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Equilibrium and kinetic studies of reactive Red 2 Dye Adsorption onto prepared activated carbons

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ABSTRACT

Three activated carbons, viz., NCDC, NCMC and NCAC, are prepared from peels of some selected citrus fruits *citrus documana*, *citrus medica* and *citrus aurantifolia* respectively and are used to adsorb commercial reactive dye, C.I. reactive red 2 (Red M5B) from aqueous solution. Out of applied Freundlich, Langmuir, Tempkin and Dubinin-Radushkevich (D-R) isotherms, Langmuir isotherm was fitted well with the adsorption equilibrium data. The kinetic process was investigated using the pseudo-first-order, pseudo-second-order, intra-particle diffusion, pore diffusion and Elovich models. The adsorption process offered excellent fit with pseudo-second-order model. SEM-EDAX and FT-IR analyses were used to study the surface characteristics of adsorbents. Amino groups present on the surface of adsorbents are electrostatically attracting the sulphonyl groups of anionic reactive red 2 dye.

Keywords: Adsorption, reactive red 2, Kinetics, SEM-EDAX, FT-IR.

INTRODUCTION

Effluents discharged from textile and dyeing industries are highly colored and are toxic to aquatic life in receiving water. Removal of synthetic reactive azo dyes from textile waste water is very difficult because the sulphonic acid groups in their chemicals make them water soluble and polar [1]. In comparison with conventional processes such as coagulation, flocculation, and biological methods, adsorption has proved to be more versatile and efficient method [2]. In the present study, activated carbons prepared from peels of some selected citrus fruits. They are used in the removal of commercially available textile reactive dye, Red M5B (RMB) in batch mode

adsorption process. Characteristics of chemical equilibrium, kinetics and mechanism were examined.

EXPERIMENTAL SECTION

Materials and Methods

The activated carbon adsorbents *viz.*, NCDC, NCMC and NCAC are prepared from the peels of citrus documana, citrus medica and citrus aurantifolia fruits respectively. The peels of selected citrus fruits were obtained from a local fruit stall at Eluru, Andhra Pradesh. The peels were dried, crushed and washed thoroughly with de-ionized water to remove adhering dirt. They were air dried in an oven at 100-120°C for 24 h. After drying, they are carbonized at 500°C in a uniform nitrogen flow and subjected to liquid phase oxidation with 1N HNO₃ (analytical grade). Further they were washed with double-distilled water to remove the excess acid and dried at 150°C for 12 h.

The RMB dye used was commercially available textile dye supplied by ATUL LIMITED, Colours Division, Atul 3962020, Gujarat, India. A stock solution of 1000 mg l⁻¹ of RMB was prepared by dissolving 1 g of the dye in double distilled water. All reagents used are of analytical grade.

Test solution of 20 mg l⁻¹ dye 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±2°C). The flasks, along with test solution and 3 g of the adsorbent at neutral pH, were shaken in horizontal shaker at 120 rpm to study the equilibration time (5-90 min) for maximum adsorption of dye and to know the kinetics of adsorption process. At the end of the desired contact time, the samples were filtered using Whatman no. 42 filter paper and the filtrate was analyzed for residual dye concentration at wavelength of 540 nm. The effect of carbon dosage (not shown) on percent removal was studied with carbon dosage varying from 0.5 to 5.5 g and the effect of dye concentration on percent removal was studied with dye concentration 1 to 60 mg l⁻¹ at initial pH 7. The effect of pH on dye removal was studied by varying the pH from 3 to 11. Effect of electrolytes NaCl and Na₂SO₄ on adsorption process was also studied by varying the concentrations of NaCl and Na₂SO₄ from 1000 to 5000 mg l⁻¹. RMB dye adsorbed activated carbons are named as NCDC-RMB, NCMC-RMB and NCAC-RMB correspondingly.

RESULTS AND DISCUSSION

Physico-chemical and surface characteristics of adsorbents:

Physico-chemical characteristics of NCDC, NCMC and NCAC are presented in Table 1. FT-IR spectra of adsorbent samples were obtained using Thermo Nicolet nexus 670 spectrometer, to confirm the presence of functional groups and the results are tabulated in Table 2. Surface morphological studies are made with SEM Hitachi 5S 520 model fitted with energy dispersive X-ray analyzer (EDAX). The scanning electron microscope (SEM) images of NCDC, NCMC, NCAC, NCDC-RMB, NCMC-RMB and NCAC-RMB are shown in Fig. 1 and the corresponding EDAX results are given in Table 3.

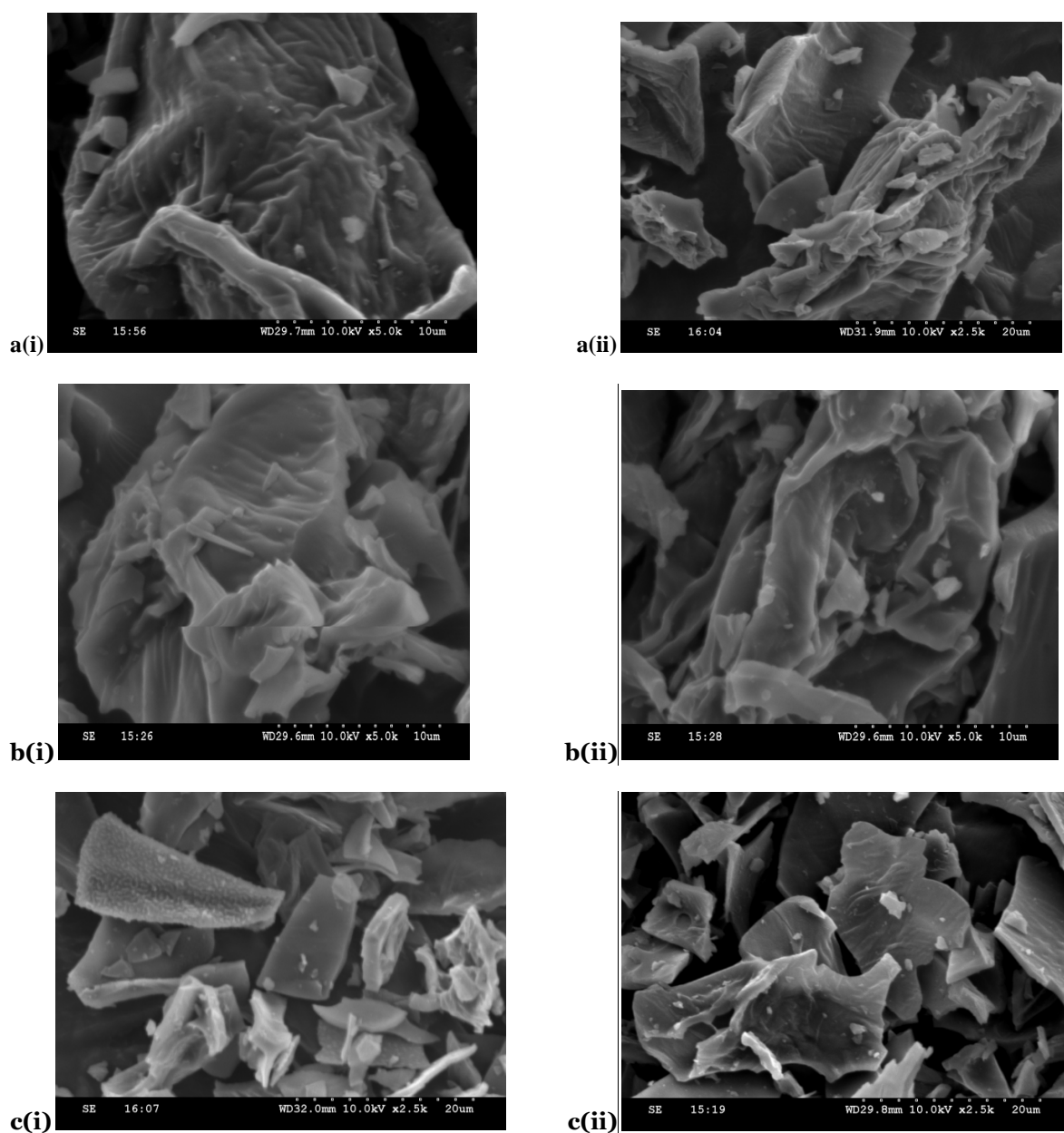


Fig.1. SEM image of a(i) NCDC, b(i) NCMC, c(i) NCAC, a(ii) NCDC-RMB, b(ii) NCMC-RMB and c(ii) NCAC-RMB

Effect of agitation time on dye adsorption:

The effect of agitation time on the percent removal of RMB dye by NCDC, NCMC and NCAC is shown in Fig. 2. The percent removal increases with time and attains equilibrium at 50 min for all three adsorbents. At this equilibrium time, the percent removal of dye is 91, 87 and 85% for NCDC, NCMC and NCAC respectively.

Table 1. Physico-chemical characteristics of NCDC, NCMC and NCAC

Parameter	Value		
	NCDC	NCMC	NCAC
Apparent density, g ml ⁻¹	0.63	0.68	0.74
Moisture content, %	6.5	8.1	7.5
Volatile matter, %	31	43	48
Ash, %	1.9	2.1	1.7
Fixed carbon, %	60.6	46.8	42.8
Matter soluble HCl, %	0.3	0.25	0.41
Matter soluble in H ₂ O, %	0.16	0.15	0.13
Decolorizing power, mg g ⁻¹	215	196	204
pH	7.1	6.9	7.2
pH _{ZPC}	9.3	9.1	8.7
<i>Surface acid groups, meq g⁻¹</i>			
I Carboxyl	0.9	1.1	0.8
II Lactonic	1.2	1.6	1.2
III Phenolic	1.4	1.3	0.9
IV Carbonyl	1.1	0.9	1.3
Total basic groups, meq g ⁻¹	6.3	5.8	6.4
Iodine number, m ² g ⁻¹	741	689	654

Table 2. Bonds assigned to functional groups of NCDC, NCMC and NCAC; NCDC-RMB, NCMC-RMB and NCAC-RMB in FT-IR study

Wave number Cm ⁻¹			BOND INDICATION	Wave number Cm ⁻¹			BOND INDICATION
NCDC	NCMC	NCAC		NCDC-RMB	NCMC-RMB	NCAC-RMB	
3428	3151	3307	O-H stretch/ N-H stretch of amines	3343	3320	3403	O-H stretch/N-H stretch of amines
2364	-	-	C=O stretch of ketene or alkyne	2571	-	2349	C=O stretch of ketene or alkyne.
1597	1584	1585	N-H in plane bending, C=C in aromatics or C=O stretch	1574	1593	1587	N-H inplane bending, C=C in aromatics or C=O stretch
1232	1262	1249	C-N stretching of aryl amines	Around 1350-1400	1383	~1380	N=N of azo group
Below 950	Below 950	Below 950	Plane deformation	1257	1240	1250	C-N stretching of aryl amines
				-	772	751	C-Cl stretching mono chlorinated aromatic
				500-1000	500-1000	500-1000	From -NH ₂ groups and traizine rings.

Adsorption kinetics:

To study the adsorption kinetics five kinetic models were used which include pseudo-first-order [3], pseudo-second-order [4], Weber and Morris intraparticle diffusion [5], Bangham's pore diffusion [6] and Elovich models [7]. The relevant equations and results are tabulated in Table 4.

In kinetic study, it was found that the correlation co-efficient (R^2) values for pseudo second-order adsorption model have high values, 0.9968, 0.9973 and 0.9967 for NCDC, NCMC and NCAC respectively. Comparatively, in each case, the R^2 value is higher than that of pseudo first-order model.

Table 3. Contents of carbon, oxygen, sulphur and chlorine on the surface from EDAX for NCDC, NCMC, NCAC, NCDC-RMB, NCMC-RMB and NCAC-RMB

Element	C	O	Ca	Mg	S	Cl
NCDC	75.15	23.1	1.43	0.32	-	-
NCDC-RMB	72.65	24.8	1.21	-	0.63	0.71
NCMC	73.35	24.99	1.66	-	-	-
NCMC-RMB	72.1	25.6	1.1	-	0.79	0.41
NCAC	77.17	21.21	1.62	-	-	-
NCAC-RMB	74.12	24.1	1.02	-	0.4	0.36

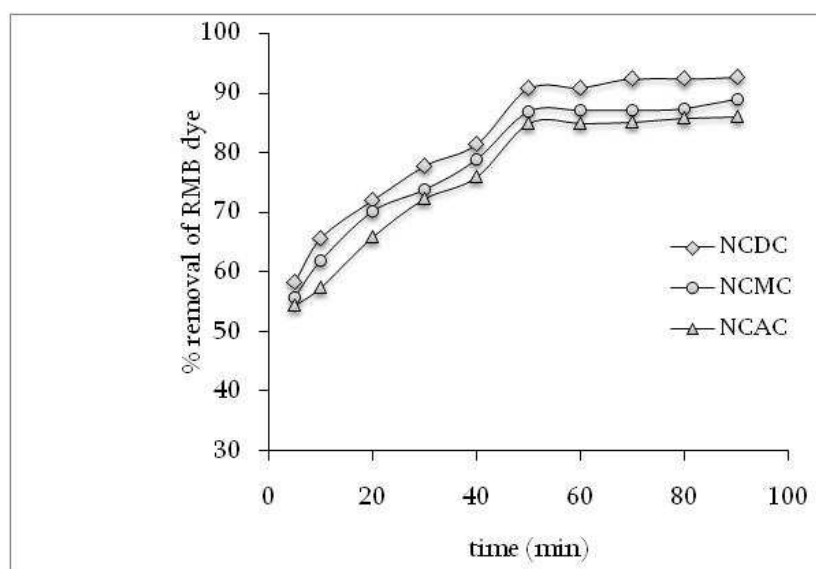


Fig. 2. Effect of contact time on adsorption of RMB dye onto NCDC, NCMC and NCAC.

The lower SSE values for pseudo second-order model also indicate that the adsorption kinetics of RMB onto NCDC, NCMC and NCAC can be better described by pseudo second-order model. Similar phenomenon was observed in the literature for the adsorption of reactive dyes on various adsorbents [8,9]. The pseudo-second order model is based on the sorption capacity on the solid phase. Contrary to other well established models, it predicts the behavior over the whole range of studies and it is in agreement with the chemisorption mechanism plays an important role in rate controlling step [10].

The plots of q versus $t^{1/2}$ for Weber and Morris intra-particle diffusion were shown in Fig. 3 and it is evident from the plots that there are two separate stages; first linear portion (Stage I) and second curved path followed by a plateau (Stage II). In Stage I, nearly 50% of dye was rapidly

up taken by carbon adsorbents within 20 min. This is attributed to the immediate utilization of the most readily available adsorbing sites on the adsorbent surfaces. In Stage II, very slow diffusion of adsorbate from surface site into the inner pores is observed. Thus initial portion of dye adsorption by carbon adsorbents may be governed by the initial intra-particle transport of dye controlled by surface diffusion process and later part is controlled by pore diffusion. Similar dual nature with initial linear and then plateau were found in the literature [11]. Though intraparticle diffusion renders straight lines with correlation coefficients (>0.94) for all the three sorbents, the intercept of the line fails to pass through the origin in each case may be due to difference in the rate of mass transfer in the initial and final stages of adsorption [12] and indicates some degree of boundary layer control which implies that intraparticle diffusion is not only the rate controlling step. The data were further used to learn about the slow step occurring in the present adsorption system using Bangham's pore diffusion model.

For all three sorbents, the lower SSE and high R^2 values (>0.96) (from Table 4) are indicating that kinetics confirmed to Bangham's equation and therefore the adsorption of dye onto NCDC, NCMC and NCAC might be pore diffusion controlled.

It was suggested that diffusion accounted for the Elovich kinetics pattern [13]; confirmation to this equation alone might be taken as evidence that the rate-determining step is diffusion in nature [14]; and that this equation should apply at conditions where desorption rate can be neglected [15]. The kinetic curve of sorption demonstrated good fitting with Elovich model ($R^2 > 0.95$) which may indicate that the diffusional rate-limiting is more prominent in dye sorption by NCDC, NCMC and NCAC.

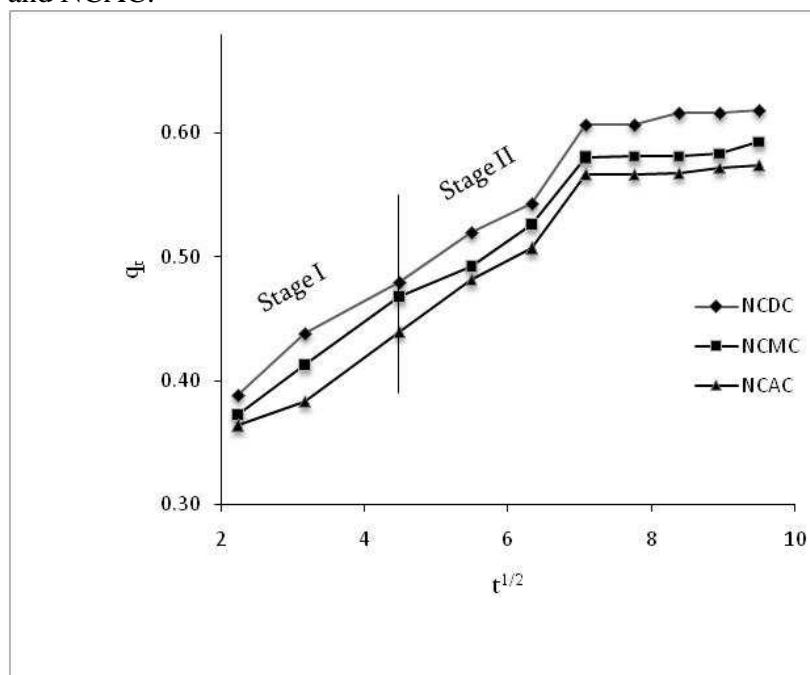


Fig. 3. Intraparticle diffusion plots of NCDC, NCMC and NCAC

Table 4. Comparison of pseudo first-order, pseudo second-order, Weber and Morris, Bangham's and Elovich models parameters, and calculated $q_{e(cal.)}$ and experimental $q_{e(expt.)}$ values at 20 mg l⁻¹ RMB dye concentration

Pseudo first-order							
Adsorbent	Equation	$q_{e(expt.)}$ (mg g ⁻¹)	$k_1 \times 10^{-1}$ (min ⁻¹)	$q_{e(cal.)}$ (mg g ⁻¹)	SSE	R ²	
NCDC	$dq_t/dt = k_1(q_e - q_t)$	0.6067	0.3455	0.2495	0.34661	0.9957	
NMC	$\log(q_e - q_t) = -k_1 t / 2.303 + \log q_e$	0.5800	0.3731	0.2463	0.33102	0.9904	
NCAC		0.5667	0.3593	0.2536	0.30522	0.9961	
Pseudo second-order							
Adsorbent	Equation	$q_{e(expt.)}$ (mg g ⁻¹)	$k_2 \times 10^{-1}$ (g mg ⁻¹ min ⁻¹)	$q_{e(cal.)}$ (mg g ⁻¹)	SSE	R ²	
NCDC	$1/(q_e - q_t) = k_2 t + 1/q_e$	0.6067	2.5549	0.6602	0.00779	0.9968	
NMC		0.5800	2.792	0.6275	0.00671	0.9973	
NCAC	$t/q_t = (1/q_e)t + 1/(k_2 q_e^2)$	0.5667	2.6131	0.6152	0.00734	0.9967	
Weber and Morris Intra-particle diffusion							
Adsorbent	Equation	$q_{e(expt.)}$ (mg g ⁻¹)	$k_{ip} \times 10^{-1}$ (mg g ⁻¹ min ^{0.5})	$q_{e(cal.)}$ (mg g ⁻¹)	SSE	R ²	
NCDC	$q_t = k_{ip} t^{1/2}$	0.6067	0.0333	0.5679	0.00408	0.9493	
NMC		0.5800	0.0315	0.564	0.000761	0.9446	
NCAC		0.5667	0.0323	0.5261	0.005125	0.9415	
Bangham's Pore diffusion							
Adsorbent	Equation	$q_{e(expt.)}$ (mg g ⁻¹)	$k_0 \text{ ml } (g \text{ l}^{-1})^{-1}$	$q_{e(cal.)}$ (mg g ⁻¹)	SSE	R ²	α
NCDC	$\log \log(C_i / (C_i - q_t)) = \alpha \log t + \log(k_0 / (2.303 V))$	0.6067	4.4812	0.5751	0.00271	0.9774	0.1789
NMC		0.5800	4.2963	0.5495	0.00277	0.9783	0.1775
NCAC		0.5667	4.0095	0.5327	0.00359	0.9657	0.1869
Elovich equation							
Adsorbent	Equation	$q_{e(expt.)}$ (mg g ⁻¹)	β	$q_{e(cal.)}$ (mg g ⁻¹)	SSE	R ²	α
NCDC	$q_t = 1/\beta \ln(1 + \alpha \beta t)$	0.6067	11.5075	0.5777	0.00228	0.9676	0.0268
NMC		0.5800	12.1359	0.5522	0.00230	0.9706	0.0268
NCAC	$q_t = 1/\beta \ln(t) + 1/\beta \ln(\alpha \beta t)$	0.5667	11.9048	0.5354	0.00304	0.9555	0.0197

Adsorption isotherms:

The experimental data obtained in the present work was tested with the Freundlich [16], Langmuir [17], Tempkin [18] and Dubinin-Radushkevich (D-R) [19] isotherms and the corresponding data is given in Table 5. Out of all applied models, Langmuir isotherm was best fitted with high R² (>0.98) and low chi-square values. This confirms the monolayer coverage of dye onto carbon adsorbents and also the homogeneous distribution of active sites on the adsorbent, since the Langmuir equation assumes that the surface is homogeneous. The dimensionless factor (R_L) values are also between 0 and 1 which indicates favourable condition for Langmuir isotherm.

However, the degree of favorability tended near to zero (the completely ideal irreversible case) rather than unity (which represents a completely reversible case) for all the sorbents at equilibrium concentration.

The above facts suggest that RMB dye is adsorbed in the form of monolayer coverage on the surface of each the adsorbent. Similar type of fitting of dye on different adsorbents has been reported [2]. The R^2 values of Tempkin isotherm are lesser than D-R isotherms. The D-R isotherms are having higher R^2 values (>0.97) than Freundlich values but lower than the Langmuir value in each case. Therefore, D-R isotherms represent a better fit of experimental data than the Freundlich but not in the case of Langmuir. The high R^2 values of Dubinin–Radushkevich isotherms in each case, indicates the applicability of some degree of heterogeneous surface factor.

The adsorption energy, E , was found to be 13.61, 14.43 and 13.87 kJ mol^{-1} for NCDC, NCMC and NCAC respectively. The value of E , for each adsorbent, is within the values of ion-exchange; therefore it is possible to say that adsorption mechanism of dye on carbon adsorbents can be explained with an ion exchange process [20].

Table 5. Results of applied adsorption isotherms

Freundlich isotherm										
Adsorbent	Equation	Graph	R^2	$\log k_F$	$1/n$	k_F ($\text{mg}^{1-1/n} \text{l}^{1/n} \text{g}^{-1}$)	n (g l^{-1})	$q_{e(\text{expt.})}$ (mg g^{-1})	$q_{e(\text{cal.})}$ (mg g^{-1})	χ^2
NCDC	$q_e = k_F C_e^{1/n}$ $\log q_e = 1/n \log C_e + \log k_F$	$\log q_e$ vs $\log C_e$	0.9734	-0.4011	0.4724	0.3971	2.1169	0.6067	0.524200	0.011210
NCMC	0.9568		-0.4866	0.4152	0.3261	2.4085	0.5800	0.484900	0.015593	
NCAC	0.9437		-0.5515	0.4328	0.2809	2.3105	0.5667	0.451900	0.023244	
Langmuir isotherm										
Adsorbent	Equation	Graph	R^2	a_L/k_L	$1/k_L$	a_L (l mg^{-1})	R_L	$q_{e(\text{expt.})}$ (mg g^{-1})	$q_{e(\text{cal.})}$ (mg g^{-1})	χ^2
NCDC	$q_e = \frac{k_L C_e}{1 + a_L C_e}$ $C_e/q_e = a_L/k_L$	C_e/q_e vs C_e	0.9845	0.7367	1.3355	0.5516	0.0831	0.6067	0.676300	0.00799
NCMC	$C_e + 1/k_L$		0.9935	0.9630	1.5109	0.6374	0.0727	0.5800	0.647600	0.00788
NCAC			0.9935	1.0230	1.8796	0.5443	0.0841	0.5667	0.606200	0.00276
Tempkin isotherm										
Adsorbent	Equation	Graph	R^2	B	$B \ln(A)$	B	A (l g^{-1})	$q_{e(\text{expt.})}$ (mg g^{-1})	$q_{e(\text{cal.})}$ (mg g^{-1})	χ^2
NCDC	$q_e = \frac{B \ln(C_e) + B \ln(A)}{RT/b}$ where $RT/b = B$	q_e vs $\ln C_e$	0.9073	0.1798	0.6230	0.1798	31.98	0.6067	0.728710948	0.024551879
NCMC			0.9438	0.1361	0.5102	0.1361	42.47	0.5800	0.640256508	0.006260081
NCAC			0.9661	0.1362	0.4482	0.1362	26.86	0.5667	0.597815915	0.001712251

Dubinin-Radushkevich (D-R) isotherm										
Adsorbent	Equation	Graph	R ²	lnq _m	β	q _m	E	q _{e(expt.)}	q _{e(cal.)}	χ ²
	$\ln q_e = -\beta \varepsilon^2 + \ln q_m$	$\ln q_e$ vs ε^2			(mol ² J ⁻²)	(mg g ⁻¹)	(kJ mol ⁻¹)	(mg g ⁻¹)	(mg g ⁻¹)	
NCDC	where $\varepsilon =$		0.9920	-11.064	0.00270	8.94	13.61	0.6067	0.5726	0.00191
NCMC	RT(1+1/C ₀)		0.9842	-11.568	0.00240	5.40	14.43	0.5800	0.5832	0.00002
NCAC			0.9751	-11.527	0.00260	5.63	13.87	0.5667	0.5824	0.00044

Effect of pH:

Fig. 4 shows the effect of pH on RMB dye removal by adsorption. Adsorption of dye decreased with increasing pH. This pH dependence of dye sorption onto carbon adsorbents could be well explained in terms of their p*H*_{ZPC} (shown in Table 1). When pH < p*H*_{ZPC}, the net surface charge on solid surface of carbon adsorbents is positive due to adsorption of excess H⁺, which favours adsorption of anion due to coulombic attraction. At pH > p*H*_{ZPC}, the net surface charge is negative due to desorption of H⁺ and adsorption must compete with coulombic repulsion. The consistent dye removal in the pH range 3–8, could be due to the combined effect of both chemical and electrostatic interactions between adsorbent surfaces and SO₃⁻ in dye ion.

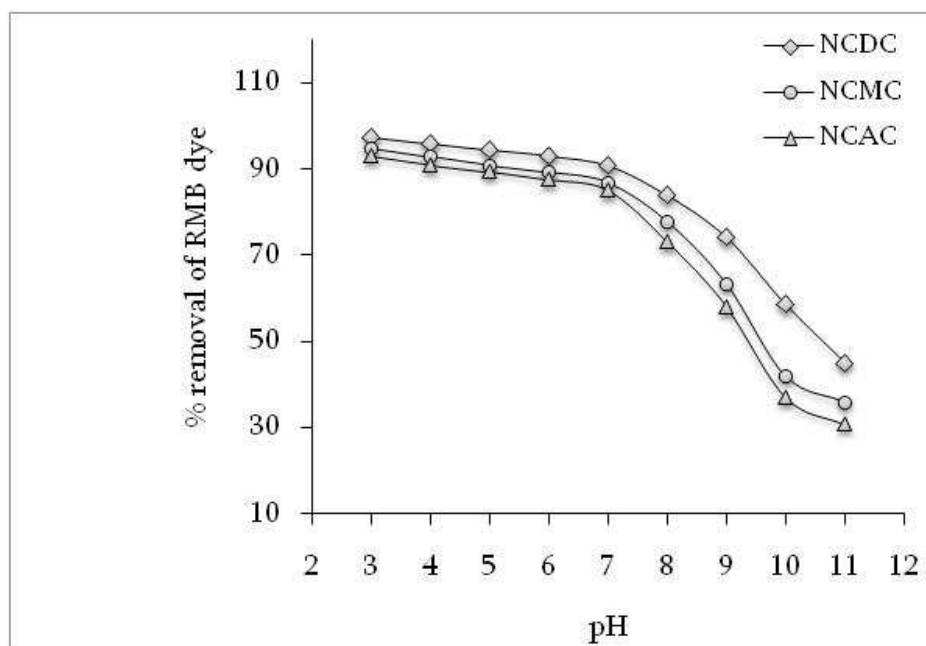


Fig. 4. Effect of pH in adsorption of RMB dye onto NCDC, NCMC and NCAC

The observed reduction in dye adsorption above pH 8 may suggest that the strong negative surface charge developed may cause repulsion for the available adsorption sites. Another factor is that in alkaline medium, lower adsorption capacity may be due to the competition of OH⁻ ions

with dye anions [21]. The decrease in dye adsorption is particularly sharp above pH 9, as the surface charge becomes more negative. Hence, dye ions would have to overcome electrostatic forces as there would be a higher density of negative charge very close to the surface, hence greater electrostatic repulsion. The results are in harmony with the previous literature [2].

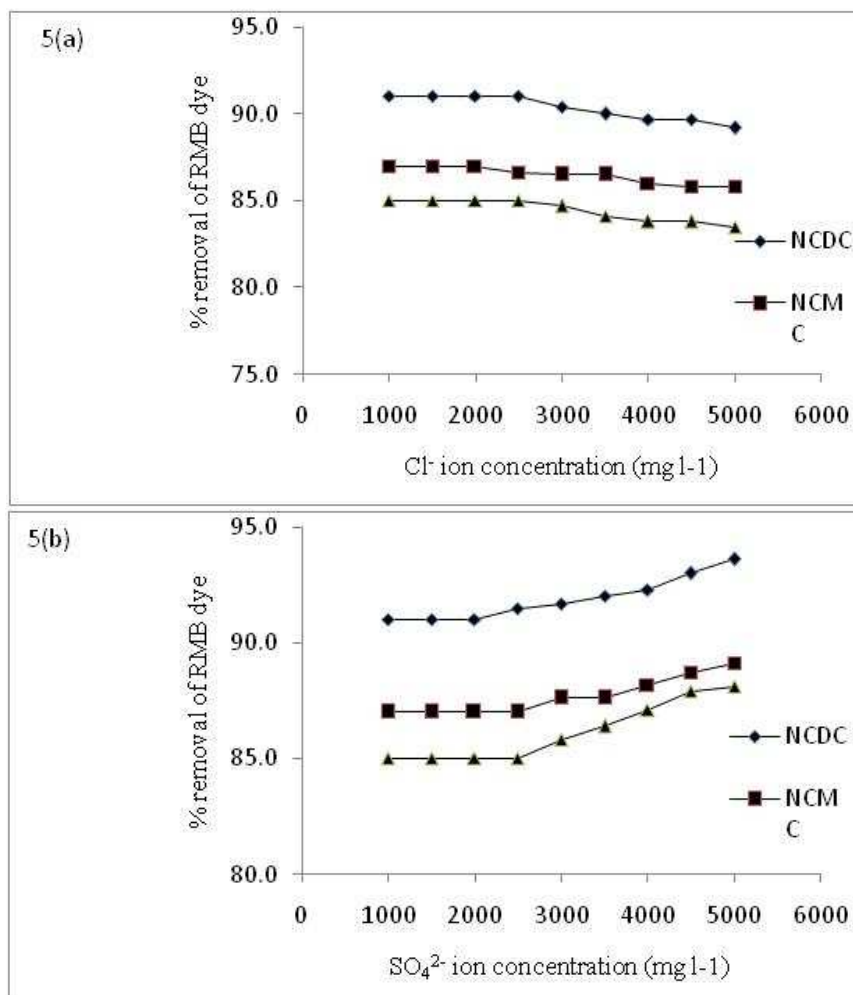


Fig.5. Effect of ionic strength (a) Chloride ion and (b) Sulphate ion on adsorption process

Effect of ionic strength:

In general, reactive dyes are applied to fabric in high salt concentrations in order to lower the dye solubility [22]. In textile effluents commonly high concentrations of chloride and sulphate ions will present. Sodium salts of these ions in the concentration range 1000 to 5000 mg l⁻¹ were introduced into dye solution and their influence was studied separately. The corresponding plot is shown in Fig. 5.

In presence of chloride ion the adsorption capacity has not significantly influenced of each adsorbent NCDC, NCM and NCAC. But for sulphate ion, little increase in adsorption capacity was observed after 2000 mg l⁻¹ and 2500 mg l⁻¹ for NCDC and for both NCM, NCAC

respectively. Similar trend was observed for reactive dye adsorption onto activated carbons in literature [23].

Possible working mechanism:

In FT-IR analysis (Table 2) for NCDC, NCMC and NCAC, bands in the range of 3300-3400 cm^{-1} this can be assigned to associated N-H stretching and from the O-H stretching vibrations due to the existence of surface hydroxyl groups were observed in all carbon samples [24]. Bands around 1580 cm^{-1} may be due to N-H in plane bending of free amines. In NCDC-RMB, NCMC-RMB and NCAC-RMB peak around 2900 cm^{-1} can be assigned to the OH stretching of $-\text{SO}_3\text{H}$ group present in RMB dye molecule and peak around 750 cm^{-1} may indicate the presence of C-Cl bond in dye molecule. Peaks corresponds to azo ($-\text{N}=\text{N}-$) group are observed around 1383 cm^{-1} . SEM images also show surface morphological changes before and after dye adsorption. In EDAX analysis (Table 3), when compared to NCDC, NCMC and NCAC, little increase in oxygen content and the presence of sulphur and chlorine was observed in RMB dye loaded carbon adsorbents.

Positively charged amine groups present on surface of carbon adsorbents could bind to anionic RMB reactive dye by electrostatic attraction. In citrus fruits, nitrogenous compounds are mainly present in the form of free amino acids and it is noted that several types of amines are present in all types of citrus fruits [25]. Thus, amine sites may play a vital role as binding sites for RMB dye. A similar phenomenon was observed in the adsorption of anionic reactive dye, C.I. Reactive Red 4, onto coke waste [24]. In zeolite and clay materials also, amine groups electrostatically attract anionic groups of dye molecules [26,27].

CONCLUSION

The prepared low cost activated carbons namely NCDC, NCMC and NCAC showed good adsorption capacity towards a reactive dye, Red M5B. Good fitting of Langmuir isotherm indicates the possibility of monolayer adsorption. From the kinetic studies it is observed that the adsorption of dye initially governed by the intraparticle transport controlled by surface diffusion and later part controlled by pore diffusion. Adsorption kinetics follows pseudo second order which points to chemisorption process. Acidic condition is more favorable than alkaline condition and presence of electrolytes also may not significantly interrupt removal of the dye by these carbon adsorbents. Amino groups present on the surface of carbon adsorbents may electrostatically attract the anionic reactive Red M5B dye.

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