹)			% removal			Amount of RB dye adsorbed (q _e) (mg g ⁻¹)		
		NLLC	NPTC	NCC	NLLC	NPTC	NCC	NLLC	NPTC	NCC
1	5	9.40	10.40	11.00	53.00	48.00	45.00	0.530	0.480	0.450
2	10	8.00	8.60	10.40	60.00	57.00	48.00	0.600	0.570	0.480
3	15	6.60	7.20	9.40	67.00	64.00	53.00	0.670	0.640	0.530
4	20	5.40	6.40	7.60	73.00	68.00	62.00	0.730	0.680	0.620
5	25	4.80	5.40	7.20	76.00	73.00	64.00	0.760	0.730	0.640
5	30	4.20	5.00	6.45	79.00	75.00	67.75	0.790	0.750	0.678
7	35	3.00	4.20	5.20	85.00	79.00	74.00	0.850	0.790	0.740
8	40	3.00	4.12	5.20	85.00	79.40	74.00	0.850	0.794	0.740
9	45	2.95	4.12	5.15	85.25	79.40	74.25	0.853	0.794	0.743
10	50	2.95	4.10	5.15	85.25	79.50	74.25	0.853	0.795	0.743

Table 3. Effect of adsorbate concentration on RB dye removal. pH is 7.0, adsorbent dose and contact time is 2 g and 35 min for all the three sorbents

S. No.	Initial conc. of RB dye (C _i) (mg l ⁻¹)	Equilibrium concentration of RB dye (C _e) (mg l ⁻¹)			% removal			Amount of RB dye adsorbed (q _e) (mg g ⁻¹)		
		NLLC	NPTC	NCC	NLLC	NPTC	NCC	NLLC	NPTC	NCC
1	1	0.07	0.12	0.17	93.00	88.00	83.00	0.047	0.044	0.042
2	5	0.45	0.70	0.94	91.00	86.00	81.20	0.228	0.215	0.203
3	10	1.10	1.58	2.00	89.00	84.20	80.00	0.445	0.421	0.400
4	15	1.90	2.60	3.40	87.33	82.67	77.33	0.655	0.620	0.580
4	20	3.00	4.20	5.20	85.00	79.00	74.00	0.850	0.790	0.740
6	25	4.20	6.50	8.00	83.20	74.00	68.00	1.040	0.925	0.850
7	30	5.70	9.00	10.72	81.00	70.00	64.27	1.215	1.050	0.964
8	35	9.00	11.80	14.20	74.29	66.29	59.43	1.300	1.160	1.040
9	40	11.80	16.40	19.60	70.50	59.00	51.00	1.410	1.180	1.020
10	45	16.40	20.60	23.70	63.56	54.22	47.33	1.430	1.220	1.065
11	50	20.50	25.50	28.50	59.00	49.00	43.00	1.475	1.225	1.075
12	60	27.20	33.00	37.00	54.67	45.00	38.33	1.640	1.350	1.150

In presence of chloride ion, the adsorption capacity has not significantly influenced for each adsorbent NLLC, NPTC and NCC for RB dye. But in presence of sulphate ion, little increase in percent removal was observed after 2500 and 3000 mg l⁻¹ for NLLC and both NPTC, NCC respectively, this increase is observed after 2000 and 2500 mg l⁻¹ for NLLC and both NPTC, NCC respectively. Similar trend was observed for reactive dye adsorption onto activated carbons in literature [12].

Table 4. Effect of pH on dye removal. Adsorbent dose and initial dye concentration are 2 g and 20 mg l⁻¹ for all the three sorbents at a contact time of 35 min

S. No.	pH	Equilibrium concentration of RB dye (C _e) (mg l ⁻¹)			% removal			Amount of RB dye adsorbed (q _e) (mg g ⁻¹)		
		NLLC	NPTC	NCC	NLLC	NPTC	NCC	NLLC	NPTC	NCC
1	3	14.20	14.80	16.00	29.00	26.00	20.00	0.290	0.260	0.200
2	4	11.50	12.60	14.20	42.50	37.00	29.00	0.425	0.370	0.290
3	5	7.90	9.20	10.30	60.50	54.00	48.50	0.605	0.540	0.485
4	6	4.20	5.60	6.10	79.00	72.00	69.50	0.790	0.720	0.695
4	7	3.00	4.20	5.20	85.00	79.00	74.00	0.850	0.790	0.740
6	8	2.80	4.10	5.00	86.00	79.50	75.00	0.860	0.795	0.750
7	9	2.60	4.00	4.90	87.00	80.00	75.50	0.870	0.800	0.755
8	10	2.50	3.80	4.80	87.50	81.00	76.00	0.875	0.810	0.760
9	11	2.20	3.60	4.75	89.00	82.00	76.25	0.890	0.820	0.763

Table 5. Effect of chloride and sulphate ions on RB dye removal. pH 7.0, adsorbent dose and initial dye concentration are 2 g and 20 mg l⁻¹ for all the three sorbents at a contact time 35 min

S.No.	Ionic strength (mg l ⁻¹)	% removal of RB dye in presence of chloride ion			% removal of RB dye in presence of sulphate ion		
		NLLC	NPTC	NCC	NLLC	NPTC	NCC
1	1000	85.0	79.0	74.0	85.0	79.0	74.0
2	1500	85.0	79.0	74.0	85.0	79.0	74.0
3	2000	85.0	79.0	74.0	85.0	79.0	74.0
4	2500	85.0	79.0	74.0	85.5	79.0	74.0
5	3000	84.4	78.5	73.7	85.7	79.6	74.8
6	3500	84.0	78.5	73.1	86.0	79.6	75.4
7	4000	83.7	78.0	72.8	86.3	80.2	76.1
8	4500	83.7	77.8	72.8	87.0	80.7	76.9

CONCLUSION

The percent removal of dye increased with increase of adsorbent dose, contact time but decreased with increase in initial concentration and particle size. The adsorption system is pH dependent, the adsorption efficiency increased when solution changed from acidic to alkaline condition. 2 g of the three adsorbents is fixed as the optimum dosage of the carbons. With this optimum adsorbent dosage, contact time is 50 min for RB dye, at pH 7, with 45 μ particle size.

These carbon adsorbents showed low adsorption capacities for further decolorization of dye solutions in continuous cycling process. The regeneration of the adsorbents carried out by changing the solution pH from acidic to alkaline. The poor efficiency of regenerated carbon adsorbents used for further dye removal indicates that dyes are strongly bound to the adsorbent surface and the availability of number of active sites are not much increased during regeneration.

In studies of ionic strength, in presence of chloride ion, with gradual increase of its concentration, considerable change in efficiency of adsorbents in decolorization is not observed and in case of sulphate ion little increase in decolorization of RB dye solution is observed.

The descending order of adsorption capacities of three activated carbons is NLLC>NPTC>NCC.

These prepared activated KAZA's carbons are low-cost biosorbents in decolorizing dye and also serve to the Green Chemistry.

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