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Sorption of cationic dyes onto activated carbon derived from agro-residues

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Abstract. Batch experiments are carried out for the sorption of cationic dyes such as crystal violet, Malachite green and Rhodamine B dyes onto corncob acid treatment. The operating variables studied are contact time and pH. Equilibrium adsorption isotherms and kinetic were investigated. The experimental data were analyzed by the Langmuir and Freundlich models and the isotherm data fitted well to the Langmuir isotherm. The kinetic data obtained were analyzed using a pseudo-first order and pseudo-second-order equation and intra particle diffusion equation. The experimental data fitted very well the pseudo-second-order kinetic model.

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Key words: cationic dyes, adsorption isotherm, equilibrium kinetic, acid activation, solid wastes

1 Introduction

Discharge of dyes onto natural water bodies represents a serious problem, since highly colored effluents can disturb aquatic life present in this compartment by decreasing sunlight penetration and/or even leading to direct poisoning of living organisms [1–3]. This problem is enhanced because some dyes cannot be degraded by chemical or photochemical processes and presents intrinsic non-biodegradable [4,5]. So that, in these cases, alternative procedures must be employed for the elimination of such dyes before disposal. Undoubtedly, in this field, the study and development of adsorption techniques is a very interesting approach, especially when solid adsorbents are cheap and commercially available. Because of their intense use in several industrial areas, cationic dyes can be considered an important class of compounds to be studied from this point of view. This statement is reinforced by the verification that current literature reports several works regarding the application of solid materials for the adsorption of cationic (or basic) dyes present in aqueous solutions [6–16]. Different materials have been applied for the adsorption of different cationic dyes.

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Many treatment processes have been applied for the removal of dyes from wastewater such as: photocatalytic degradation [3,4], sonochemical degradation [5], micellar enhanced ultrafiltration [6], cation exchange membranes [7], electrochemical degradation [8], adsorption/precipitation processes [9], integrated chemical-biological degradation [10], integrated iron(III) photoassisted-biological treatment [11], solar photo-Fenton and biological processes [12], Fenton-biological treatment scheme [13] and adsorption on activated carbon [14,15]. As synthetic dyes in wastewater cannot be efficiently decolorized by traditional methods, the adsorption of synthetic dyes on inexpensive and efficient solid supports was considered as a simple and economical method for their removal from water and wastewater [16].

The high cost of removal of dyes from aqueous solutions using adsorption on commercial activated carbons though very effective has motivated the search for alternatives adsorbents. Such alternatives include: waste metal hydroxide sludge [17], oil palm trunk fibre [18], broad bean peels [19], biomass fly ash [20], rice straw-derived char [21], durian (Durio zibethinus Murray) peel [22], chitosan bead [23], rice husk [24] and palm kernel fibre [25]. Recently, an extensive list of alternative and cheaper adsorbents for dyes removal has been compiled by Allen and Koumanova [26].

The main objective of this study was to investigate the potentiality of using corncobs acid treatment for the adsorption of cationic dyes such as crystal violet CV, Malachite green MG and Rhodamine B, RB dyes from aqueous solutions. The effects of initial dye concentrations, contact time and pH on the selective cationic dyes were studied. Adsorption isotherms and kinetics parameters were also calculated and discussed.

2 Material and methods

2.1 Adsorbate

Basic dye used in this study was Crystal Violet, CV; Malachite Green, MG, Rhodamine B, RB, purchased from Sigma-Aldrich. The maximum wavelength of these dyes are “586, 620 and 459 n” for CV, MG and RB, respectively. The dye stock solution was prepared by dissolving accurately weight dye in distilled water to the concentration of 1 g/L.

The experimental solutions were obtained by diluting the dye stock solution in accurate proportions to needed initial concentrations.

2.2 Preparation of adsorbent

Corncobs, agro-waste was collected from nearby market as solid wastes. The collected materials were then washed with distilled water for several times to remove all the dirt particles. The washed materials were cut into small pieces (1-3 cm) and dried in a hot air oven at 70 °C for 24 h. activated carbon were prepared by impregnating of the precursor with H_3PO_4 (50 vol.%) followed by thermal treatment at 700 °C for two hours. The cooled activated mass was subjected to through washing with distilled water, so as get rid of extra acid and to attain pH values ≤ 5.5 in the washing solution, and finally dried at 110 °C.

2.3 Equilibrium studies

A fixed amount of adsorbent (0.30 g) was added into a set of each 250 mL Erlenmeyer flasks containing 200 mL of different initial concentrations (25, 50, 100, 150, 200, 250 and 300 mg/L) of dye solution without adjusting pH. The flaks were agitated in an isothermal water bath shaker at 120 rpm and 30°C for 5 h and 30 min until equilibrium was reached. At time $t=0$ and equilibrium, the dye concentrations were measured by a double beam UV/Vis spectrophotometer (Shimadzu, Model UV 1601, Japan). Each experiment was duplicated under identical conditions. The amount of adsorption at equilibrium, q_e (mg/g), was calculated by

$$q_e = \frac{(C_0 - C_e)V}{W}, \tag{1}$$

where C_0 and C_e (mg/L) are the liquid-phase concentrations of dye at initial and equilibrium time t, respectively. V (L) is the volume of the solution, and W (g) is the mass of adsorbent used.

The removal percentage of the selective dyes can be calculated as follows

$$\text{Removal percentage} = \left(\frac{C_0 - C_t}{C_0}\right) \times 100, \tag{2}$$

where C_t (mg/L) is the liquid-phase concentrations of dye at time t.

2.4 pH effect

The effect of pH on the amount of dye removal was studied over the pH range from 2 to 10. The pH was adjusted by adding a few drops of 1.0 N NaOH or 1.0 N HCl. In this study, 200 mL of a fixed initial concentration of dye solution at different pH were agitated with 0.30 g of adsorbent using water-bath shaker at 30 °C. Agitation was provided at a constant speed of 120 rpm for 5 h 30min. The concentrations at equilibrium were determined.

2.5 Batch kinetic studies

The procedure of kinetic tests was identical to those of equilibrium tests. The aqueous samples were taken at preset time intervals and the concentrations of dye solutions were similarly measured. The amount of adsorption at time t, q_t (mg/g), was calculated by

$$q_t = \frac{(C_0 - C_t)V}{W}. \tag{3}$$

3 Results and discussion

3.1 Effect of contact time on cationic dyes adsorption

The adsorption of MG, CV and RB dyes onto corncobs-carbon that derived by chemical activation, at initial concentration of 100 mg/L, was studied at different contact time (0-1400 min, Fig. 1). It was observed that dye uptake was rapid for the first 200 min, and there after proceeded at a slower rate and finally attains saturation. The curves are smooth, and continuous, leading to saturation, suggesting the possible monolayer coverage of the dyes on the carbon surface (Senthikumar *et al.*, 2005). The contact time of cationic dyes were needed to less than 3 hour and half to reach equilibrium. However, the experimental data were measured overnight to be sure that full equilibrium was attained.

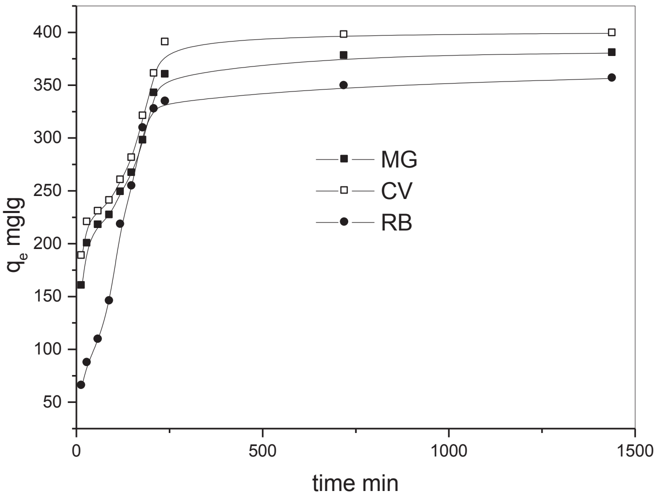

Figure 1: Effect of contact time on the adsorption of cationic dyes onto cobs-carbon.

3.2 Effect of solution pH on dyes adsorption

The effect of solution pH on the equilibrium uptake capacity of MG, CV and RB cationic dyes was studied at 100 mg/L initial dye concentration and temperature 25°C between pH value of 2 and 10. As shown in Fig. 2, the dye uptake was found to increase with an increase in pH. A consistent increase in adsorption capacity of the cationic dyes were noticed as the pH increased from 2 to 4, but further increase in pH from 4 to 10 seemed that was no affected on the sorption in any wise. At lower pH as 2, the surface charge may be positively, thus making (H+) ions compete effectively with cationic dyes causing a decrease in the amount of dye adsorbed. At higher pH the surface of on corncobs-carbon, may be negatively charged which enhance the positively charged on cationic dyes through electrostatic force at attraction

[32]. A similar trend was also observed for adsorption of MB onto beech sawdust [33] and malachite green onto treated sawdust [21]. Present result is in good agreements with the above previous findings. A similar trend was reported for the adsorption of MB onto wheat shells [31].

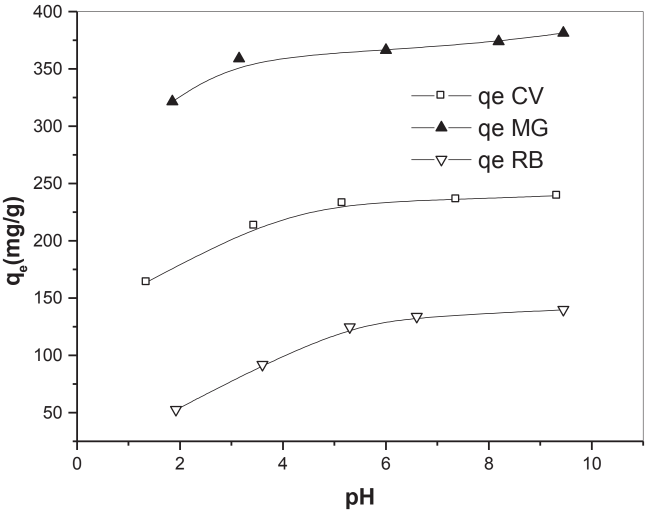

Figure 2: Effect of pH on the adsorption of cationic dyes from aqueous solutions by cobs-carbon.

3.3 Adsorption isotherms

In order to establish the most appropriate correlations for the equilibrium data in the design of adsorption system, two common isotherm models were tested: the Langmuir and Freundlich models. The applicability of the isotherm equations was compared by judging the correlation coefficients, R^2. The Langmuir adsorption [34] model is based on the assumption that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface. The linear form of the Langmuir equation can be described by

$$\frac{C_e}{q_e}=\left(\frac{1}{Q_0 b}\right)+\left(\frac{1}{Q_0}\right)C_e, \tag{4}$$

where C_e (mg/L) is the equilibrium concentration of the adsorbate, q_e (mg/g) is the amount of adsorption per unit mass, Q^0 and b are Langmuir constants related to adsorption capacity and rate of adsorption, respectively. Fig. 3 shows the adsorption isotherm of cationic dyes "MG, CV and RB" onto cabs-carbon. The linear plot of specific adsorption (C_e/q_e) against the equilibrium concentration C_e (Fig. 4) shows that the adsorption obeys the Langmuir model. The Langmuir constants Q^0 and b were determined from the slope and intercept of the plot and are presented in Table 1. The R^2 values (0.998) suggest that the Langmuir isotherm

Table 1: Langmuir and Freundlich isotherm constants and correlation coefficients for adsorption of "MG, CV and RB" dyes onto cobs-carbon.

Dyes	Langmuir constants			Frundlish constants		
	b (mg/L)$^{-1}$	q^0 (mg/g)	R^2	K_f (mg/g)	n	R^2
CV	0.48	320.5	0.995	89.13	2.60	0.668
MG	0.99	209.2	0.996	79.70	3.76	0.870
RB	0.88	95.1	0.999	41.35	4.10	0.813

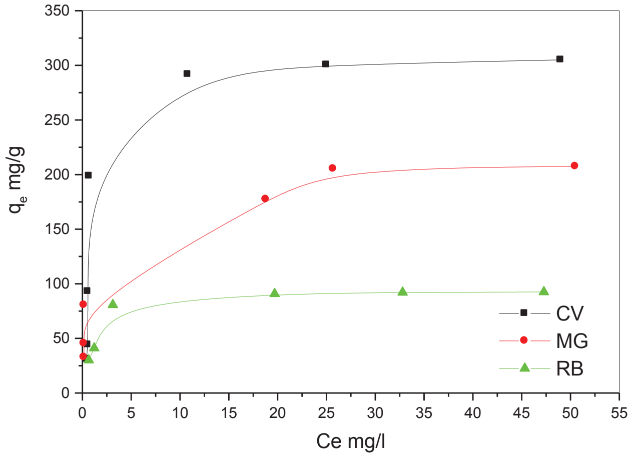

Figure 3: Adsorption isotherm of cationic dyes "MG, CV and RB" onto cabs-carbon.

provides a good fit to the isotherm data. A similar observation was reported for adsorption of MB on fly ash [35], pomelo (Citrus grandis) [24], silk worm [36], cedar sawdust and crushed brick [37].

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor RL [38] given by

$$R_l = \frac{1}{1+bC_0}, \tag{5}$$

where C_0 (mg/L) is the highest initial concentration of adsorbent, and b (L/mg) is Langmuir constant. The parameter R_L indicates the nature of shape of the isotherm accordingly

$R_L > 1$,	Unfavorable adsorption,
$0 < R_L < 1$,	Favorable adsorption,
$R_L = 0$,	Irreversible adsorption,
$R_l = 1$,	Linear adsorption.

The value of RL in the present investigation has been found to be 0.9737 at 30°C showing that the adsorption of MG, CV and RB dyes on Cob-carbon is favorable at the temperature studied.

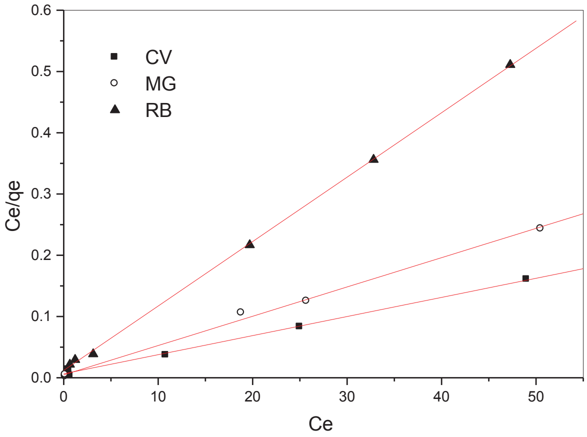

Figure 4: Langmuir isotherm for "MG, CV and RB" dyes onto cobs-carbon.

The Freundlich isotherm [39] is the earliest known relationship describing the sorption equation. The fairly satisfactory empirical isotherm can be used for non-ideal sorption that involves heterogeneous surface energy systems and is expressed by the following equation

$$q_e = K_F C_e^{1/n}, \tag{6}$$

where K_F (mg/g), is roughly an indicator of the adsorption capacity and 1/n is the adsorption intensity. In general, as the K_F value increases the adsorption capacity of adsorbent for a given adsorbate increases. The magnitude of the exponent, $1/n$ gives an indication of the favorability of adsorption. As the values of $n > 1$ represents favorable adsorption condition [40,41]. The linear form of Eq. (6)

$$\log q_e = \log K_f + \left(\frac{1}{n}\right) \log C_e. \tag{7}$$

Values of K_F and n are calculated from the intercept and slope of the plot (Fig. 5) and are listed in Table 1. The R^2 value is lower than Langmuir isotherm. The value of Freundlich exponent n is the range of $n > 1$, indicating a favorable adsorption [40,41].

The best equilibrium model was determined based on the linear square regression correlation coefficient R^2. From Table 1, it was observed that the equilibrium sorption data were very best represented by the Langmuir isotherm. The best fit isotherm expressions confirm the monolayer coverage process of MG, CV and RB dyes onto activated carbon prepared. A similar result was reported for adsorption of methylene blue on adsorbents materials produce from sewage sludge [42].

3.4 Adsorption kinetics

Pseudo-first-order and second-order models were applied to test experimental data and thus elucidated the kinetic adsorption process. Lagergren proposed a method for adsorption anal-

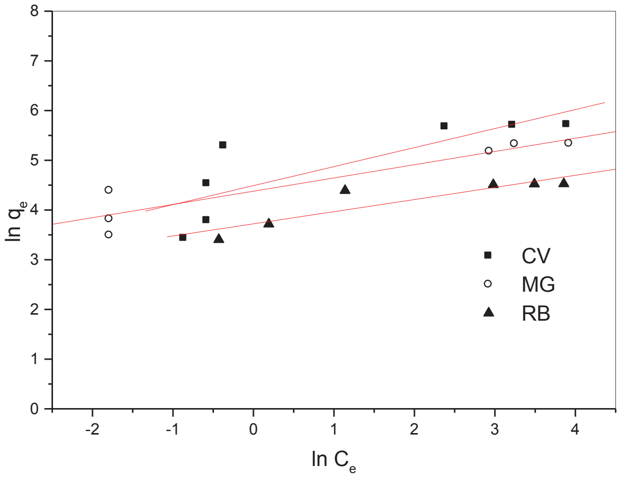

Figure 5: Freundlich isotherm for "MG, CV and RB" dyes on cobs-carbon.

ysis which is the pseudo-first-order kinetic equation of Lagergren [49] in the form

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t, \tag{8}$$

where k_1 (1/min), is the rate constant, q_e (mg/g) is the amount of solute adsorbed on the surface at equilibrium and q_t (mg/g) is the amount of solute adsorbed at time t (min). The value of k_1 for dye adsorption by Cob-carbon was determined from the plot of $\log(q_e - q_t)$ against t (Fig. 6). The parameters of pseudo-first-order model are summarized in Table 2. Although the correlation coefficients (R^2) are generally greater than 0.858 for all the initial concentrations of dyes under the limit of the experimental q_e for the pseudo-first-order kinetic model. As such, the adsorption of MG, CV and RB dyes on Cob-carbon cannot be the best described by the pseudo-first-order kinetic. In many cases the first-order equation of Lagergren does not fit well to the whole range of contact time and is generally applicable over the initial stage of the adsorption processes [50]. Therefore, the pseudo-second-order kinetic model [41,51] as shown in Eq. (9) was used to study the adsorption kinetic of the present system,

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right) t, \tag{9}$$

where k_2 (g/mg min) is the second-order rate constant. The q_e and k_2 can be calculated from the slope and intercept of the plots t/q_t versus t.

The constant k_2 is used to calculate the initial sorption rate h (mg/g min), as $t \rightarrow 0$ as follows

$$h = k_2 q_e^2. \tag{10}$$

The pseudo-second-order rate constants k_2, the calculated h values, and the corresponding linear regression correlation coefficients R^2 are given in Table 2. The R^2 values were found to be in the range 0.994-1.000. Moreover, the variations between the calculated q_e and experimental q_e were very minimal for this model. The high correlations coefficient and high agreement that exist between the calculated and experimental q_e values of the pseudo second-order kinetic model over the other model renders it is the best in adsorption of MG, CV and RB dyes on Cob-carbon. This confirms that the sorption data are well represented by the pseudo-second-order kinetics for the entire sorption period.

Table 2: Comparison between pseudo-first, second-order adsorption rate constant calculated and experimental q_e values.

Dyes	Pseudo-first-order kinetic model				Pseudo-second-order kinetic model			
	q_e(exp)	q_e(calc)	K_1	R^2	q_e(calc)	K_2	R^2	h
MG	380.4	222.4	0.0064	0.93	393.7	$5.55*10^{-5}$	0.998	8.6
CV	399.1	233.1	0.0074	0.88	413.2	$5.66*10^{-5}$	0.998	9.66
RB	356.1	22.8	0.0056	0.8	383.14	$3.1*10^{-5}$	0.991	4.56

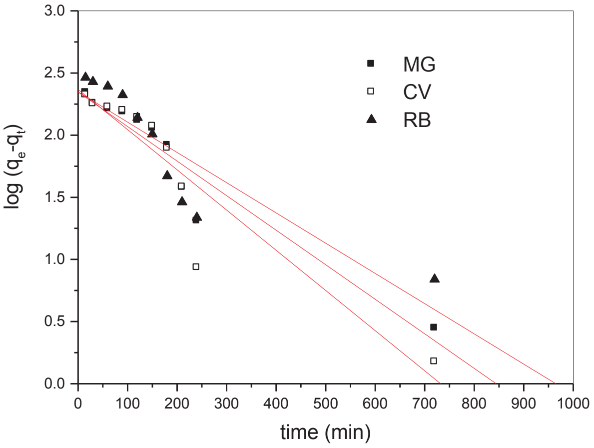

Figure 6: Pseudo-first-order kinetics for adsorption of "MG, CV and RB" dyes on cobs-carbon.

The kinetic results were further analyzed by the intraparticle diffusion model to elucidate the diffusion mechanism [54],

$$q_t = k_{\mathrm{id}} t^{1/2} + C, \tag{11}$$

where C is the intercept and k_{id} is the intraparticle diffusion rate constant (mg/g min 0.5), which can be evaluated from the slope of the linear plot of q_t versus $t^{1/2}$ (Fig. 7). If the regression of q_t versus $t^{1/2}$ is linear and passes through the origin, then intraparticle diffusion is the sole rate-limiting step [55]. For intraparticle diffusion plots, the first, sharper region is the instantaneous adsorption or external surface adsorption. The second region is the gradual adsorption stage where intraparticle diffusion is the rate limiting. In some cases, the third region exists, which is the. Final equilibrium stage where intraparticle diffusion starts to slow down due to the extremely low adsorbate concentrations left in the solutions [56]. As seen from Fig. 7, the plots were not linear over the whole time range, implying that more than one process affected the adsorption.

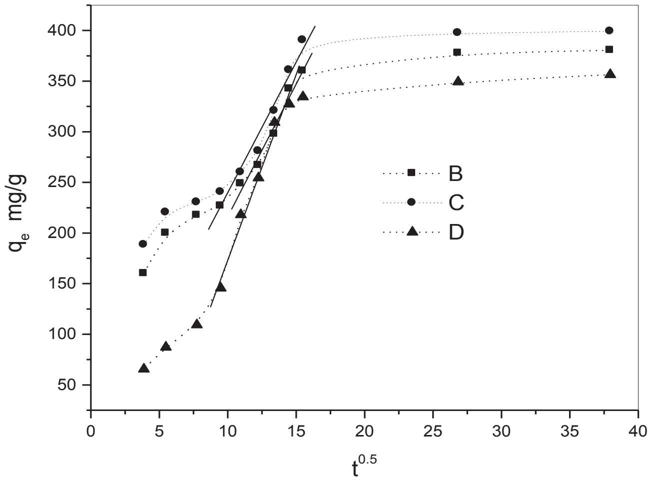

Figure 7: Intraparticle diffusion constants for different initial concentrations of"MG, CV and RB" dyes on cobs-carbon.

4 Conclusions

The results revealed that the potential of corncob, as agricultural waste material, to be a low-cost adsorbent for removing cationic dyes from aqueous media. Equilibrium data agreed well with Langmuir isotherm model with monolayer adsorption capacity of 320.5, 209.2 and 95.1 for MG, CV and RB dyes respectively. The values of the separation factor, RL, indicated that the dye/Cob-system was a favorable adsorption. The suitability of pseudo-first-order kinetic and pseudo-second-order kinetic models for the sorption of MG, CV and RB dyes on Cob-carbon were also discussed. The kinetic modeling study has shown that the experimental data were found to follow the pseudo-second-order model suggesting a chemisorption process.

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