ADSORPTION OF DISPERSE BLUE DYE ON IRAQI DATE PALM SEEDS ACTIVATED CARBON

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ABSTRACT

In this paper, adsorption isotherm and kinetics of disperse blue dye on activated carbon prepared from Iraqi date seeds (Zahdi date seeds ZDS) were determined from batch tests. The effect of different parameters, such as, different doses, pH and contact time were investigated. Equilibrium adsorption data for synthesized activated carbon (ZDSAC) were analyzed by Langmuir and Freundlich isotherm. The equilibrium data were best fitted with Langmuir isotherm model, showing maximum monolayer adsorption capacity of 8.13 mg/g. Kinetic analyzes were tested using pseudo-first order, pseudo-second order and the intraparticle diffusion model. Kinetic studies showed that the adsorption kinetics was more accurately represented by a pseudo-second order model. Among ZDSAC removes 66.47% of disperse blue at the dose of 0.3 g, whereas the commercial activated carbon removes 54.33% of disperses blue.

Key words: Adsorption, Date palm seeds, Activated carbon, Disperse blue, Kinetics, Isotherms.

INTRODUCTION

Activated carbon is the most popular and widely used adsorbent in wastewater treatment throughout the world. Activated carbon is cheap, easily available, high capacity of adsorption and surface reactive[1]. Adsorption is an important technology and effective method for purification process of water and wastewater in industrial application such as odor, oil, and colors of organic pollutants. Several researchers used the activated carbon as an adsorbent for water and air purification[2]. Adsorption onto activated carbon prepared from date palm seeds has been proven to be an effective process for disperse dye removal, but it is an expensive process. This has largely been associated with the cost of producing activated carbon, and the lack of suitable and inexpensive regeneration procedures for these

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adsorbents. The activation method to be proposed is important for the cost of producing activated carbons. In this respect, these have led many researchers to use low-cost plant and wood-based materials for activated carbon production. Numerous low-cost plants such as pistachio shells[3], palm kernel shell[4], coconut husk[5], bamboo waste[6], coir pith[7], rice husk[8] and oil palm shell activated carbon[9], have been used for the production of activated carbon for the removal of the textile dye effluents.

Disperse dyes are extensively used in different types of industries, such as textiles, paper and leather. Disperse dyes are non-ionic aromatic compounds, scarcely soluble in water, but soluble in organic solvent. Majority of them are azo and anthraquinone dyes. These dyes can be applied to synthetic fibers such as nylon, polyester, cellulose, acrylic and acetate[10,11]. During dye production and textile manufacturing processes, a large quantity of wastewater containing high concentration of organic compounds difficult removal of these dyes due to high solubility in water[12-18]. Many researchers are devoted in recent years to remove dyes from wastewaters, using different techniques such as adsorption technique. Adsorption removal is an effective and simple technique for dye treatment, but usually produces large amount of sludge, which may cause secondary pollution. The individual treatment technique is not perfect enough to remove the dyes from wastewaters in high efficiency without produced a secondary contaminants. As a result combining two or more treatment techniques such as using the adsorption with the photodegradation technique is more effective to get high removal of dyes from wastewater[19-23].

The main objective of this research was to evaluate the ability of using activated carbon prepared from Iraqi date palm seeds (*Phoenix dactylifera*); as one of the most important fruit crops grown in the Iraq, by phosphoric acid activation for the adsorption of disperse dye from aqueous solutions.

EXPERIMETNAL

Materials and methods

Adsorbate

Disperse blue 26 dye (DB26), 1, 5-Dihydroxy-4,8-bis (methylamino) anthracene-9,10-dione was used as an adsorbate and was not purified prior to use. Distilled water was used to prepare all the solutions and reagents. DB26 has a chemical formula of $C_{16}H_{14}N_2O_4$, with molecular weight of 298.29336 g/mol. The chemical structure of DB26 dye is illustrated in Fig. 1.
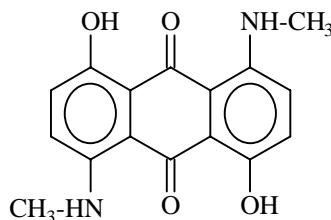
Fig. 1: Chemical structure of disperse blue

Preparation of activated carbon

Zahdi date seeds (ZDS) were used to prepare the activated carbon ZDSAC. The seeds were washed with hot distilled water to remove dust and other impurities, dried at 105°C. 40% phosphoric acid (purity 85% Merck, Germany) was added to it during the chemical activation process. The activation was completed by heating at temperature 700°C for 1 hour. After cooling, the activated carbon was repeatedly washed with hot distilled water until the pH of the washing solution reached 6-6.5. The product was dried at 105°C for 2 hours and kept in tightly closed plastic container.

Adsorption studies

The adsorption experiments in this work were done for the study the effect of experimental conditions on disperse blue adsorption and determining the conditions that achieve the maximum removal of disperse blue. The adsorption tests were conducted in magnetic mixer. The concentration of disperse blue was 20 ppm and the amount of adsorbent was included the ratio 0.1, 0.15, 0.2, 0.25, 0.3, and 0.35 g for activated carbon. In all experiments, the required amount of the adsorbent was suspended in 100 cm^3 of aqueous solution of disperse blue. 2 mL was taken from the reaction suspension, centrifuged at 6,000 rpm for 15 minutes in an 800 B centrifuge, and filtered to remove the particles. The second centrifuge was found necessary to remove fine particle of the activated carbon. After the second centrifuge, the absorbance of the disperse blue was measured at 570 nm, using 1650 PC UV-visible spectrophotometer Shimadzu. The efficiency for removal of disperse blue, (% Removal), was calculated as follows[24-26]:

$$\% \text{ Removal} = \frac{C_i - C_f}{C_i} \text{ x } 100 \qquad \ldots(1)$$

where C_i is the initial concentration and C_f is the final concentration. q is the amount of metal adsorbed per specic amount of adsorbent (mg/g).The sorption capacity at time t, q_t (mg/ g) was obtained as follows:

$$q_t = \frac{(C_i - C_t) \times V}{m} \qquad \qquad \ldots(2)$$

where C_i is the initial concentration of disperse blue, C_t represents disperse blue concentration at time t., V was the solution volume and m the mass activated carbon (g). The amount of adsorption at equilibrium, (q_e) was calculated by the following equation :

$$q_e = \frac{(C_i - C_e) \times V}{m} \qquad \qquad \ldots(3)$$

where C_e was the disperse blue concentration at equilibrium.

RESULTS AND DISCUSSION

Effect of contact time

Fig. 2 shows the effects of contact time on disperse blue dye removal. Removal percentage was increased with an increase in contact time. Adsorption was very rapid in the first 20 min for activated carbon, and then it was increased slowly with time until reaching equilibrium. It was found that the equilibrium time was more than 20 min for both activated carbons. To ensure full equilibration, a shaking time of 60 min was used for all concentrations of activated carbon in this study[27-29].
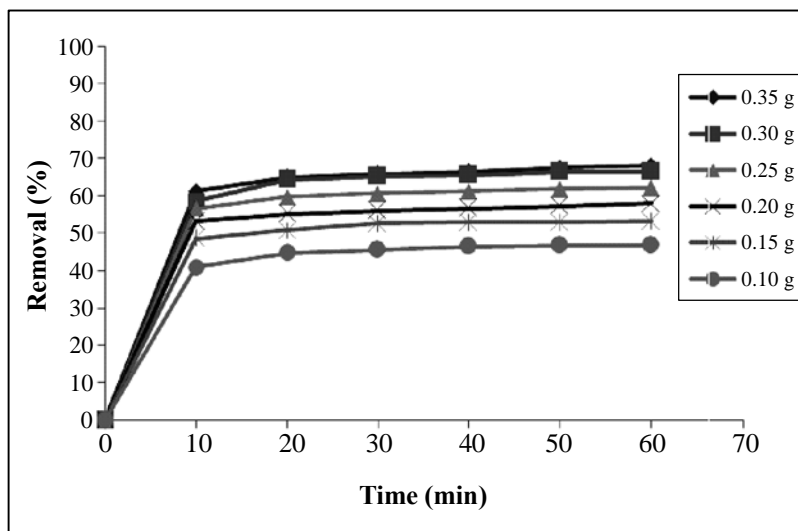

Fig. 2: Effect of contact time on disperses blue dye removal by ZDSAC

Comparison between the removal efficiency of ZDSAC and commercial activated carbon

Fig. 3 represents the comparison of effect of synthesized ZDSAC and commercial activated carbon on disperses blue. Fig. 3 indicates that the maximum disperse blue removal was found at 0.3 g of synthesized ZDSAC i.e. 66.47% whereas 54.33% for commercial AC.
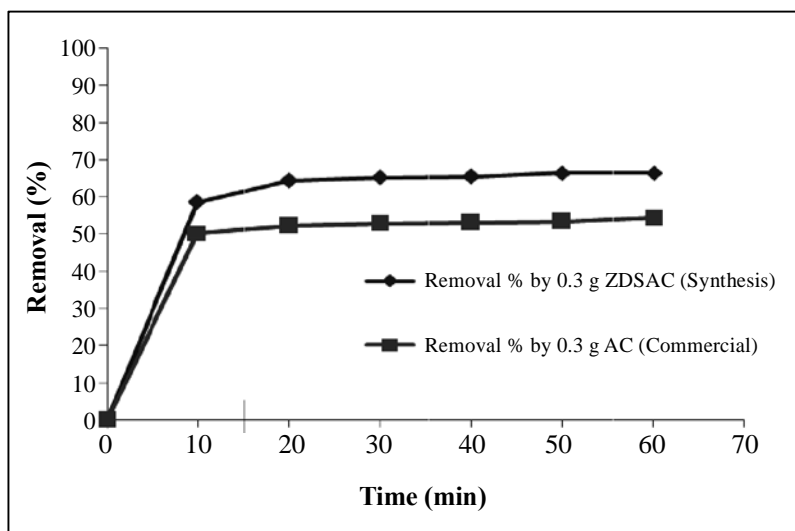

Fig. 3: Comparison between the removal efficiency of ZDSAC and commercial activated carbon

Effect of activated carbon dosage

The effect of activated carbon dose was studied by varying the dose between 0.1 g and 0.35 g in 100 mL aqueous solution of disperse blue dye. These tests were conducted at a temperature of 25°C, with pH 5.5 for disperse blue dye. The initial disperse blue concentration was 20 ppm. It was observed that the adsorption efficiency percentage of disperse blue dye onto the activated carbon increased rapidly with the increase of adsorbent concentration as shown in Fig. 4. This result was expected because the increase of adsorbent dose leads to greater surface area. When the adsorbent concentration was increased from 0.1 g to 0.35 g, the percentage of disperse blue adsorption increased from 44.79 to 65.02 at higher concentrations, however the equilibrium uptake of disperse blue dye did not increase significantly with increasing activated carbon. There was no any appreciable increase in the effective surface area resulting due to the conglomeration of exchanger particles, so 0.3 g/100 mL was considered as optimum dose[30].
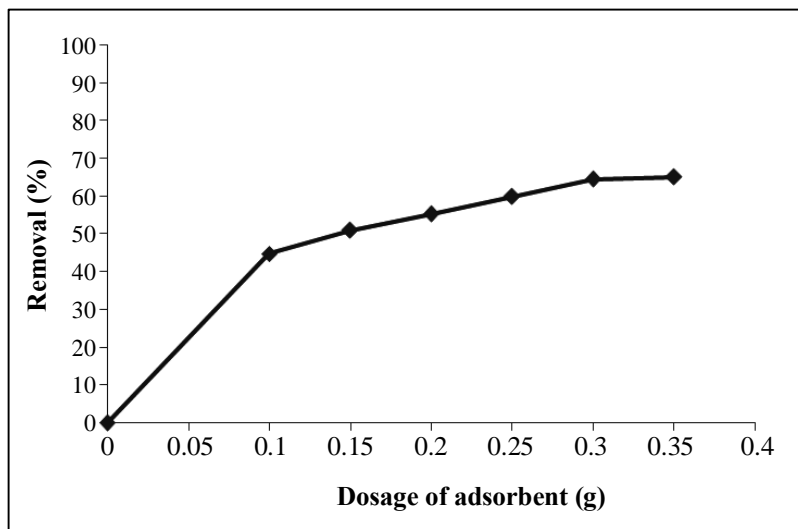
**Fig. 4: The effect of dosage of adsorbent on the removal of disperses
blue dye**

Effect of pH

The pH of solution is an important factor in the adsorption process. Fig. 5 shows the effect of pH on the removal of the disperse blue dye onto synthesized activated carbon. It was observed that the adsorption of disperse blue dye is unaffected by changing solution pH and remained nearly constant over the pH ranges from 3-11.
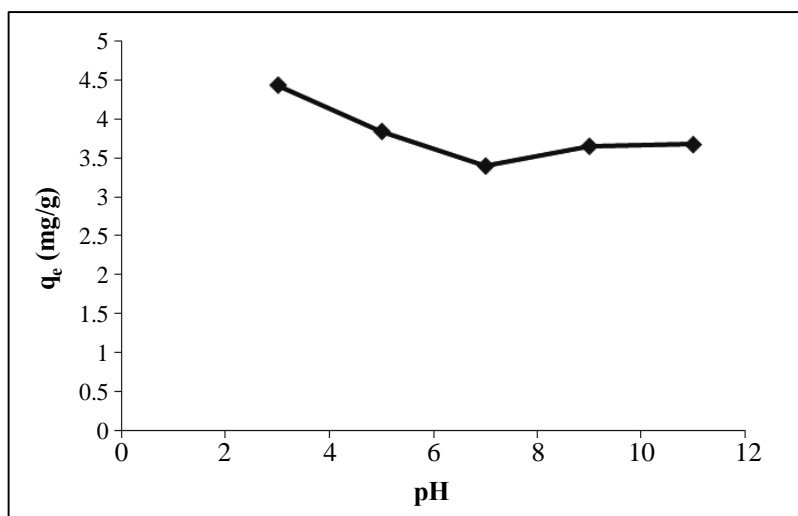

Fig. 5: Effects of pH for adsorption of disperse blue on ZDSAC

The percentage adsorption of disperse blue was not significantly changed when the initial pH was increased from 3 to 11. Thus pH 7 was selected as the optimum pH value for all further experiments due to the advantage of neutral pH value. As the solubility of disperse dyes in aqueous solution is low, they have a tendency to accumulate at the surface of adsorbents[31]. It was found that the adsorption of disperse blue onto activated carbon remained approximately constant in the pH range of 3-11. When the adsorbing species is not ionized, no such electrical repulsion exists, and thus the packing density on the surface can be higher[32].

Kinetics of disperse blue dye adsorption

The kinetics of disperse blue dye adsorption on synthesized activated carbon ZDSAC were determined under the conditions: initial disperse blue concentration 20 ppm, pH 5.5 and temperature 25°C. It was found that the equilibrium time for both activated carbon used in this study was more than 20 min. To ensure full equilibration, a shaking time of 60 min was used for all concentrations of activated carbon in this study. The experimental data were processed with respect to three different kinetic models namely pseudo-first order[33], pseudo-second order[34], and intra-particle diffusion[35]. The equations 4 and 5 represent the linear forms of the pseudo-first order and pseudo-second order models, respectively.

$$\ln (q_e - q_t) = \ln q_e - k_1 t \qquad \qquad \ldots (4)$$

$$\frac{t}{q_t} = \frac{1}{k_2 \, q_e^2} + \frac{t}{q_e} \qquad \qquad \ldots (5)$$

where, q_e (mg/g) and q_t (mg/g) are amounts of disperse blue adsorbed at equilibrium and at time t, respectively. k_1 (min^{-1}) and k_2 (g/min.mg) are the pseudo-first order and pseudo-second order adsorption rate constant, respectively. Fig. 6 and Fig. 7 show pseudo-first order and pseudo-second order plots for the experimental data. Various rate constants derived from the slopes and intercepts along with correlation coefficients are given in Table 1 and Table 2. The pseudo-second order plot in Fig. 7 has better correlation coefficient (R^2). The calculated value of adsorption capacity from the plot in Fig. 7 was found to be closer to the experimentally determined value than that calculated from Fig. 6. This suggests that the pseudo-second order model represents the kinetic data more accurately.
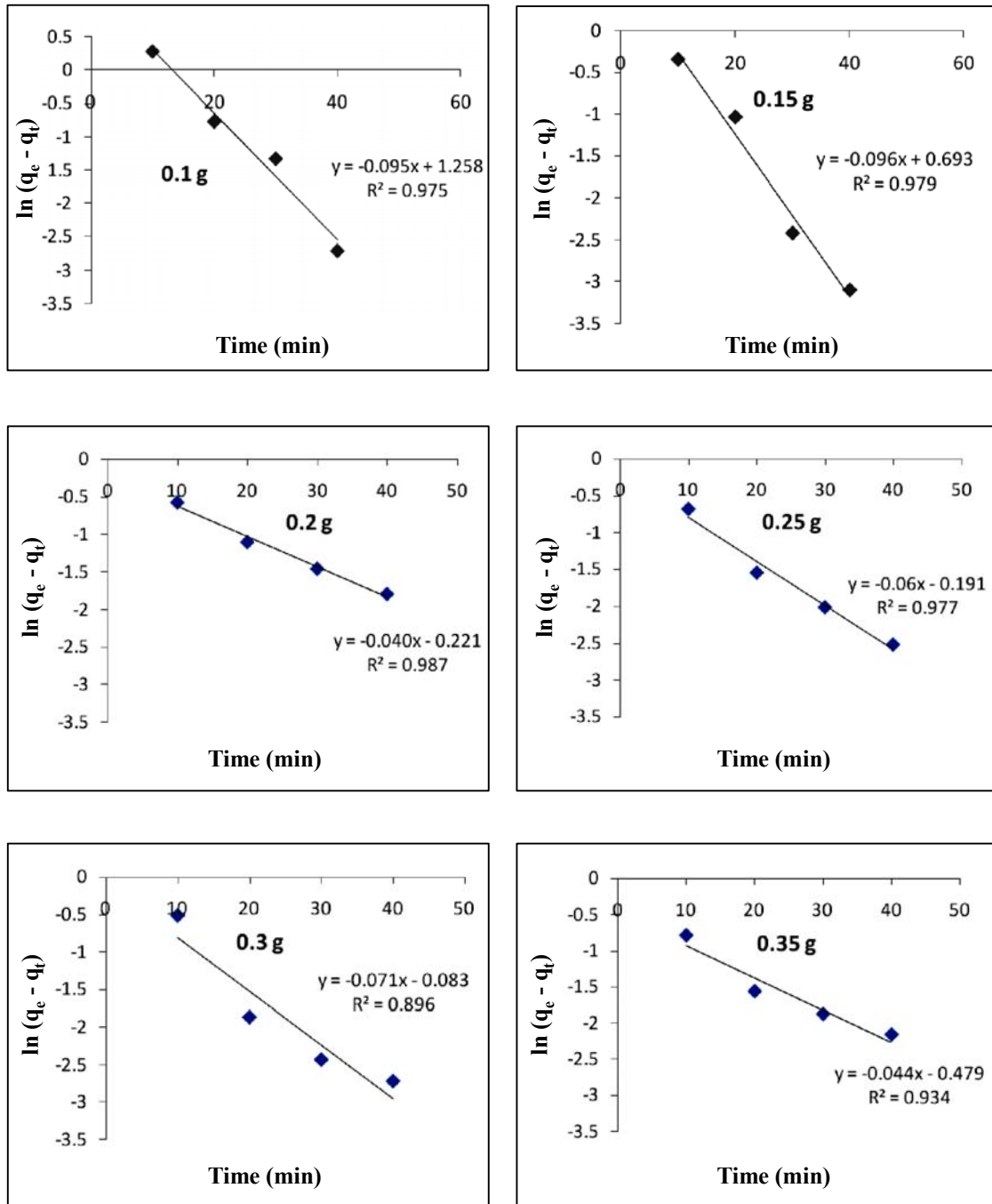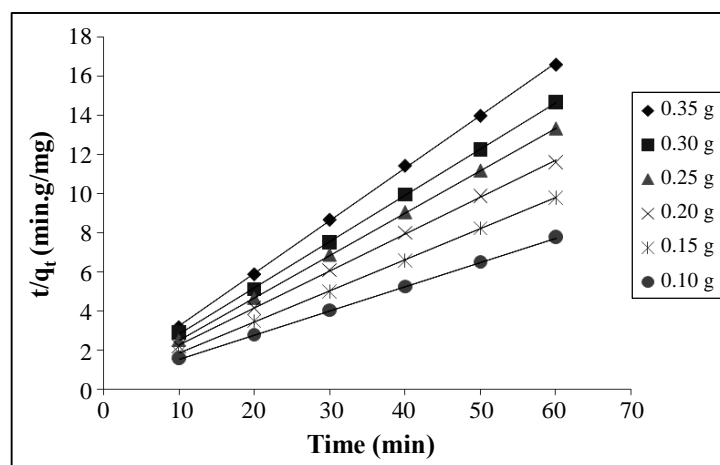
Fig. 6: Pseudo-first-order-kinetic model for the adsorption of disperse blue dye onto ZDSAC

Table 1: The pseudo-first-order-kinetic models, for the adsorption of disperse blue dye onto ZDSAC at different adsorbent dose

Adsorbent dose (g/100 mL)	Pseudo-first-order kinetic			
	q_e, exp (mg/g)	q_e, calc. (mg/g)	k_1 (min^{-1})	R^2
0.10	7.733	3.518	0.095	0.975
0.15	6.133	1.999	0.096	0.979
0.20	5.166	1.247	0.040	0.987
0.25	4.506	1.210	0.060	0.977
0.3	4.088	1.086	0.071	0.896
0.35	3.619	1.614	0.044	0.934

Fig. 7: Pseudo-second order kinetic model for the adsorption of disperse blue dye onto ZDSAC

Table 2: The pseudo-second order kinetic model for the adsorption of disperse blue dye onto ZDSAC at different adsorbent dose

Adsorbent dose (g/100 mL)	Pseudo-second order kinetic			
	$q_{e,exp}$ (mg/g)	$q_{e,calc.}$(mg/g)	K_2 (g/mg.min)	R^2
0.10	7.733	8.130	0.414	0.999
0.15	6.133	6.329	0.632	0.999

| Adsorbent dose | Pseudo-second order kinetic | | | |
(g/100 mL)	$q_{e,exp}$ (mg/g)	$q_{e,calc.}$ (mg/g)	K_2 (g/mg.min)	R^2
0.20	5.166	5.291	0.543	0.999
0.25	4.506	4.629	0.624	1
0.30	4.088	4.219	0.558	0.999
0.35	3.619	3.717	0.510	0.999

The intraparticle diffusion model, is expressed as[34] –

$$q_t = k_{id}t^{1/2} + C \qquad \qquad …(6)$$

where, k_{id} is the intraparticle diffusion rate constant (mg/g.min$^{1/2}$) and C is a constant related to boundary layer thickness (mg/g). If intraparticle diffusion is involved in the adsorption process, the q_t versus $t^{1/2}$ plot should be linear and should go through the origin, if intraparticle diffusion is the sole rate-controlling step. Fig. 8 shows that the plot of q_t vs. $t^{1/2}$ is not linear over the entire time period. This implies that more than one process is controlling the adsorption. The dotted line is indicative of the intraparticle diffusion on the activated carbon, for which the rate constant and intercept are given in Table 3.
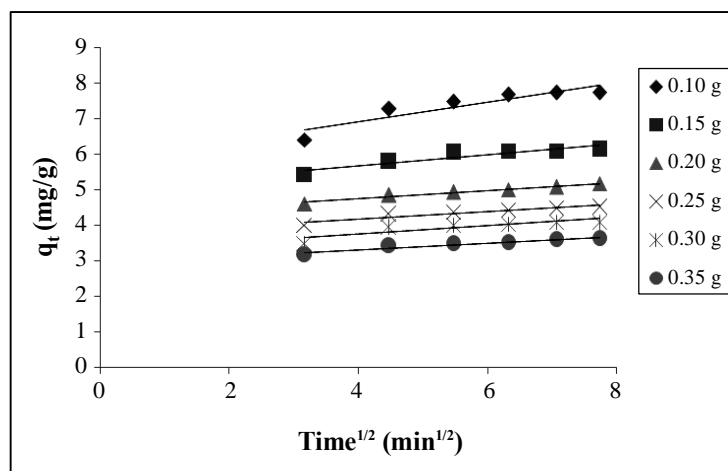

Fig. 8: Intraparticle diffusion model, for the adsorption of disperse blue dye onto ZDSAC

Table 3: The intraparticle diffusion model, for the adsorption of disperses blue dye onto ZDSAC at different adsorbent dose

Adsorbent dose (g/100 mL)	Intraparticle diffusion			
	$q_{e,exp}$ (mg/g)	C (mg/g)	K_{id} (mg/g.min$^{1/2}$)	R^2
0.10	7.733	5.800	0.276	0.840
0.15	6.133	5.063	0.151	0.854
0.20	5.166	4.274	0.115	0.976
0.25	4.506	3.754	0.103	0.896
0.3	4.088	3.265	0.117	0.773
0.35	3.619	2.928	0.092	0.896

Adsorption isotherms

The adsorption isotherms were studied through various models such as the Langmuir and Freundlich isotherms. The Langmuir model is based on the assumption of homogeneous monolayer coverage with all sorption sites to be identical and energetically equivalent. The Freundlich model assumes physicochemical adsorption on heterogeneous surfaces. The linear forms of the two models are[36-42]:

Langmuir $1/q_e = 1/q_m + 1/K_L q_m C_e$ ...(7)

Freundlich $\log q_e = \log K_F + 1/n \log C_e$ ...(8)

where, q_e (mg/g) is amounts of disperse blue adsorbed at equilibrium, q_m (mg/g) is the monolayer adsorption capacity, K_L (L/mg) is the Langmuir adsorption constant related to the free energy of adsorption and C_e (mg/L) is equilibrium disperse blue concentration in the solution. K_F and $(1/n)$ are Freundlich adsorption isotherm constants being indicative of extent of adsorption and intensity of adsorption, respectively. The Langmuir isotherm equation was used to estimate the maximum adsorption capacity of the activated carbon under the following conditions 25°C, pH 5.5 and 20 ppm initial disperse blue concentration while varying adsorbent dose from (0.1 to 0.35 g). The values of the isotherm constants and R^2 are given in Table 4. The linear plot is shown in Fig. 9, of $1/q_e$ versus $1/C_e$ along with high value correlation coefficient indicate that Langmuir isotherm provides a better fit with the equilibrium data. The adsorption data when fitted to the Langmuir isotherm the plot of $1/q_e$ versus $1/C_e$ in Figure 9 shows that Langmuir isotherm gives a poor fit to the experimental data as compared to Freundlich isotherm. The isotherm parameters as derived from the slope and intercept of the plots are listed in Table 4.

Table 4: Langmuir and Freundlich isotherm constants

Isotherm constants	Langmuir			Freundlich		
Constants/Correlation coefficients	R^2	q_m	K_L	R^2	K_F	n
Values	0.995	8.130	0.004	0.990	8.749	0.616
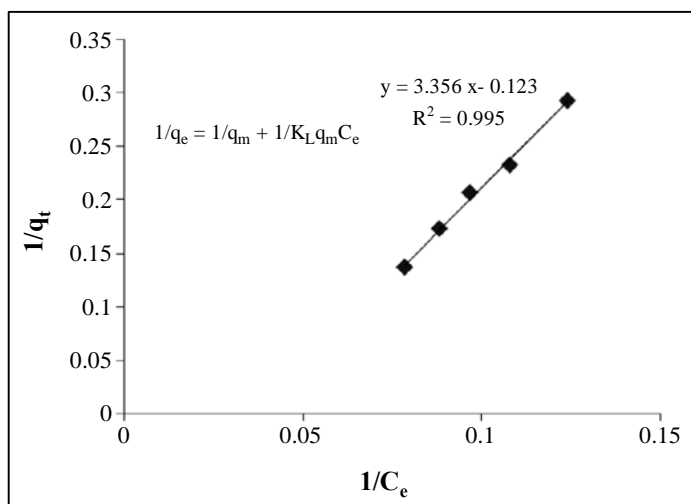
Fig. 9: Langmuir adsorption isotherms for disperse blue dye adsorption onto ZDSAC
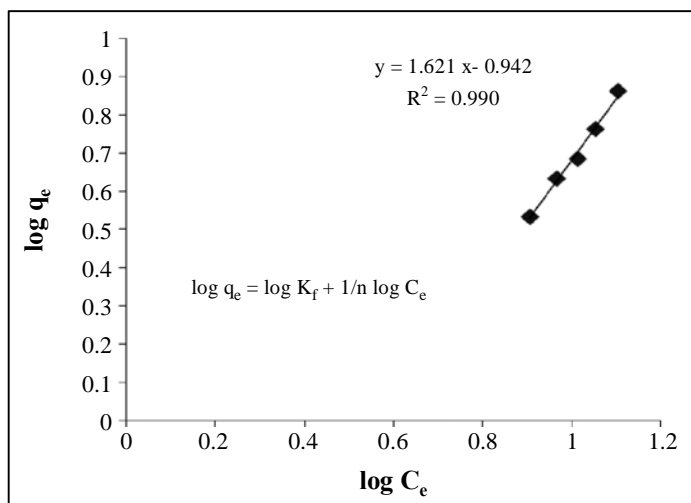
Fig. 10: Freundlich adsorption isotherms for disperse blue adsorption onto ZDSAC

CONCLUSION

The results indicate that ZDSAC is a promising adsorbent for disperse dyes. The pseudo-second order kinetic model equation is the best to describe adsorption of disperse blue dye on activated carbon. The results show that the best fit was achieved with the Langmuir isotherm equation. Also application of activated carbon shows high efficiency for the disperse blue removal in the wastewater. The removal efficiency of disperse blue dye was found equal to 66.47% for ZDSAC the synthesized whereas 54.33% for AC the commercial. The results indicate that the adsorption efficiency percentage of disperse blue dye with ZDSAC the synthesized was markedly higher than of AC the commercial.

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