

Equilibrium, Kinetic and Thermodynamic Study on Methylene Blue from Aqueous Solution Using Low Cost Adsorbent

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Abstract

The research of the present work was to investigate the removal of methylene blue dyes from aqueous solution by using Acid Activated Carica Papaya (ACPCNC). Generally, dyes are organic compounds used as colouring products in chemical, textile, paper, printing, leather, plastics and various food industries. The need for the treatment of dye contaminated waste water passed out from the industry. In this study, Acid Activated Carica Papaya was studied for its potential use as an adsorbent for removal of a cationic dye methylene blue. The various factors affecting adsorption, such as initial dye concentration, contact time, adsorbent dose and effect of temperature, were evaluated. The experimental data were fitted into the pseudo-second order kinetic model. The equilibrium of adsorption was modeled by using the Langmuir and Freundlich isotherm models. The objective of the present work suggests the ACPCNC may be utilized as a low cost adsorbent for methylene blue dyes removal from aqueous solution.

Keywords: Activated Acid Activated Carica Papaya (ACPCNC); Methylene blue; Adsorption isotherm; Kinetics; Equilibrium models

Abbreviation

ACPCNC – Acid Activated Carica Papaya

MB - Methylene blue

K - Kelvin

INTRODUCTION

Dyes are widely used, generally in the textiles, plastics, paper, leather, food industry to color products. In process of washing and finishing coloured products, waste water contaminated with dyes is generated. The contaminated waste waters are hazardous, which is a great threat to environment [1-3]. Dye contamination in wastewater causes problems in various ways: the presence of dyes in water, even in very low quantities, is highly visible and undesirable; color interferes with penetration of sunlight into waters; retards photosynthesis; inhibits the growth of aquatic biota and interferes with gas solubility in water bodies. These materials are the complicated organic compounds and they resist against light, washing and microbial invasions [4-7]. The need for the treatment of dye contaminated waste water arose from the environmental impact [8]. Activated minerals are one of the most popular adsorbents used for the removal of toxic

substances from waste water. This could be related to their extended surface area [9]. The major use of activated Acid Activated Carica Papaya is in solution purification and for the removal of colour, odors and other unpleasant impurities from liquids, water supplies and vegetable and animal oils.

In recent years it has been increasingly used for the prevention of environmental pollution and antipollution laws have increased the sales of low-cost activated minerals for control the of air and water pollution. Various techniques like precipitation, ion exchange, chemical oxidation and adsorption have been used for the removal of toxic pollutant from, wastewater. Methylene blue (MB) is selected as a model compound for evaluating the potential of ACPCNC to remove dye from aqueous solution.

MATERIALS AND METHODS

Adsorption studies

Methylene blue (MB) was employed for the adsorbates in the adsorption experiments. Adsorption from the liquid phase was carried out to verify the nature the porosity and the capacities of the samples. An aqueous solution with a concentration of 50-250 mg/L was prepared by mixing an appropriate amount of MB with distilled water adsorption experiments were conducted by placing 0.025 g of the ACPCNC samples and 50 ml of the aqueous solution in a 250 ml of glass-stoppered flask. The flask was then put in a constant-temperature shaker bath with a shaker speed of 150 rpm. The isothermal adsorption experiments were performed at $30 \pm 2^\circ\text{C}$.

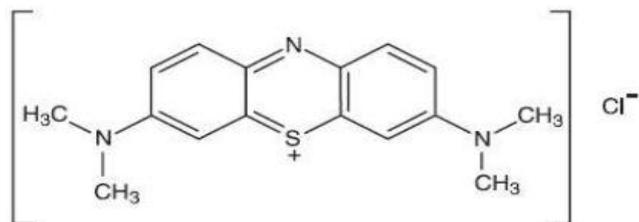
Preparation of adsorbent materials

The Acid Activated Carica Papaya obtained from Agriculture area was activated around 400°C in a muffle furnace for 5 hrs the it was taken out, ground well to fine powder and stored in a vacuum desiccators.



Preparation of adsorbate

Methylene blue was chosen in this work because of its strong adsorption onto solids and it recognized usefulness in characterizing adsorptive material [10, 11] Methylene blue is employed to evaluate the adsorption characteristics of carbon. A known weight of 1000 mg of MB was dissolved in about one litre of distilled water to get the stock solution.



Structure of Methylene Blue

ADSORPTION DYNAMIC EXPERIMENTS

Batch equilibrium method

The adsorption experiments were carried out in a batch process at 30, 40, 50 and 60° C. A known weight of ACPCNC was added to 50 ml of the dye solutions with an initial concentration of 50 mg/L to 250 mg/L, which is prepared from 1000 mg/L of methylene blue stock solution. The contents were shaken thoroughly using a mechanical shaker with a speed of 150 rpm. The solution was then filtered at present time intervals and the residual dye concentration was measured.

RESULT AND DISCUSSIONS

Characteristics of the adsorbent

Activated Acid Activated Carica Papaya is an effective adsorbent for the abatement of many pollutant compounds (organic, inorganic, and biological) of concern in water and wastewater treatment. Most of the solid adsorbents possess micro porous fine structure, high adsorption capacity, high surface area and high degree of surface, which consists of pores of different sizes and shapes [12]. The wide usefulness of ACPCNC is a result of their specific surface area, high chemical and mechanical stability. The chemical nature and pore structure usually determines the sorption activity. The physico-chemical properties of the chosen adsorbent are listed in Table 1.

Table 1. Characteristics of the Adsorbent

Properties	ACPCNC
Particle size(mm)	0.0150
Density (g/cc)	0.2025
Moisture content (%)	0.1827
Loss in ignition (%)	0.0130
pH of aqueous solution	6.3000

Effect of adsorbent dosage

The adsorption of the methylene blue dye on ACPCNC was studied by varying the adsorbent dose (50–250 mg/50ml) for 50 mg/L of dye concentration. The percentage of adsorption increased with increases in the ACPCNC concentration, which is attributed to increased carbon surface area and the availability of more adsorption sites [13, 14]. Hence, all studies were carried out with 0.025g of adsorbent /50 ml of the varying adsorbate solutions. 50, 100, 150, 200 and 250. The Results obtained from this study are shown in figure (2). The amount of MB adsorbed per gram reduced with increase in the dosage of ACPCNC. This reveals that the direct and equilibrium capacities of MB are functions of the activated ACPCNC dosage.

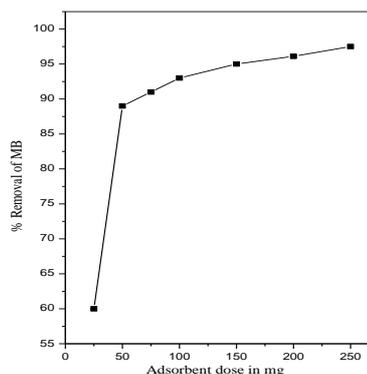


Fig:2- Effect of Adsorbent dose on the removal of MB Dye [MB]=50mg/L:Contact Time 50min:Temperature 30°C

Effect of contact time and initial dye concentration

The effect of contact time on the amount of dye adsorbed was investigated at 1000 mg/L concentration of the dye fig (1). It is observed that the percentage removal of dye increases rapidly with an increase in contact time initially, and thereafter, beyond a contact time of about 45 min, no noticeable change in the percentage removal is observed the percentage removals after 45 min were 85%. Therefore, the optimum contact time is considered to be 45 min. this is also the equilibrium time of the batch adsorption experiments, since beyond a contact time of 45 min, adsorption is not changed. The rapid removal of dye is observed at the beginning of the contact time due to the percentage of large number of binding sites available for adsorption. The experimental results of adsorptions at different concentrations (50, 100, 150, 200 and 250 mg/L) collected in Table 2 observed that percent adsorption decreased with increase in initial dye concentration, but the actual amount of dye adsorbed per unit mass of ACPCNC increased leads to increase in dye concentration. This means that the adsorption is highly dependent on initial concentration of dye. At lower concentration, the ratio of the initial number of dye molecules to the available surface area is low. Subsequently, the fractional adsorption becomes independent of initial concentration. However, at high concentration the available sites of adsorption become less and hence the percentage removal of dye is dependent upon initial concentration [15, 16].

Table 2. Equilibrium Parameters for Adsorption of MB Dye Onto ACPCNC Adsorbent

MB ₀	C _e (Mg / L)				Q _e (Mg / g)				Removed (%)			
	30° C	40° C	50° C	60° C	30° C	40° C	50° C	60° C	30° C	40° C	50° C	60° C
25	1.45	1.26	1.03	1.09	47.09	47.47	47.92	47.81	94.18	94.94	95.84	95.62
50	5.28	4.84	3.21	3.00	89.43	90.30	93.56	93.98	89.43	90.30	93.56	93.98
75	11.63	10.35	10.00	9.07	126.7	129.2	129.98	131.8	84.48	86.18	86.65	87.89
100	25.76	23.26	10.00	19.62	148.4	153.4	179.98	160.7	74.23	76.73	89.99	80.37
125	41.87	37.76	21.76	30.76	166.2	174.4	206.47	188.4	66.50	69.78	82.58	75.38

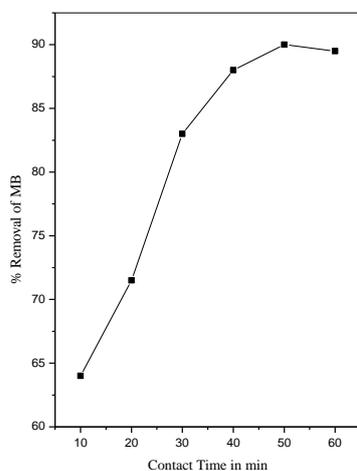


Fig-1- Effect of Contact Time on the Removal of MB Dye [MB]=50 mg/L; Temperature 30°C; Adsorbent dose=25mg/50ml

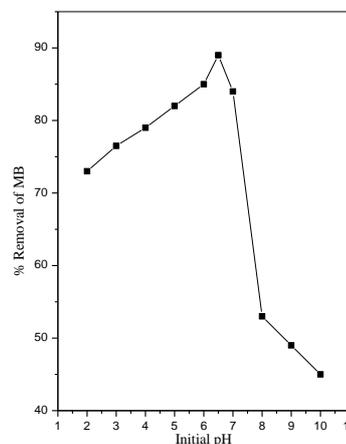


Fig-3- Effect of Initial pH on the removal of MB Dye [MB]=50 mg/L; Temperature 30°C; Adsorbent dose=25mg/50ml

Effect of solution pH

The solution pH is one of the most important factors that control the adsorption of dye on the sorbent material. The adsorption capacity can be attributed to the chemical form of dye in the solution at specific pH. In addition, due to different functional groups on the adsorbent surface, which become active sites for the dye binding at a specific pH the effect of adsorption can vary substantially. Therefore, an increase in pH may cause an increase or decrease in the adsorption, resulting different optimum pH values dependent on the type of adsorbent. To examine the effect of pH on the % removal of MB dye, the solution pH were varied from 2.0 to 10.0 by adding acid and base to the stock solution This increases may be due to the presence of negative charge on the surface of the adsorbent ACPCNC that may be responds for the dye binding. However, as the pH is lowered, the hydrogen ions compete with dye for the adsorption sites in the adsorbent ACPCNC, the overall surface charge on the particles become positive and hinds the binding of positively charged dye. On other hand, decrease in the adsorption under pH >6.3 may be due to occupation of the adsorption sites by OH⁻ ions which retard the approach of such dye further toward the adsorbent ACPCNC surface. From the experimental results, the optimum pH range for the adsorption of the MB dye is 2.0 to 6.3 shown in Figure.3.

Adsorption isotherms

Langmuir isotherm

The theoretical Langmuir isotherm is used for adsorption of a solute from a liquid solution as monolayer adsorption on a surface containing a finite number of identical sites. Therefore, the Langmuir isotherm model was chosen for estimation of the maximum adsorption capacity corresponding to complete monolayer coverage on the adsorbent surface. The Langmuir non-linear equation is commonly expressed as follows:

$$C_{eq}/Q_{eq} = 1/Q_m b + C_{eq}/Q_m \quad (4.1)$$

Where C_{eq} is the equilibrium concentration of adsorbate in the solution (mg/L), Q_{eq} is the amount adsorbed at equilibrium (mg/g), Q_m and b are Langmuir constants related to adsorption efficiency and energy of adsorption, respectively. The linear plots of C_{eq}/Q_{eq} vs. C_{eq} suggest the applicability of the Langmuir isotherms. The values of Q_m and b were calculated from slope and intercepts of the plots are given in Table 3. From the results, it is obvious that the value of adsorption efficiency Q_m and adsorption energy b of the ACPCNC increases on increasing the temperature. The values can conclude that the maximum adsorption corresponds to a saturated monolayer of adsorbate molecules on adsorbent surface with endothermic nature of adsorption [17, 18]. To confirm the favourability of the adsorption process, the separation factor (R_L) was determined and given in Table 4. The values were established to be between 0 and 1 and confirm that the ongoing adsorption process is favorable [19].

Table 3. Langmuir and Freundlich Isotherm Parameter for Adsorption of MB ONTO ACPCNC

TEMP. (°C)	LANGUMUIR PARAMETERS		FRUENDLICH PARAMETERS	
	Q _m	b	K _f	N
30°	183.88	0.19	5.20	2.66
40°	193.91	0.20	5.31	2.60
50°	249.85	0.18	5.45	2.08
60°	207.88	0.23	5.58	2.56

Table 4. Dimensionless Separation Factor (R_L) for Adsorption of MB ONTO ACPCNC

(C _i)	TEMPERATURE °C			
	30°C	40°C	50°C	60°C
25	0.17	0.16	0.17	0.14
50	0.09	0.09	0.09	0.07
75	0.06	0.06	0.06	0.05
100	0.04	0.04	0.05	0.04
125	0.03	0.03	0.04	0.03

The Freundlich isotherm

The Freundlich isotherm model is the earliest known equation describing the adsorption process. It is an empirical equation and can be used for non-ideal sorption that involves heterogeneous adsorption. The Freundlich equation was employed for the adsorption of methylene blue dye on the adsorbent. The Freundlich isotherm was represented by the following equation.

$$\log Q_e = \log K_f + 1/n \log C_e \quad (4.2)$$

Where Q_e is the amount of methylene blue dye adsorbed (mg/g), C_e is the equilibrium concentration of dye in solution (mg/L), and K_f and n are constants incorporating the factors affecting the adsorption capacity and intensity of adsorption, respectively. Linear plots of log Q_e versus log C_e shows that the adsorption of methylene blue obeys the linear plots of log Q_e versus log C_e shows that the adsorption of methylene blue dye obeys the Freundlich adsorption isotherm. The values of K_f and n are given in Table 4 shows that the increase of negative charges on the adsorbent surface makes electrostatic force like Vanderwaal's between the ACPCNC surface and dye ion. The molecular weight and size either limit or increase the possibility of the adsorption of the dye onto adsorbent. However, the values clearly show the dominance in adsorption capacity.

The intensity of adsorption is an indication of the bond energies between dye and adsorbent, and the possibility of slight chemisorptions rather than physisorption [17, 20]. However, the multilayer adsorption of methylene blue through the percolation process may be possible. The values of n are less than one, indicating the physisorption is much more favorable [21].

Effect of temperature

To study the effect of temperature on the adsorption of dye adsorption by ACPCNC, the experiments were performed at

temperatures of 30, 40, 50, 60°C. As it was observed that, the equilibrium adsorption capacity of MB onto ACPCNC was found to increase with increasing temperature, especially in higher equilibrium concentration, or lower adsorbent dose because of high driving force of adsorption. This fact indicates that the mobility of dye molecules increased with the temperature. The adsorbent shows the endothermic nature of adsorption. The adsorption capacity of the ACPCNC increased with increase of the temperature in the system from 30° to 60°C. Thermodynamic parameters such as change in free energy (ΔG°) (kJ/mol), enthalpy (ΔH°) (kJ/mol) and entropy (ΔS°) (J/K/mol) were determined using the following equations.

$$K_0 = C_{\text{solid}}/C_{\text{liquid}}$$

$$\Delta G^\circ = -RT \ln K_0$$

$$\log K_0 = \Delta S^\circ / (2.303R) - \Delta H^\circ / (2.303RT) \quad 4.5$$

Where K₀ is the equilibrium constant, C_{solid} is the solid phase concentration at equilibrium (mg/L), C_{liquid} is the liquid phase concentration at equilibrium (mg/L), T is the temperature in Kelvin, and R is the gas constant. The ΔH° and ΔS° values obtained from the slope and intercept of Van't Hoff plots are given in Table 5. The values of ΔH° is the range of 1 to 93 kJ/mol, indicate the physisorption. The results show that physisorption is much feasible for the adsorption of methylene blue. The positive values of ΔH° show the endothermic nature of adsorption which governs the possibility of physical adsorption [19, 22]. Because in the case of physical adsorption, while increasing the temperature of the system, the extent of dye adsorption increases, there is no possibility of chemisorption. The negative values of ΔG° (Table 5) show that the adsorption is highly favorable and spontaneous. The positive values of ΔS° (Table 5) show the increased disorder

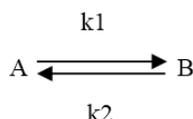
and randomness at the solid solution interface of methylene blue with ACPCNC adsorbent. The enhancement of adsorption capacity of the activated ACPCNC at higher temperatures was ascribed to the enlargement of pore size and activation of the adsorbent surface [23].

Table 5. Thermodynamic Parameter for the Adsorption of MB ONTO ACPCNC

C ₀	ΔG°				ΔH°	ΔS°
	30° C	40° C	50° C	60° C		
25	-7015.00	-7630.64	-8429.44	-8540.5	9.38	54.37
50	-5380.48	-5808.03	-7188.37	-7608.42	19.13	80.61
75	-4269.3	-4764.78	-5024.06	-5489.47	7.59	39.24
100	-2665.32	-3105.22	-5898.05	-3903.43	17.73	68.00
125	-1727.31	-2178.32	-4180.44	-3099.26	17.24	63.02

Kinetics of Adsorption

Kinetics of sorption describes the solute uptake rate, which in turn governs the residence time or sorption reaction. It is one of the important characteristics in defining the efficiency of sorption. In this study, the kinetics of the methylene blue dye removal was carried out to understand the behavior of this low-cost ACPCNC adsorbent. The adsorption of methylene blue dye from an aqueous solution follows reversible second-order kinetics, when a single species is considered on a heterogeneous surface. The heterogeneous equilibrium between the methylene blue dye solution and the ACPCNC was represented in the following equation.



Where k_1 is the forward rate constant and k_2 is the backward rate constant. A represents the methylene blue remaining in the aqueous solution and B represents the methylene blue adsorbed on the surface of the activated ACPCNC. The rate constants were calculated as earlier [18, 24]. The data (Table 6) show that the forward rate constant is much higher than the backward rate constant, suggesting that the rate of adsorption is clearly dominant.

In order to study the kinetics of the adsorption process, the following kinetic equation proposed by Natarajan and Khalaf, as cited in literature, has been employed [25].

$$\log C_0/C_t = (K_{ad}/2.303)t \quad 4.6$$

Where C_0 and C_t are the concentration of the dye (in mg/L) at the time of zero and time t respectively. The rate constants (K_{ad}) for the adsorption processes have been calculated from the slope of the linear plots of $\log C_0/C_t$ versus t for different concentrations and temperatures. The determination of rate constants as described in literature is given by the following equation.

$$K_{ad} = k_1 + k_2 = k_1 + (k_1/K_0) = k_1 [1 + 1/K_0] \quad 4.6.1$$

The overall rate constant k_{ad} for the adsorption of dye at different temperatures are calculated from the slopes of the linear Natarajan-Khalaf plots. The rate constant values are collected in Table 6 shows that the rate constant (k_{ad}) increases with increase in temperature suggesting that the adsorption process is endothermic in nature. The overall rate of adsorption is separated into the rate of forward and reverse reactions using the above equation. The rate constants for the forward and reverse processes are also collected in Table 6, indicate that, at all initial concentrations and temperatures, the forward rate constant is much higher than the reverse rate constant suggesting that the rate of adsorption is clearly dominant [22, 26].

Table 6. The Kinetic Parameters for the Adsorption of MB ONTO ACPCNC

C ₀	Temp °C	PSEUDO SECOND ORDER				ELOVICH MODEL			INTRAPARTICLE DIFFUSION		
		q _e	k ₂	γ	h	α	β	γ	K _{id}	γ	C
25	30	51.96	29×10 ⁻³	0.996	7.91	64.98	0.13	0.9921	1.65	0.9912	0.18
	40	50.27	46×10 ⁻³	0.993	11.83	1656.7	0.21	0.9924	1.78	0.9914	0.10
	50	50.93	44×10 ⁻³	0.991	11.53	1383.8	0.20	0.9930	1.78	0.9915	0.10
	60	50.43	46×10 ⁻³	0.9960	11.86	4751.2	0.23	0.9915	1.80	0.9917	0.09
50	30	97.30	17×10 ⁻³	0.994	16.85	260.38	0.07	0.9940	1.67	0.9918	0.15
	40	97.13	23×10 ⁻³	0.9955	22.21	1107.8	0.09	0.9923	1.73	0.9919	0.12
	50	100.16	20×10 ⁻³	0.9952	20.47	1697.7	0.09	0.9928	1.75	0.9921	0.11
	60	99.30	22×10 ⁻³	0.9953	22.30	3591.8	0.10	0.9927	1.77	0.9923	0.10
75	30	135.80	14×10 ⁻³	0.9942	25.96	1134.4	0.06	0.9926	1.69	0.9925	0.12
	40	139.10	13×10 ⁻³	0.9961	25.49	831.93	0.06	0.9933	1.68	0.9928	0.13
	50	138.33	15×10 ⁻³	0.9956	28.84	2021.4	0.07	0.9935	1.72	0.9938	0.11
	60	140.62	14×10 ⁻³	0.9974	28.64	1588.2	0.06	0.9936	1.71	0.9945	0.12
100	30	160.07	11×10 ⁻³	0.9941	29.07	874.81	0.05	0.9939	1.62	0.9961	0.13
	40	166.49	10×10 ⁻³	0.9944	29.11	683.98	0.05	0.9940	1.62	0.9967	0.14

C ₀	Temp °C	PSEUDO SECOND ORDER				ELOVICH MODEL			INTRAPARTICLE DIFFUSION		
		q _e	k ₂	γ	h	α	β	γ	K _{id}	γ	C
	50	168.18	11×10 ⁻³	0.9922	31.21	951.56	0.05	0.9941	1.64	0.9969	0.13
	60	172.95	10×10 ⁻³	0.9932	31.38	1046.2	0.05	0.9943	1.65	0.9968	0.13
125	30	175.27	12×10 ⁻³	0.9973	39.39	5003.1	0.06	0.9937	1.62	0.9977	0.10
	40	188.12	9×10 ⁻⁴	0.9935	33.28	914.40	0.04	0.9928	1.58	0.9975	0.13
	50	194.22	9×10 ⁻⁴	0.9936	33.94	867.17	0.04	0.9920	1.59	0.9974	0.14
	60	203.84	8×10 ⁻⁴	0.9939	34.47	922.38	0.04	0.9919	1.62	0.9978	0.14

Evidences for adsorption

The Scanning Electron Microscope (SEM) diagrams of raw activated Acid Activated Carica Papaya and dye -adsorbed activated ACPCNC are shown in Fig. 4 and Fig.5. The bright spots, shows the presence of tiny holes on the ACPCNC, after treatment with dye the bright spots become black shows the adsorption of the dyes on the surface of the ACPCNC.

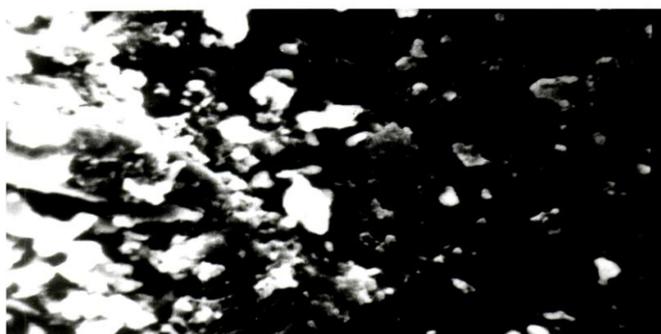


Figure 4. Scanning electron microscope of ACPCNC before adsorption



Figure 5. Scanning electron microscope of ACPCNC after adsorption

CONCLUSION

The present study has shown the effectiveness of using ACPCNC in the removal of methylene blue dye from aqueous solutions. Activated Acid Activated Carica Papaya in different forms has a great role in modern life to clean environment. Acid Activated Carica Papaya can be good precursors for producing highly porous activated Acid

Activated Carica Papaya by simple preparative methods. An adsorption test has been carried out for industrial pollutants (methylene blue) under different experimental conditions in batch mode. The adsorption of methylene blue was dependent on adsorbent surface characteristics, adsorbent dose, methylene blue concentration, time of contact and temperature. A study of the kinetic models on sorption showed that sorption fitted the pseudo second- order kinetics model. The ΔG , ΔH , and ΔS reveal's the favorability of adsorption. The thermodynamic parameters suggested that the adsorption on ACPCNC was a spontaneous and endothermic process.

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