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EQUILIBRIUM AND KINETIC STUDIES OF METHYLENE BLUE AND RHODAMINEB ONTO PREPARED ACTIVATED KAZA'S CARBONS

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ABSTRACT: Three Activated Kaza's Carbons viz. NPTC, NLLC andNCC, are prepared from some Bio- Materials – Phaseolus trilobus, Leucena leucocephala and Casurina. These carbonsare used to adsorb dyes Methylene blue and Rhodamine B from aqueous solution. Adsorption equilibrium data and kinetic processes were studied. The Langmuir isotherm provides the best correlation for the experimental data, where as Temkin and Dubinin – Radushkevich (D-R) isotherms also fit to the experimental data. In the kinetic studies the best fit Model was assessed by the squared some of errors (SSE) values. Adsorption of dyes, Methylene Blue (MB) and Rhodamine B (RB) ,on to adsorbents could be described by pseudo-second order equation. The adsorption process has good co-ordinance with pore diffusion and Elovich equations.

Key words: Methylene Blue, Rhodamine B, Kinetic Studies,Activated Kaza's Carbons

INTRODUCTION

Adsorption of dye molecules onto the surface of non-conventional sorbents is a complicated process, in which various mechanisms may be effective. The analysis of adsorption data is important to develop an equation which accurately represents the results and which could be used for design purposes. Equilibrium isotherm equations are used to describe experimental adsorption data.. The importance of obtaining the 'best-fit' isotherm becomes more and more significant, because as more applications are developed, more accurate and detailed isotherm descriptions are required for the adsorption system designs. One of the most important factors in designing an adsorption system is predicting the rate at which adsorption takes place, referred to the 'kinetics of sorption'. In the present study, prepared activated Kaza's carbons are used in the removal of commercial dyes-methylene blue (MB)and rhodamine B (RB) in batch mode adsorption process. Characteristics of chemical equilibrium, kinetics and mechanism were examined.

MATERIALS AND METHODS

Preparation of activated carbons:

The raw materials, *Phaseolus trilobus*, *Leucena leucocephala* and *Casuarina* were collected, crushed into small pieces, washed with water and dried under sunlight for two days. The dried materials were carbonized in uniform nitrogen flow in a horizontal tube furnace electrically heated at 500ºC for 4 h, cooled to room temperature and ground to 45 mesh.

These powdered carbons were subjected to liquid phase oxidation with 1N HNO_3. After that the carbons were washed with double-distilled water to remove the excess acid and dried at 150°C for 12h. These activated carbons are named as NPTC, NLLC and NCC respectively. These are also collectively named as Kaza's carbons after the name of Kaza Somasekhara Rao.

Stock solutions of selected reactive dyes prepared separately. 1g of methylene blue 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 MB. This solution is said to be stock solution of Methylene Blue (MB). The stock solution of Rhodamine B (RB) is also prepared in the same procedure.

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 ± 2^0C). 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[1,2]. The samples were filtered using Whatman no. 42 filter paper, the first part of the filtrate was discharged 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. The optimum conditions taken in the equilibrium and kinetic studies are – the dose of the adsorbent is 2g , pH is 7.0 ,dyes concentration is 20mg l^{-1} ,contact time for MB is 60min. and RB is 50min, particle size is 45µ .

RESULTS AND DISCUSSION

Adsorption isotherms:
The most commonly applied isotherms, in solid/liquid system, are the theoretical equilibrium isotherm: the Freundlich, Langmuir, Temkin and Dubinin- Radushkevich. In this work, attempts have been made to analyze adsorption by these four models. The linear regression was used to determine the most fitted model among all the four above written isotherms.The experimental data obtained in the present work was tested with the Freundlich[3], Langmuir[4], Tempkin[5], Dubnin – Radushkevich[6] isotherms on the sorption of dyes onto NLLC,NPTC and NCC .

From the Freundlich plots between $log q_e$ and $log C_e$ for the adsorption of MB & RB dyes for all three sorbents , the values of k_F and 1/n were obtained from the slope and the intercept of the linear Freundlich plots and are listed in Tables 1 and 2 for MB and RB dyes respectively. The equilibrium data were analyzed according to the linear form of the Freundlich isotherm . In case of MB dye adsorption, from Table 1, the Freundlich correlation coefficients are 0.9443, 0.9267 and 0.9110 and in case of RB dye adsorption, from Table 2, these are 0.9338, 0.9213 and 0.9086 for NLLC, NPTC and NCC respectively. In relevant comparison with other adsorption isotherms applied in this study, χ^2 values of Freundlich isotherm are higher in each case. The lesser R^2 (<0.99) indicate that Freundlich model may not be applicable to present study in adsorption of both dyes.
The Langmuir plots of C_e/q_e as a function of C_e for the adsorption of MB and RB dyes respectively for all the three sorbents NLLC, NPTC and NCC are drawn.

The values of monolayer capacity (q_m) and Langmuir constant (a_L) have been evaluated from intercept and slope corresponding plots and are given in Tables 1 and 2 for MB and RB dyes respectively. In all cases, values of q_e calculated from Langmuir isotherm were all close to experimental values as evident from low chi-square values.In case of MB dye, the R^2 values are 0.9950, 0.9970 and 0.9979; and in case of RB dye, the values are 0.9964, 0.9974 and 0.9970 for NLLC, NPTC and NCC respectively. The plots were found linear (in both cases) with good correlation coefficients implies that Langmuir isotherm fits the experimental data very well. The influence of isotherm shape on whether adsorption is favorable or unfavorable has been considered. For a Langmuir type adsorption process, the isotherm shape can be classified by a dimensionless constant separation factor (R_L). It was observed that the value of R_L (for both MB and RB dyes) is in the range 0–1 at equilibrium concentration calculated from corresponding graphs confirms the favorable uptake of the dyes in adsorption process. 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 for both dyes.
The resulted best fit of Langmuir isotherm, in all cases for all three sorbents, suggest that dyes adsorption is limited with monolayer coverage and the surface may be relatively homogenous in terms of active sites. Similar results were found for adsorption reactive red dye from aqueous phase onto activated carbon prepared from agricultural waste[7].

The Temkin plots of $\ln(C_e)$ vs q_e for the adsorption of MB and RB dyes are drawn respectively, for all the three sorbents NLLC, NPTC and NCC. From Table**s** 1 and 2, good fitting of Temkin isotherm is observed with high R^2 and low chi-square values for both dyes. Tempkin isotherm model contains a factor that explicitly takes into account adsorbing species–adsorbate interactions. This model assumes the following: (i) the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbant–adsorbate interactions, and (ii) adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy [5,8].

The Dubinin–Radushkevich (D-R) constants are calculated for all three sorbents and the results are listed in Tables 1 and 2. In case of MB dye, the determined correlation coefficients are 0.9756, 0.9619 and 0.9485; and for RB dye, the values are 0.9653, 0.9549 and 0.9442 for NLLC, NPTC and NCC respectively. In all cases, the D-R isotherms possess competing R^2 and low χ^2 values with Langmuir isotherm, indicating the applicability of some degree of heterogeneous surface factor. In case of MB dye, the adsorption energy, E, was found to be 12.31, 11.95 and 11.62 kJ mol^{-1}; and in case of RB dye, the values are 11.62, 11.47 and 11.32 kJ mol^{-1} for NLLC, NPTC and NCC respectively. The value of E, for each case and for all adsorbents, is within the values of ion exchange; therefore it is possible to say that adsorption mechanism of dyes on carbon adsorbents can be explained with an ion exchange process [9].

Adsorption kinetics:

Five simplified kinetic models namely pseudo-first-order [10],pseudo-second-order [11],Weber and Morris intra-particle diffusion model [12],Bangham's pore diffusion model [13] and Elovich equations[14] have been studied to identify the rate and kinetics of sorption of dye onto NLLC, NPTC and NCC. The relevantEquations and results are dicussed
The pseudo-first-order rate constant (k_1) and $q_{e(cal.)}$ values were determined for each adsorbent from the slope and the intercept of corresponding plots and are listed in Table 3 and4 for MB and RB dyes respectively.The values of $q_{e(cal.)}$ and k_2 were determined for each adsorbent from the slope and intercept of the corresponding plots obtained and are compiled in Table 3 and4 for MB and RB dyes respectively.

Table 1. Comparison of Freundlich, Langmuir, Temkin and Dubinin Radushkevich isotherm parameters, and calculated $q_{e(cal)}$ and experimental $q_{e(expt)}$ values for adsorption of MB dye.

Adsorbent	Equation	Graph	R^2	$\log k_F$	1/n	k_F ($mg^{1-1/n} l^{1/n} g^{-1}$)	N ($g l^{-1}$)	$q_{e(expt.)}$ ($mg\ g^{-1}$)	$q_{e(cal.)}$ ($mg\ g^{-1}$)	χ2
	Freundlich isotherm: $q_e = k_F C_e^{1/n}$ $\log q_e = 1/n \log C_e + \log k_F$	$\log q_e$ vs $\log C_e$								
NLLC	y = 0.5173x -0.3379		**0.9443**	-0.3379	0.5173	**0.4593**	**1.9331**	0.8900	0.6906	0.0447
NPTC	Y = 0.5308x -0.4537		**0.9267**	-0.4537	0.5308	**0.3518**	**1.8839**	0.8500	0.6303	0.0568
NCC	y = 0.5498x-0.5530		**0.9110**	-0.5530	0.5498	**0.2799**	**1.8188**	0.8100	0.5831	0.0636
Adsorbent	**Equation**	**Graph**	R^2	a_L/k_L	$1/k_L$	a_L ($l\ mg^{-1}$)	R_L	$q_{e(expt.)}$ ($mg\ g^{-1}$)	$q_{e(cal.)}$ ($mg\ g^{-1}$)	χ2
	Langmuir isotherm: $q_e = k_L C_e/(1+a_L C_e)$ $C_e/q_e = a_L/k_L\ C_e + 1/k_L$	C_e/q_e vs Ce								
NLLC	y = 0.5511x + 1.1329		**0.9950**	0.5511	1.1329	**0.4865**	**0.0932**	0.8900	0.9380	0.00259
NPTC	y = 0.6424x + 1.6355		**0.9970**	0.6424	1.6355	**0.3928**	**0.1129**	0.8500	0.8420	0.00008
NCC	y = 0.6919x + 2.2034		**0.9979**	0.6919	2.2034	**0.3140**	**0.1374**	0.8100	0.7863	0.00069

Adsorbent	Equation	Graph	R^2	B	Bln(A)	B	A ($l\ g^{-1}$)	$q_{e(expt.)}$ ($mg\ g^{-1}$)	$q_{e(cal.)}$ ($mg\ g^{-1}$)	χ2
	Temkin equation: $q_e = RT/b\ln(Ac_e)$ $q_e = B\ln(C_e) + B\ln(A)$ *where* $RT/b = B$	q_e vs $\ln C_e$								
NLLC	y = 0.2786x + 0.7599		0.9458	0.2786	0.7599	0.2786	15.30	0.8900	0.9796	0.0090204
NPTC	y = 0.2607x + 0.5951		0.9671	0.2607	0.5951	0.2607	9.80	0.8500	0.8814	0.0011600
NCC	y = 0.2472x + 0.4770		0.9724	0.2472	0.4770	0.2472	6.89	0.8100	0.8071	0.0000104
Adsorbent	Equation	Graph	R^2	$\ln q_m$	β ($mol^2 J^{-2}$)	q_m ($mg\ g^{-1}$)	E ($kJ\ mol^{-1}$)	$q_{e(expt.)}$ ($mg\ g^{-1}$)	$q_{e(cal.)}$ ($mg\ g^{-1}$)	χ2
	D-R equation: $q_e = q_m e^{-\beta\varepsilon^2}$ $\ln q_e = -\beta\varepsilon^2 + \ln q_m$ where $\varepsilon = RT(1+1/C_e)$	$\ln q_e$ vs ε^2								
NLLC	y = -0.0033x-9.9454		0.9756	-9.9454	0.00330	13.67	12.31	0.8900	0.7514	0.02158
NPTC	y = -0.0035x-10.0136		0.9619	-10.0136	0.00350	12.76	11.95	0.8500	0.7469	0.01251
NCC	y = -0.0037x-10.0347		0.9485	-10.0347	0.00370	12.5	11.62	0.8100	0.7111	0.01208

In case of MB dye, the correlation co-efficient (R^2) values for pseudo-second-order adsorption model have high values, 0.9960, 0.9975 and 0.9931; and for RB dye, the values are 0.9960, 0.9982 and 0.9913 for NLLC, NPTC and NCC respectively. Comparatively for all three sorbents and for adsorption of MB and RB dyes, the R^2 value is higher than that of pseudo-first-order model. The lower SSE values for pseudo-second-order model also indicate that the adsorption kinetics of dyes onto NLLC, NPTC and NCC can be better described by pseudo-second-order model in all cases. Similar phenomenon has been observed in the literature for the adsorption of dyes on various adsorbents [7].The pseudo-second-order model is based onto 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 being the rate controlling step [15,16].

Table 2. Comparison of Freundlich, Langmuir, Temkin and Dubinin Radushkevich isotherm parameters, and calculated $q_{e(cal.)}$ and experimental $q_{e(expt.)}$ values for adsorption of RB dye.

Adsorbent	**Equation**	**Graph**	**R^2**	**$\log k_F$**	**1/n**	**k_F ($mg^{1-1/n} l^{1/n} g^{-1}$)**	**n ($g\,l^{-1}$)**	**$q_{e(expt.)}$ ($mg\,g^{-1}$)**	**$q_{e(cal.)}$ ($mg\,g^{-1}$)**	**χ2**
	Freundlich isotherm: $q_e = k_f C_e^{1/n}$ $\log q_e = 1/n \log C_e + \log k_F$	$\log q_e$ vs $\log C_e$								
NLLC	y= 0.5769x - 0.4601		**0.9338**	-0.4601	0.5769	**0.3467**	**1.7334**	0.8500	0.6534	0.0455
NPTC	Y = 0.5801x - 0.5988		**0.9213**	-0.5988	0.5801	**0.2519**	**1.7238**	0.7900	0.5791	0.0563
NCC	y= 0.5862x-0.6972		**0.9086**	-0.6972	0.5862	**0.2008**	**1.7059**	0.7400	0.5279	0.0608
Adsorbent	**Equation**	**Graph**	**R^2**	a_L/k_L	$1/k_L$	**a_L ($l\,mg^{-1}$)**	**R_L**	**$q_{e(expt.)}$ ($mg\,g^{-1}$)**	**$q_{e(cal.)}$ ($mg\,g^{-1}$)**	**χ2**
	Langmuir isotherm: $q_e = k_L C_e/(1+a_L C_e)$ $C_e/q_e = a_L/k_L\, C_e + 1/k_L$	C_e/q_e vs Ce								
NLLC	y= 0.5677x + 1.7365		**0.9964**	0.5677	1.7365	**0.3269**	**0.1327**	0.8500	0.8722	0.00058
NPTC	y= 0.6818x + 2.5886		**0.9974**	0.6818	2.5886	**0.2634**	**0.1595**	0.7900	0.7703	0.00049
NCC	y= 0.7877x + 3.3417		**0.9970**	0.7877	3.3417	**0.2357**	**0.1750**	0.7400	0.6992	0.00225
Adsorbent	**Equation**	**Graph**	**R^2**	B	Bln(A)	**B**	**A ($l\,g^{-1}$)**	**$q_{e(expt.)}$ ($mg\,g^{-1}$)**	**$q_{e(cal.)}$ ($mg\,g^{-1}$)**	**χ2**
	Temkin equation: $q_e = RT/b \ln(Ac_e)$ $q_e = B\ln(C_e) + B\ln(A)$ where $RT/b = B$	q_e vs $\ln C_e$								
NLLC	y= 0.2949x + 0.6008		**0.9500**	0.2949	0.6008	**0.2949**	**7.67**	0.8500	0.9248	0.006582
NPTC	y= 0.2565x + 0.4339		**0.9638**	0.2565	0.4339	**0.2565**	**5.43**	0.7900	0.8021	0.000185
NCC	y= 0.2300x + 0.3403		**0.9634**	0.2300	0.3403	**0.2300**	**4.39**	0.7400	0.7194	0.000573
Adsorbent	**Equation**	**Graph**	**R^2**	$\ln q_m$	**β ($mol^2 J^{-2}$)**	**q_m ($mg\,g^{-1}$)**	**E ($kJ\,mol^{-1}$)**	**$q_{e(expt.)}$ ($mg\,g^{-1}$)**	**$q_{e(cal.)}$ ($mg\,g^{-1}$)**	**χ2**
	D-R equation: $q_e = q_m e^{-\beta\varepsilon^2}$ $\ln q_e = -\beta\varepsilon^2 + \ln q_m$ where $\varepsilon = RT(1+1/C_e)$	$\ln q_e$ vs ε^2								
NLLC	y= -0.0037x-10.0435		0.9653	-10.043	0.00370	19.31	11.62	0.8500	0.6936	0.02878
NPTC	y= -0.0038x-10.2367		0.9549	-10.2367	0.00380	15.92	11.47	0.7900	0.6322	0.03152
NCC	y= -0.0039x-10.3544		0.9442	-10.3544	0.00390	14.15	11.32	0.7400	0.6135	0.02162

From the Weber and Morris plots of q_t versus $t^{1/2}$, the results are tabulated in Tables 3 and 4 for MB and RB dyes sorption respectively, for all three sorbents. 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 few minutes. 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 intraparticle 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 for adsorption of reactive orange onto sugarcane bagasse pith [1]. Though intraparticle diffusion renders straight lines with correlation co-efficients (>0.9) for all the three sorbents in MB and RB dye cases, 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 [17]and indicates some degree of boundary layer control which implies that intraparticle diffusion is not only the rate controlling step [18].The data were further used to learn about the slow step occurring in the present adsorption system using pore diffusion model.

From the Bangham's plots of log(t) versus $\log[\log(C_i/(C_i\text{-}q_t m)]$, the results obtained are tabulated in Tables 3 and 4 for MB and RB dyes respectively, for all three sorbents. The Bangham's plots were found to be linear for each adsorbent with good correlation co-efficient (>0.9) and low SSE values indicating that kinetics may be confirmed to Bangham's equation and therefore the adsorption of dye onto NLLC, NPTC and NCC may be pore diffusion controlled for both dyes.

From the Elovich plots of q_t versus ln(t) ,the results obtained are compiled in Tables 3 and 4 respectively, for all three sorbents. In case of MB dye, the R^2 values are 0.9553, 0.9672 and 0.9400; and for RB dye, the values are 0.9781, 0.9846 and 0.9412 for NLLC, NPTC and NCC respectively. High R^2 values suggest that diffusion accounted for Elovich kinetics pattern; confirmation to this equation alone might be taken as evidence that the rate-determining step is diffusion in nature [19] and that this equation should apply at conditions where rate of desorption can be neglected [20].

For both MB and RB dye sorption (separately) onto NLLC, NPTC and NCC, the fitting of the kinetic data demonstrate that the dynamics of sorption could be better described by pseudo-second-order model indicating a chemisorptive rate-limiting. Though the plots of intraparticle diffusion render straight lines with good correlation coefficients, they fail to pass through origin in each case. This suggests that the process is 'complex' with more than one mechanism limiting the rate of sorption. The good fitting of the kinetic data, to Bangham's and Elovich equations indicate that pore diffusion plays a vital role in controlling the rate of reaction.

In order to study the thermodynamic parameters, the adsorption experiments were also carried out at different temperatures 298–318 K. From Vant Hoff plots of ln(t) versus q_t ,for MB and RB dyes and for all three sorbents. Values of ΔH^0, ΔS^0 and ΔG^0 are listed in Tables 5(a) and 5(b) for MB and RB dyes respectively.

The endothermic nature of adsorption is indicated by the positive value of ΔH^0 which implies that the amount of dye adsorbed on adsorbent increases with temperature. The positive value of ΔS^0 which is a measure of randomness at the solid/liquid interface during dye sorption indicates that the sorption process is possibly irreversible and stable [21].The values of ΔG^0 are negative, which is indicative of spontaneous nature of sorption process. Similar endothermic and spontaneous nature was observed for adsorption of reactive blue 221 onto kaolinite [22].

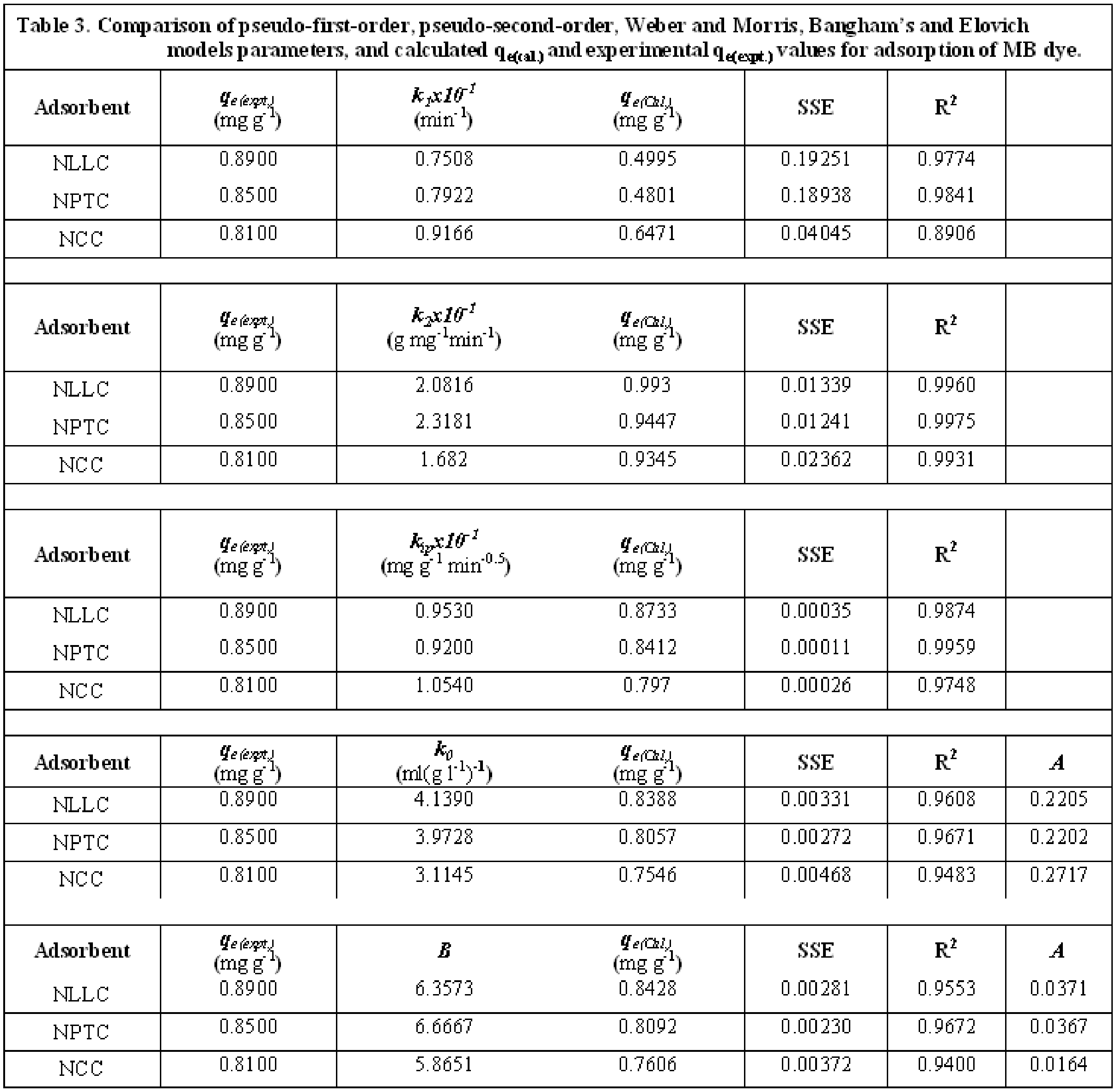

Table 3. Comparison of pseudo-first-order, pseudo-second-order, Weber and Morris, Bangham's and Elovich models parameters, and calculated $q_{e(cal.)}$ and experimental $q_{e(expt.)}$ values for adsorption of MB dye.

Adsorbent	$q_{e(expt.)}$ (mg g^{-1})	k_1x10^{-1} (min^{-1})	$q_{e(Cal.)}$ (mg g^{-1})	SSE	R^2	
NLLC	0.8900	0.7508	0.4995	0.19251	0.9774	
NPTC	0.8500	0.7922	0.4801	0.18938	0.9841	
NCC	0.8100	0.9166	0.6471	0.04045	0.8906	

Adsorbent	$q_{e(expt.)}$ (mg g^{-1})	k_2x10^{-1} (g mg^{-1}min^{-1})	$q_{e(Cal.)}$ (mg g^{-1})	SSE	R^2	
NLLC	0.8900	2.0816	0.993	0.01339	0.9960	
NPTC	0.8500	2.3181	0.9447	0.01241	0.9975	
NCC	0.8100	1.682	0.9345	0.02362	0.9931	

Adsorbent	$q_{e(expt.)}$ (mg g^{-1})	$k_{ip}x10^{-1}$ (mg g^{-1} min$^{-0.5}$)	$q_{e(Cal.)}$ (mg g^{-1})	SSE	R^2	
NLLC	0.8900	0.9530	0.8733	0.00035	0.9874	
NPTC	0.8500	0.9200	0.8412	0.00011	0.9959	
NCC	0.8100	1.0540	0.797	0.00026	0.9748	

Adsorbent	$q_{e(expt.)}$ (mg g^{-1})	k_0 (ml(g l^{-1})$^{-1}$)	$q_{e(Cal.)}$ (mg g^{-1})	SSE	R^2	A
NLLC	0.8900	4.1390	0.8388	0.00331	0.9608	0.2205
NPTC	0.8500	3.9728	0.8057	0.00272	0.9671	0.2202
NCC	0.8100	3.1145	0.7546	0.00468	0.9483	0.2717

Adsorbent	$q_{e(expt.)}$ (mg g^{-1})	B	$q_{e(Cal.)}$ (mg g^{-1})	SSE	R^2	A
NLLC	0.8900	6.3573	0.8428	0.00281	0.9553	0.0371
NPTC	0.8500	6.6667	0.8092	0.00230	0.9672	0.0367
NCC	0.8100	5.8651	0.7606	0.00372	0.9400	0.0164

The adsorption capacity largely depends on the chemical interaction of carbon surface groups and the sorbate ions. So the adsorption increased with temperature may be due to the increase in chemical interaction between sorbate ions and surface functionalities of the active carbons or due to the increase of the intraparticle diffusion rate of sorbate ions into the pores at higher temperature as diffusion is an endothermic process [23]

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 for adsorption of RB dye.

Adsorbent	$q_{e(expt.)}$ (mg g^{-1})	$k_1 x 10^{-1}$ (min^{-1})	$q_{e(Cal.)}$ (mg g^{-1})	SSE	R^2	
NLLC	0.8500	0.6541	0.4618	0.20858	0.9942	
NPTC	0.7900	0.7945	0.4832	0.15082	0.9847	
NCC	0.7400	0.6333	0.4584	0.14481	0.9614	
Adsorbent	$q_{e(expt.)}$ (mg g^{-1})	$k_2 x 10^{-1}$ (g mg^{-1}min^{-1})	$q_{e(Cal.)}$ (mg g^{-1})	SSE	R^2	
NLLC	0.8500	1.9005	0.9533	0.01477	0.9960	
NPTC	0.7900	2.1653	0.8858	0.01471	0.9982	
NCC	0.7400	1.6248	0.8562	0.02466	0.9913	
Adsorbent	$q_{e(expt.)}$ (mg g^{-1})	$k_{ip} x 10^{-1}$ (mg g^{-1} min$^{-0.5}$)	$q_{e(Cal.)}$ (mg g^{-1})	SSE	R^2	
NLLC	0.8500	0.8290	0.8358	0.00028	0.9930	
NPTC	0.7900	0.8300	0.7966	0.00007	0.9924	
NCC	0.7400	0.8050	0.7208	0.00067	0.9648	
Adsorbent	$q_{e(expt.)}$ (mg g^{-1})	k_0 (ml(g l^{-1})$^{-1}$)	$q_{e(Cal.)}$ (mg g^{-1})	SSE	R^2	*A*
NLLC	0.8500	3.7144	0.8157	0.00163	0.9829	0.2332
NPTC	0.7900	3.4229	0.7669	0.00086	0.9801	0.2381
NCC	0.7400	2.8549	0.6996	0.00298	0.9532	0.2623
Adsorbent	$q_{e(expt.)}$ (mg g^{-1})	*B*	$q_{e(Cal.)}$ (mg g^{-1})	SSE	R^2	*A*
NLLC	0.8500	6.4103	0.816	0.00160	0.9781	0.0238
NPTC	0.7900	6.7613	0.7664	0.00089	0.9846	0.0215
NCC	0.7400	6.6401	0.7019	0.00265	0.9412	0.0130

Table 5(a). Effect of temperature on MB dye removal. pH 7.0, adsorbent dose and initial dye concentration are 2g and 20 mg l^{-1} at contact time of 30 min for all the three sorbents;and Thermodynamic parameters of this sorption process.

S.No	Temp. (K)	Equilibrium conc. of MB dye (C_e mg l^{-1})			% removal			? H^0 (kJ mol^{-1})	? S^0 (J mol^{-1}K^{-1})	? G^0 (kJ mol^{-1})		
		NLLC	NPTC	NCC	NLLC	NPTC	NCC			NLLC	NPTC	NCC
1	298	2.20	3.00	3.80	89.00	85.00	81.00	47.42	175.61	-5.18	-4.30	-3.59
2	308	1.70	2.00	3.20	91.50	90.00	84.00	25.38	99.94	-5.89	-5.44	-4.11
3	318	0.71	1.70	2.90	96.45	91.50	85.50	12.81	55.16	-8.18	-5.89	-4.40

Table 5(b). Effect of temperature on RB dye removal. pH 7.0, adsorbent dose and initial dye concentration are 2g and 20 mg l^{-1} at contact time of 35 min for all the three sorbents; and Thermodynamic parameters of this sorption process.

S.No.	Temp. (K)	Equilibrium conc. of RB dye (C_e mg l^{-1})			% removal			? H^0 (kJ mol^{-1})	? S^0 (J mol^{-1}K^{-1})	? G^0 (kJ mol^{-1})		
		NLLC	NPTC	NCC	NLLC	NPTC	NCC			NLLC	NPTC	NCC
1	298	3.00	4.20	5.20	85.00	79.00	74.00	49.09	178.35	-4.30	-3.28	-2.59
2	308	2.22	3.00	3.90	88.90	85.00	80.50	24.53	93.54	-5.15	-4.30	-3.51
3	318	0.96	2.50	3.60	95.20	87.50	82.00	18.64	71.60	-7.40	-4.82	-3.76

CONCLUSIONS

Equilibrium isotherm equations used to describe experimental adsorption data are Freundlich, Langmuir, Temkin and Dubinin- Radushkevich. Basing on correlation co-efficient and chi-square analysis, it is observed that Langmuir isotherm provides the best correlation for experimental data, whereas the Temkin and Dubinin–Radushkevich isotherms also fit to the experimental data. This suggests that adsorption of dyes is limited with monolayer coverage and the surface is relatively homogenous in terms of active sites.

In kinetic studies pseudo-first-order, pseudo-second-order, Weber and Morris intraparticle diffusion model, Bangham's pore diffusion model and Elovich equations have been applied to identify the rate and kinetics of sorption of dye onto NLLC, NPTC and NCC. The best-fit among the kinetic models was assessed by the squared sum of errors (SSE) values. Adsorption of dyes onto adsorbents could be described by pseudo-second-order equation. Though the plots of intraparticle diffusion renders straight lines with good correlation co-efficients, they fail to pass through origin in each case. This suggests that the process is 'complex' with more than one mechanism limiting the rate of sorption. The adsorption process has also good co-ordinance with pore diffusion and Elovich equations which indicates that pore diffusion plays a vital role in controlling the rate of the reaction.

In the study of effect of temperature on adsorption process, it is observed that percent removal increased with increase of temperature. Adsorption of reactive dyes, MB and RB on to NLLC, NPTC and NCC is endothermic, irreversible and spontaneous which are indicated by the positive values of ΔH^0 and ΔS^0 and by the negative value of ΔG^0 respectively.

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