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Production and Characterization of Activated Carbon From Iraqi Palm Fiber

ZAHRAA H. ATHAB

Environmental Researches Center, Babylon University, Hilla, Iraq

Corresponding author: E-mail: ahmed_zazaza@yahoo.com

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In this work, activated carbon was prepared from Iraqi palm fiber by zinc chloride activation. Activated cabon Iraqi palm fiber (PFAC) was used as low cost adsorbent material for removal of Brilliant Cresyl Blue dye (BCB) from aqueous media using batch adsorption technique. The effect of different parameters, such as, amount of adsorbent, contact time and pH were investigated. The removal efficiency of Brilliant Cresyl Blue was found equal to 98 % by using activated cabon Iraqi palm fiber. Langmuir and Freundlich models were applied in the present study to describe the adsorption isotherm. The isotherms of adsorption were fitted to the Langmuir equation better than Freundlich equation. Three kinetic models include pseudo-first order, pseudo-second order and intra-particle diffusion were applied to analyze Brilliant Cresyl Blue adsorption process. Kinetic studies showed that the adsorption kinetics was more accurately represented by a pseudo-second order model.

Keywords: Palm fiber, Activated carbon, Adsorption, Brilliant cresyl blue, Kinetics, Isotherms.

INTRODUCTION

Dyes are extensively used in different types of industries, such as paper, leather and textiles[1,2]. Synthetic dyes usually have a complex aromatic molecular structure which possibly obtained from coal tar based hydrocarbons such as benzene, naphthalene, antracene, toluene, xylene, *etc*[3]. The complex aromatic molecular structures of dyes make them more stable and difficult to biodegrade. The extensive use of dyes often poses pollution problems in the form of colored wastewater discharged into environmental water bodies[4]. Many of these dyes are also toxic and even carcinogenic and poses a serious hazard to aquatic living organisms[5]. However, wastewater containing dyes is very difficult to treat, as the dyes are recalcitrant organic molecules, resistant to aerobic digestion and are stable to light, heat and oxidizing agents[6,7]. Therefore, removal of such dyes from wastewater is very important to the environment. Several treatment techniques have been applied to remove the dyes from wastewater such as adsorption technique[8,9].

Adsorption technique is the most favorable method for removal of dyes because of its simple design, easy operation and relatively simple regeneration[10]. The fact that wastewater industries may contain a variety of organic compounds and toxic substances that exhibit toxic effects toward microbial populations, which can be toxic and carcinogenic to animals[11]. Previous investigation deals with equilibrium isotherms and kinetic studies in presence of Brilliant Cresyl Blue dye adsorption onto activated carbon prepared from various agricultural wastes such as oil palm fiber[12], pistachio shells[13], palm kernel shell[14], coconut husk[15], bamboo waste[16], coir pith[17], rice husk[18] and oil palm shell activated carbon[19].

Fig. 1 shows a fiber as important product of the palm, it has several names such as Aren, Gomuti and Black and locally known as the Ijuk fiber.

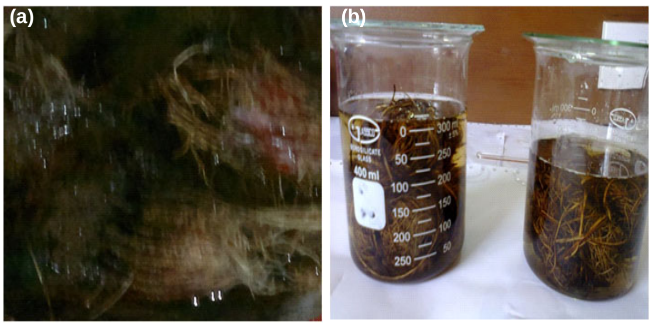

Fig. 1. A bundle of palm fiber

These fibers are known for their high durability and their resistance to sea water. In past, palm fibers were used to make ropes for ship cordages which were proven to have good properties in sea water. Other than that, the preparation for palm fibers is effortless as the fibers do not require any secondary processes such as water retting or mechanical decorticating process to yield the fiber[20]. This is due to the fact that the fibers, originally wrapped around the palm trunk from the bottom to the upper part of the tree as shown in Fig. 2.

Fig. 2. Palm fiber

In this paper, activated cabon Iraqi palm fiber was developed by zinc chloride activation and applied to remove Brilliant Cresyl Blue from aqueous solutions. The effects of various operating parameters on the adsorption such as amount of adsorbent, contact time and pH were investigated in controlled batch experiments. Finally, the isotherm and kinetics in the adsorption process were evaluated.

EXPERIMENTAL

The molecular weight of Brilliant Cresyl Blue was 317.8 g/mol. Distilled water was used to prepare all the solutions and reagents in this work. The chemical structure of Brilliant Cresyl Blue is shown in Fig. 3.

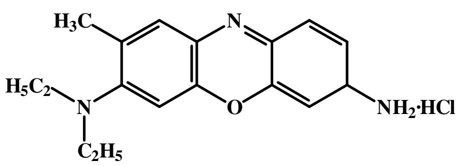

Fig. 3. Chemical structure of Brilliant Cresyl Blue dye

Preparation of activated carbon from fiber palm: Palm fiber was obtained from Iraq, washed many times by distilled water to remove all foreign materials and clay and left to dry in a drying oven at 110 °C, after that impregnation palm fiber with the required amount of $ZnCl_2$ (necessary of the desired ratio of $ZnCl_2$ to palm fiber) and then mixed thoroughly. The mixture was left overnight before carbonization. The impregnated palm fiber was then loaded into crucible. The required numbers of reactors were placed in a muffle furnace and heating started by adjusting the furnace temperature to the desired value. The furnace took about 1 to 1.5 h to reach the desired temperature (the average heating rate was 5 °C/min). The activation was completed by heating at temperature 400 °C for 2 h. The carbonization times was measured from the moment the furnace reached the desired temperature. At prescribed times a sample of each ratio was withdrawn from the furnace and allowed to cool. The activated carbon was then extracted from the reactor and kept in a carefully labeled and tightly closed plastic bottles. The next step is the removal of the activator from the carbonization products by washing. First the pyrolysis products were grinded into fine powder and the required concentration of HCl (0.1 M) was added to it the mixture was then left overnight at room temperature in a conical flask. Next morning supernatant liquid was decanted in a filter paper followed by three successive washings and decantation using distilled water. In the third step, the washing, the whole carbon was transferred to the filter paper and washing using distilled water was continued on the filter paper till free of chloride ion as indicated by silver nitrate test. Finally the carbon was dried at 110 °C.

Adsorption experiments: Adsorption experiments were carried out by mixing a fixed amount of activated cabon Iraqi palm fiber with 100 mL of Brilliant Cresyl Blue solution of different initial concentration into a number of 100 mL stoppered flasks. The desirable initial pH was measured by pH meter. The initial pH was regulated using different concentrations of hydrochloric acid or sodium hydroxide. The adsorption tests were conducted in magnetic mixer. The concentration of Brilliant Cresyl Blue dye was 60 ppm and the amount of adsorbent was included the ratio 0.05, 0.1, 0.15, 0.2 and 0.3 g for activated carbon. In all experiments, the required amount of the adsorbent was suspended in 100 cm^3 of aqueous solution of Brilliant Cresyl Blue dye. 2 mL was taken from the reaction suspension, centrifuged at 4,000 rpm for 15 min in an 800 B centrifuge and filtered to remove the particles. The second centrifuge was found necessary to remove fine particle of the activated cabon Iraqi palm fiber. After the second centrifuge, the absorbance of the Brilliant Cresyl Blue dye was measured at 624 nm, using Cary 100 Bio UV-visible spectrophotometer Shimadzu. The efficiency of Brilliant Cresyl Blue dye, % removal, was calculated as[21,22]:

$$\text{Removal (\%)} = \frac{C_i - C_f}{C_i} \times 100 \quad (1)$$

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:

$$q_t = \frac{(C_i - C_t) \times v}{m} \quad (2)$$

where C_i is the initial concentration of Brilliant Cresyl Blue dye, C_t represents Brilliant Cresyl Blue dye concentration at time t, V was the solution volume and m the mass activated cabon Iraqi palm fiber (g). The amount of adsorption at equilibrium, q_e was given by:

$$q_e = \frac{(C_i - C_e) \times v}{m} \quad (3)$$

where C_e was the Brilliant Cresyl Blue dye concentration at equilibrium.

RESULTS AND DISCUSSION

Scanning electron microscope analysis: The surface morphological changes of activated cabon Iraqi palm fiber samples were investigated using a scanning electron microscope. Fig. 4 shows palm fibers modified with zinc chloride. Figure shows a significantly good bonding between fiber and matrix.

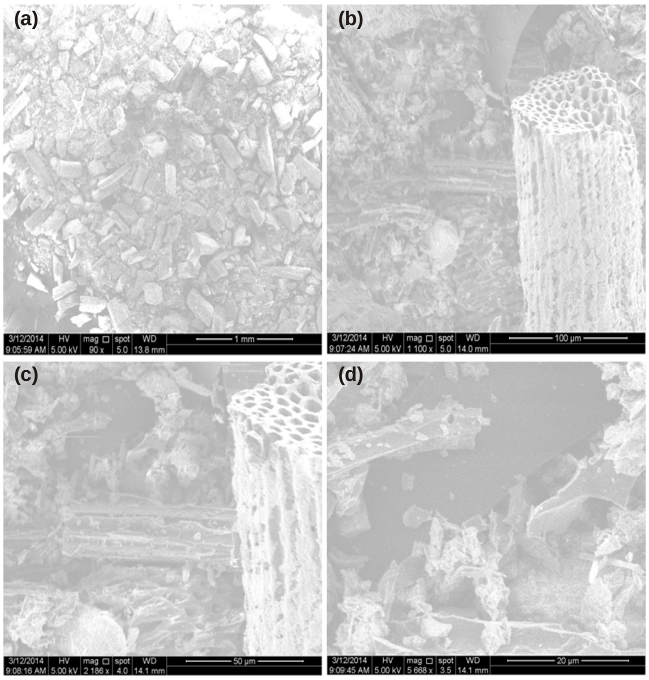

Fig. 4. SEM micrographs of carbon samples from Iraqi palm fiber: 200 mesh (a, b, c and d at different magnifications)

Effect of activated cabon Iraqi palm fiber dosage on adsorption of Brilliant Cresyl Blue: The effect of activated cabon Iraqi palm fiber dose was studied for varying the dose between 0.05 g and 0.3 g in 100 mL aqueous solution of dye. These tests were conducted at a temperature of 25 °C, with pH 6.5 for Brilliant Cresyl Blue. The initial Brilliant Cresyl Blue concentration was 60 ppm. It was observed that the adsorption efficiency percentage of Brilliant Cresyl Blue onto the activated cabon Iraqi palm fiber increased rapidly with the increase of adsorbent concentration as shown in Fig. 5. This result is expected because the increase of adsorbent dose leads to greater surface area. When the adsorbent concentration was increased from 0.05 to 0.3 g, the percentage of Brilliant Cresyl Blue adsorption increased from 50.08 to 98.59 At higher concentrations, the equilibrium uptake of Brilliant Cresyl Blue did not increase significantly with increasing activated cabon Iraqi palm fiber. So, there was no any appreciable increase in the effective surface area resulting due to the conglomeration of exchanger particles. Thus, 0.15 g/100 mL was considered as optimum dose[23].

Effect of contact time: Fig. 6 shows the effect of contact time on Brilliant Cresyl Blue removal. Removal of dye increased with an increase in contact time. Adsorption was very rapid in the first 10 min for activated cabon Iraqi palm fiber the synthesized and then increased slowly with time until reaching equilibrium. It was found that the equilibrium time for activated

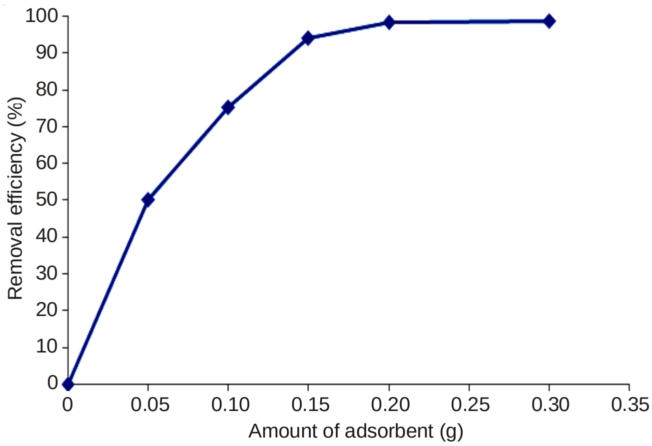

Fig. 5. Effect of dosage of activated cabon Iraqi palm fiber on the removal efficiency of Brilliant Cresyl Blue

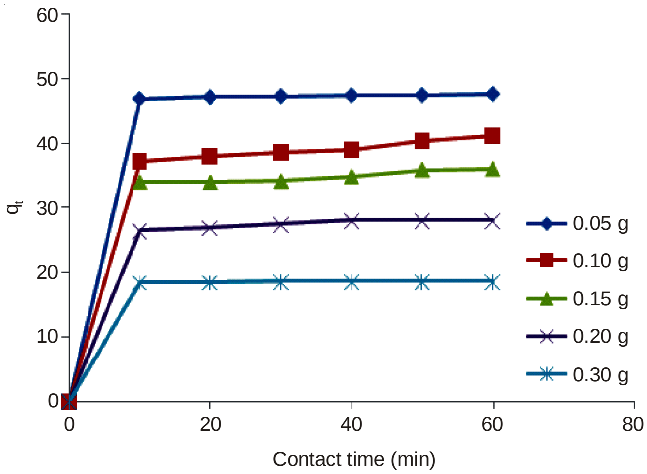

Fig. 6. Effect of contact time on Brilliant Cresyl Blue removal by activated cabon Iraqi palm fiber

cabon Iraqi palm fiber was more than 20 min. To ensure full equilibration, a shaking time of 60 min was used for all concentrations of activated cabon Iraqi palm fiber in this study[24,25].

Effect of initial pH: Effect of initial pH of Brilliant Cresyl Blue solution on adsorption capacity of treated activated cabon Iraqi palm fiber is shown in Fig. 7. The adsorption capacity was found to increase with increasing initial pH and reached maximum value at initial pH of 5.5. Low values of adsorption capacity at acid initial pH is probably due to the excess of H^+ ions competing with Brilliant Cresyl Blue cations for active sites of treated activated cabon Iraqi palm fiber. At initial pHs (5.5-6.5) the adsorption capacity of Brilliant Cresyl Blue onto treated activated cabon Iraqi palm fiber was almost constant. For initial pH values higher than 6.5, it was noticed a decrease in the adsorption capacity. This is mainly due to the solubility of the organic groups present on the surface of treated activated cabon Iraqi palm fiber[26].

Adsorption isotherms: The adsorption isotherms are 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 physico-chemical adsorption on heterogeneous surfaces. The linear forms of the two models are[27,28]:

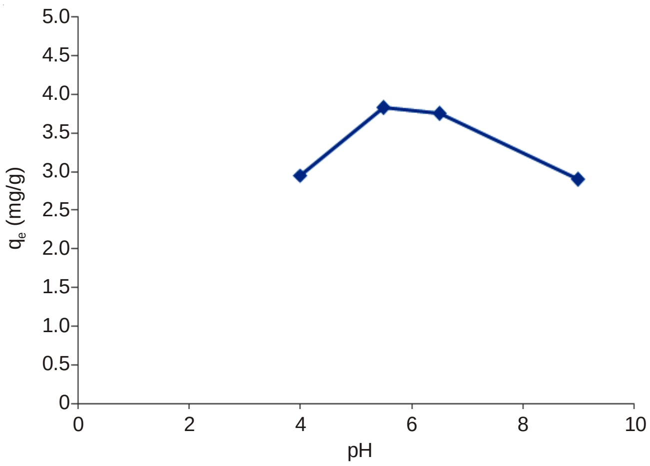

Fig. 7. Effects of pH for adsorption of Brilliant Cresyl Blue on activated cabon Iraqi palm fiber

$$\text{Langmuir} \quad 1/q_e = 1/q_m + 1/K_L\, q_m\, C_e \tag{4}$$

$$\text{Freundlich} \quad \log q_e = \log K_F + 1/n \log C_e \tag{5}$$

where, q_e (mg/g) is amounts of Brilliant Cresyl 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 Brilliant Cresyl 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 cabon Iraqi palm fiber under the conditions 25 °C, pH 6.5 and 60 ppm initial Brilliant Cresyl Blue concentration while varying adsorbent dose from (0.05 to 0.3 g). The values of the isotherm constants and R^2 are given in Table-1. The linear plot is shown in Fig. 8, 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 Freundlich isotherm the plot of log q_e *versus* log C_e in Fig. 9 shows that Freundlich isotherm gives a poor fit to the experimental data as compared to Langmuir isotherm. The isotherm parameters as derived from the slope and intercept of the plots are listed in Table-1.

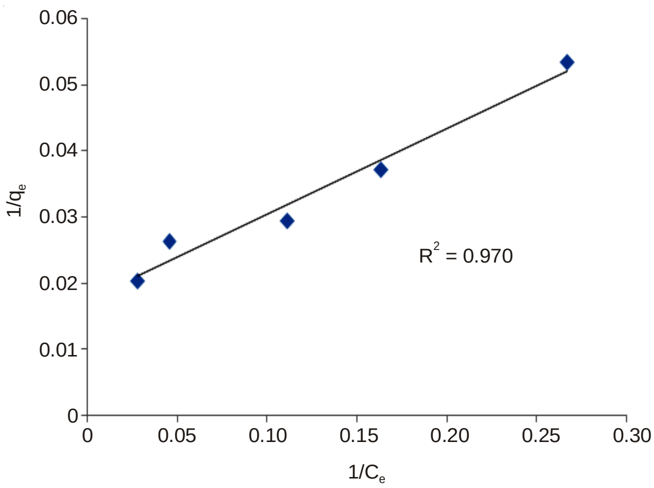

Fig. 8. Linear Langmuir adsorption isotherms for Brilliant Cresyl Blue adsorption by the activated cabon Iraqi palm fiber

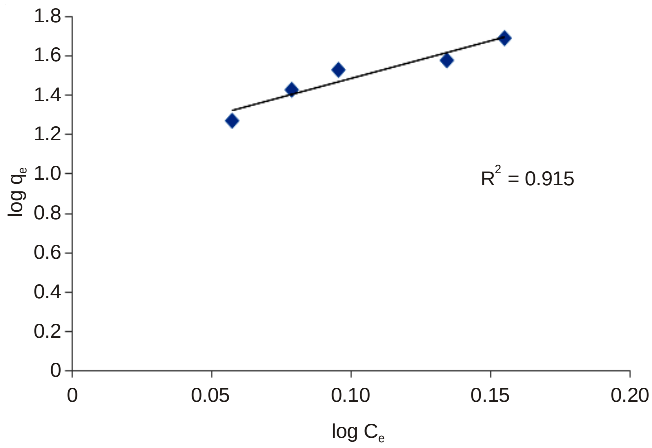

Fig. 9. Linear Freundlich adsorption isotherms for Brilliant Cresyl Blue adsorption by the activated cabon Iraqi palm fiber

TABLE-1
LANGMUIR AND FREUNDLICH ISOTHERM CONSTANTS

Isotherms	Constants/correlation coefficients	Values
Langmuir	R^2	0.9701
	q_m	57.8034
	K_L	0.0355
Freundlich	R^2	0.9153
	K_F	12.7555
	n	2.6315

Kinetics of Brilliant Cresyl Blue adsorption on activated cabon Iraqi palm fiber: The kinetics of Brilliant Cresyl Blue adsorption on activated cabon Iraqi palm fiber were determined under the conditions: Initial Brilliant Cresyl Blue concentration 60 ppm, pH 6.5 and temperature 25 °C. It was found that the equilibrium time for activated cabon Iraqi palm fiber was more than 20 min. To ensure full equilibration, a shaking time of 60 min was used for all concentrations of activated cabon Iraqi palm fiber in this study. The experimental data were processed with respect to three different kinetic models namely pseudo-first order[29], pseudo-second order[30] and intra-particle diffusion[31]. The eqns. 6 and 7 represent the linear forms of the pseudo-first order and pseudo-second order models respectively.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{6}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{7}$$

where, q_e (mg/g) and q_t (mg/g) are amounts of Brilliant Cresyl 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. Figs. 10 and 11 show pseudo-first order and pseudo-second order plots respectively for the experimental data. Various rate constants derived from the slopes and intercepts along with correlation coefficients are given in Tables 2 and 3. The pseudo-second order plot in Fig. 11 has better correlation coefficient (R^2). The calculated value of adsorption capacity from the plot in Fig. 11 is found to be closer to the experimentally determined value than that calculated from Fig. 10. This suggests that the pseudo-second order model represents the kinetic data more accurately.

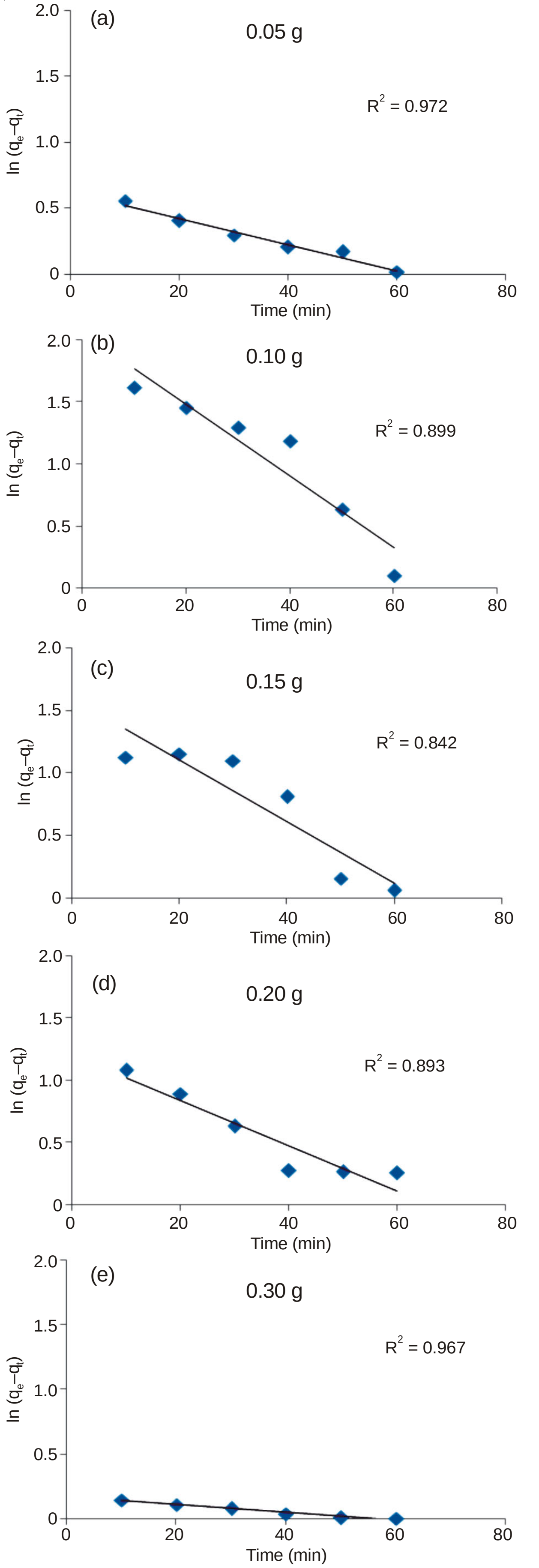

Fig. 10. Plot of (a, b, c, d and e) pseudo-first-order-kinetic model, for the adsorption of Brilliant Cresyl Blue onto activated cabon Iraqi palm fiber

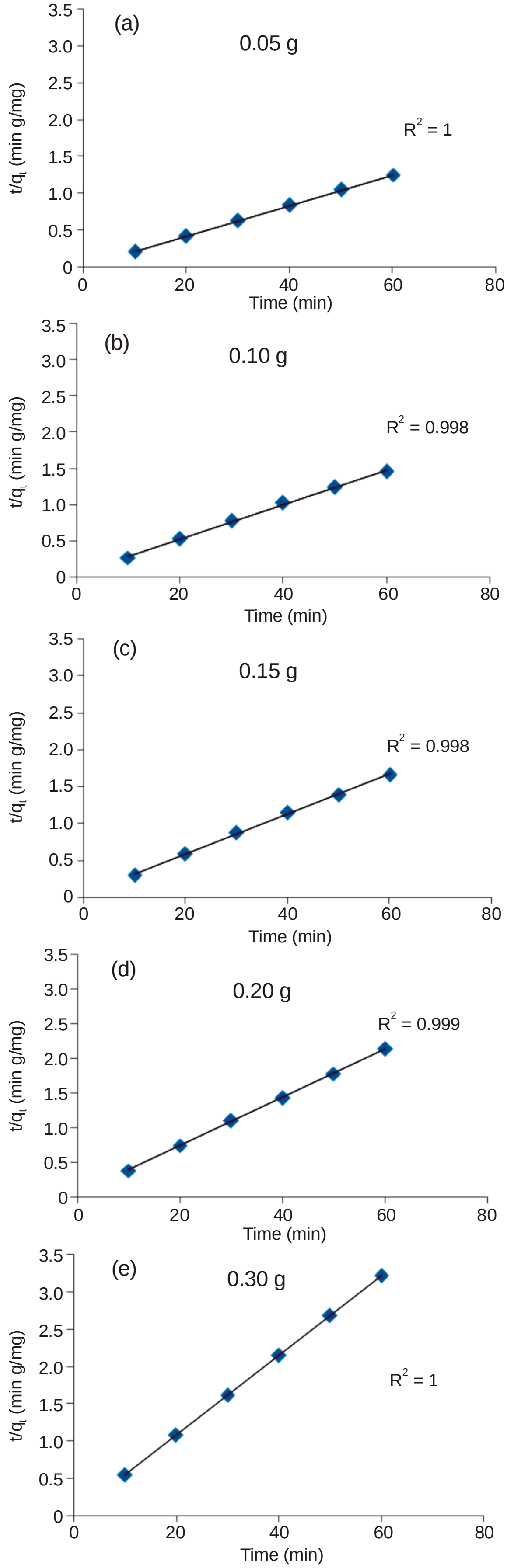

Fig. 11. Plot of (a, b, c, d and e) pseudo-second-order-kinetic model, for the adsorption of Brilliant Cresyl Blue onto activated cabon Iraqi palm fiber

TABLE-2
PSEUDO-FIRST-ORDER-KINETIC MODEL, FOR THE ADSORPTION OF BRILLIANT CRESYL BLUE ONTO ACTIVATED CABON IRAQI PALM FIBER 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
0.050	48.750	1.870	0.010	0.9726
0.100	42.250	7.803	0.029	0.8990
0.150	37.166	4.931	0.024	0.8424
0.200	29.375	3.321	0.018	0.8933
0.300	19.666	1.187	0.003	0.9671

TABLE-3
PSEUDO-SECOND-ORDER-KINETIC MODEL, FOR THE ADSORPTION OF BRILLIANT CRESYL BLUE ONTO ACTIVATED CABON IRAQI PALM FIBER 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
0.050	48.750	47.846	4.098	1
0.100	42.250	42.016	0.486	0.9985
0.150	37.166	36.764	0.655	0.9989
0.200	29.375	28.571	1.000	0.9999
0.300	19.666	18.691	6.687	1

The intraparticle diffusion model is expressed as

$$q_t = k_{id} t^{1/2} + C$$

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 *vs.* $t^{1/2}$ plot should be linear and should go through the origin if intraparticle diffusion is the sole rate-controlling step. Fig. 12 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 cabon Iraqi palm fiber, for which the rate constant and intercept are given in Table-4.

TABLE-4
INTRAPARTICLE DIFFUSION MODEL, FOR THE ADSORPTION OF BRILLIANT CRESYL BLUE ONTO ACTIVATED CABON IRAQI PALM FIBER 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
0.050	48.750	46.554	0.150	0.9831
0.100	42.250	34.314	0.833	0.9374
0.150	37.166	31.983	0.507	0.7952
0.200	29.375	25.255	0.396	0.9317
0.300	19.666	18.390	0.036	0.9815

Conclusion

In this work, activated cabon Iraqi palm fiber was used as a adsorbent for the removal of Brilliant Cresyl Blue from aqueous solution in the present study. The optimum conditions of adsorption were found to be: A adsorbent dose of 0.15 g in 100 mL of solution. The optimum contact time and pH were 20 min and 6.5, respectively. The pseudo-second-order-kinetic model equation is the best to describe adsorption of Brilliant Cresyl Blue on activated cabon Iraqi palm fiber. Adsorption

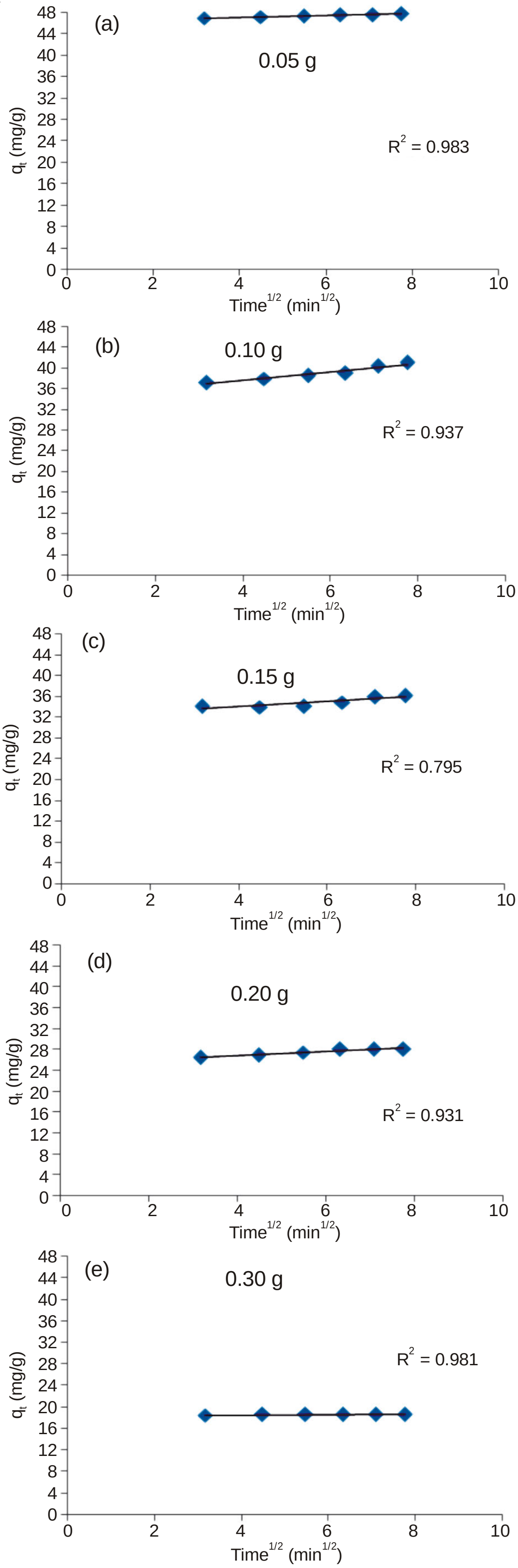

Fig. 12. Plot of (a, b, c ,d and e) Intraparticle diffusion model, for the adsorption of Brilliant Cresyl Blue onto activated cabon Iraqi palm fiber

equilibrium data were fitted by adsorption models, Langmuir and Freundlich. Langmuir equation represents the adsorption equilibrium better than Freundlich. The application of activated cabon Iraqi palm fiber shows high efficiency for the Brilliant Cresyl Blue removal in the wastewater. The efficiency of color removed increase with increasing adsorbent dosage, increase with increasing contact time. The removal efficiency of Brilliant Cresyl Blue was found equal to 98 % by using activated cabon Iraqi palm fiber.

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