

Kinetic investigation of methyl violet dye adsorption on agar-agar impregnated activated carbon

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Agar-agar-impregnated activated carbon (AA-AC) which is a biopolymer-based adsorbent was prepared, characterized *via* FTIR-ATR and used for the adsorption of methyl violet (MV) dye from synthetic waste water. The effects of different reaction parameters such as initial MV concentration, contact time and solution temperature on the adsorption of MV onto AA-AC at constant adsorbent dose were investigated. To determine the best adsorption equilibrium the Freundlich, Langmuir and Temkin models were applied and to determine the adsorption kinetics the pseudo first-order, pseudo second-order and Weber-Morris intraparticle diffusion models were applied.

Keywords: Methyl violet dye; Agar-agar impregnated activated carbon; Dye removal; Adsorption isotherms; Kinetic parameters

INTRODUCTION

Adsorption technique is widely used to cleaning waste water from dyes on industrial and lab scale as it is simple, cost-effective and easily applicable [1]. Activated carbons in granular or powdered form obtained from waste materials or commercially available are the most widely used sorbents in adsorption technique because of their excellent sorption capability for inorganic pollutants in industry [2, 3]. Especially dyes are a problem of the waste water in the textile industry [4]. Methyl violet (MV) dye, a harmful basic dye, is used in textile industry. *Saba senegalensis* shell residue-based activated carbon [5] and hydrolyzed polyacrylamide nanocomposite grafted onto xanthan gum, or incorporated in nanosilica [6] were successfully used to remove MV from waste water. Agar-agar is a porous galactose polymer. Agar-agar-impregnated activated carbon (AA-AC) is a biopolymer-based adsorbent which has been successfully used to remove Pb^{+2} from water [7].

In the present study, the preparation of agar-agar-embedded activated carbon adsorbent obtained by

physical mixing of activated carbon with an agar-agar solution is reported. FTIR-ATR spectral analysis was used to confirm the presence of agar-agar on the activated carbon. The AA-AC adsorbent was used to remove MV from synthetic waste water solutions. Three kinetic and isotherm models were applied.

EXPERIMENTAL

Activated carbon, methyl violet ($C_{24}H_{27}N_3ClH$) and agar-agar were purchased from Fluka, Merck and Sigma-Aldrich, respectively (Fig. 1). Activated carbon powder (5 g) was impregnated by mixing with 3.75 g of agar-agar in 50 ml of hot water at 85 °C for 24 h. After impregnation, AA-AC was washed three times with cold water to remove non-adsorbed agar-agar from the medium and was dried in a vacuum oven at 100 °C. Thermo Fischer brand Nicolet 10 model FTIR-ATR spectrophotometer, Sigma brand 3-18K model ultracentrifuge device, Shimadzu brand Uvmini-1240 UV-Visible spectrophotometer and Daihan Scientific multi-heat mixer were used.

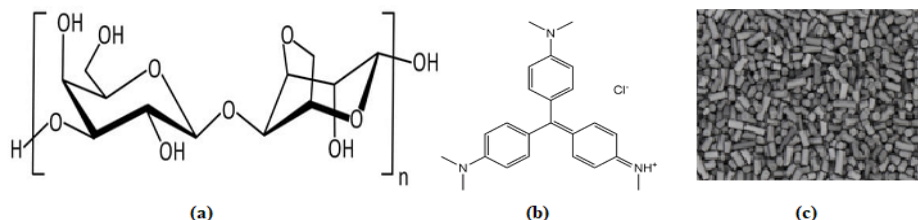


Figure 1. Chemical structures of agar-agar (a), methyl violet dye (b) and image of granulated activated carbon (c)

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The concentrations of methyl violet in synthetic waste water solution and in an aqueous solution were determined using a double-beam visible spectrophotometer at a wavelength of 578 nm (Figure 2).

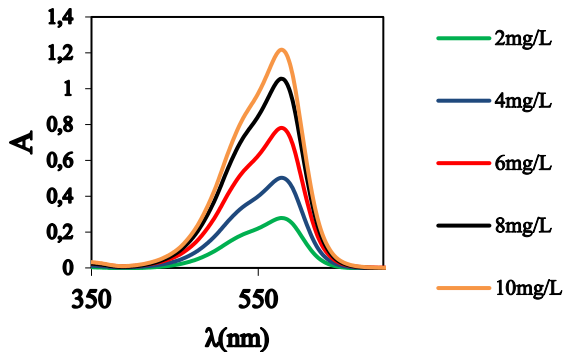


Figure 2. Absorbance changes of different concentrations of MV in pure water

A calibration curve ($A=0.1215C+0.0379$, $R^2 = 0.993$) (Figure 3) was constructed from the absorbance values of 2-4-6-8-10 mg/l of MV dye solutions prepared by dilution from 1000 mg/l stock solution in water.

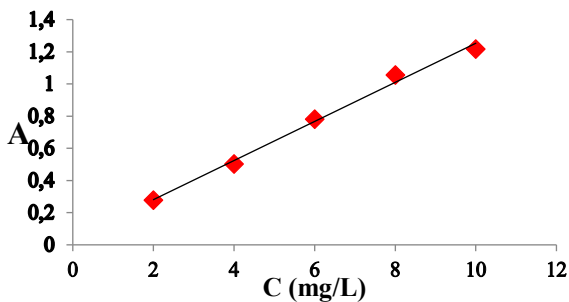


Figure 3. Calibration curve for MV in pure water

Methyl violet removal was carried out from synthetic wastewater solutions by adsorption on AC and AA-AC. In all measurements, the amount of adsorbent was kept constant at 80 mg and the mixing speed was kept constant at 300 rpm. In the adsorption experiments, the effects of time (30-60-90-120-150-180-210-240 min at room temperature in 50 mg/L MV solution), temperature (20-25-30-35-40-45-50 °C in 50 mg/L MV solution for 150 min) and initial concentration (50-100-150-200-250-300-350-400-450-500 mg/L for 150 min at room temperature) were examined.

The dye removal yield percentage (RY, %) of MV was calculated by using Eq.1 [8]:

$$\%RY = \frac{(C_o - C_e)}{C_o} \cdot 100 \quad (1)$$

The adsorption capacity of AC and AA-AC, the amount of MV adsorbed at equilibrium, was calculated by using Eq. 2:

$$q_e = \frac{(C_o - C_e) \cdot V}{w} \quad (2)$$

where q_e (mg/g) is the adsorbed amount of MV per gram adsorbent, C_o (mg/L) and C_e (mg/L) are MV dye solution concentration at the initial and equilibrium stages, respectively. V (L) is the volume of the MV solution, and w (g) is the amount of the AC and AA-AC adsorbents.

RESULTS AND DISCUSSION

To determine the chemical composition of the agar-agar-impregnated activated carbon adsorbent, FTIR-ATR analysis was conducted and the FTIR-ATR spectra of AC and AA-AC are given in Figure 4.

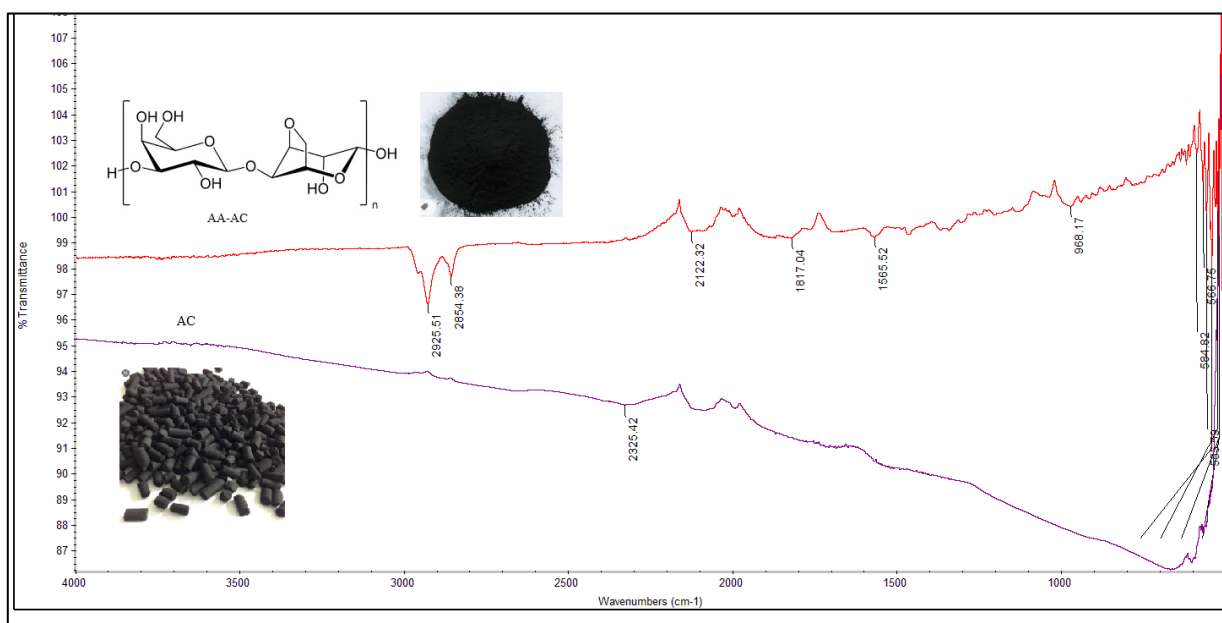


Figure 4. FTIR-ATR spectra of AC and AA-AC

The new peaks observed are: the absorption peak of agar-agar at 2925 cm⁻¹ (O–H stretching vibration of hydroxyl group), and at 968 cm⁻¹ (C–O stretching vibration of pyranose ring). In order to investigate the effect of contact time on dye adsorption and to determine the optimum retention time for the adsorption capacity, the adsorption removal efficiencies of AC and AA-AC were examined for 30-60-90-120-150-180-210-240 min from a solution containing 50 mg/L of dye. After the corresponding

time passed, the batches were centrifuged for 10 min, the adsorption values of the solutions were taken on a UV-VIS spectrophotometer, C_e values were found from the calibration curve according to their absorbance at 578 nm, and dye removal yield percentage (RY, %) and adsorption capacity, q_e of AC and AA-AC adsorbents were calculated according to Eqs. 1 and 2, respectively. The results are given in Table 1.

Table 1. Contact time effect: MV dye solution concentration at the equilibrium stage, dye removal yield percentage and adsorption capacity of AC and AA-AC adsorbents

t (min)	AC				AA-AC			
	A	C _e (mg/L)	RY (%)	q _e (mg/g)	A	C _e (mg/L)	RY (%)	q _e (mg/g)
30	3.84	31.3	37.4	29.2	2.84	23.1	53.9	42.1
60	4.87	39.8	20.5	15.9	3.24	26.4	47.2	36.9
90	4.77	38.9	22.0	17.2	2.95	23.9	52.1	40.7
120	4.27	34.9	30.2	23.6	2.97	24.1	51.7	40.4
150	3.25	26.5	47.0	36.8	3.01	24.5	50.9	39.8
180	4.34	35.4	29.2	22.8	2.76	22.4	55.1	43.1
210	5.06	41.4	17.2	13.4	2.90	23.5	52.9	41.3
240	5.09	41.6	16.8	13.1	3.08	25.0	49.9	38.9

Table 2. Effect of temperature on adsorption of MV by AC and AA-AC

T (°C)	AC				AA-AC			
	A	C _e (mg/L)	RY (%)	q _e (mg/g)	A	C _e (mg/L)	RY (%)	q _e (mg/g)
20	3.85	31.4	37.2	29.1	3.78	30.8	38.5	30.0
25	3.82	31.2	37.6	29.4	3.70	30.6	38.7	30.0
30	3.83	31.3	37.4	29.2	3.77	30.8	38.5	30.1
35	3.81	31.1	37.7	29.5	3.79	30.9	38.1	29.8
40	3.78	30.9	38.3	29.9	3.78	30.8	38.5	30.0
45	3.80	30.9	38.0	29.7	3.70	30.6	38.7	30.3
50	3.80	31.0	38.0	29.7	3.70	30.6	38.7	30.4

The optimum removal efficiency was determined at 150 min for AC and at 180 min for AA-AC.

The rate of MV adsorption on AA and AA-AC adsorbents was investigated at temperatures of 20-25-30-35-40-45-50 °C in a 50 mg/L MV solution for 150 min. As seen in Table 2, dye removal yield percentage and adsorption capacity of adsorbents at equilibrium did not significantly change with increased temperature.

Adsorption isotherms

The adsorption isotherm expresses the relationship between the amount of substance adsorbed at constant temperature and the equilibrium pressure or equilibrium concentration. In this study, the Freundlich and Temkin adsorption isotherms were applied. The non-linear Freundlich equation is given according to Eq. 3[9]:

$$q_e = K_F C_e^{1/n} \quad (3)$$

where K_F(L/mg) is the Freundlich constant. The linear Freundlich equation is given in Eq. 4 and applied for MV dye adsorption (initial MV concentrations: 50-100-150-200-250-300-350-400-450-500 mg/L for 150 min at room temperature) on AC and AA-AC adsorbents.

$$\log q_e = \log K_F + \left(\frac{1}{n}\right) \log C_e \quad (4)$$

For the Freundlich adsorption isotherm, the linear log q_e versus log C_e plot was drawn and the kinetic parameters, n and K_F, were obtained from the slope and the intersection point of the linear plot, respectively, and are given in Table 3.

The Freundlich isotherms for AC and AA-AC are given in Figs. 5 and 6.

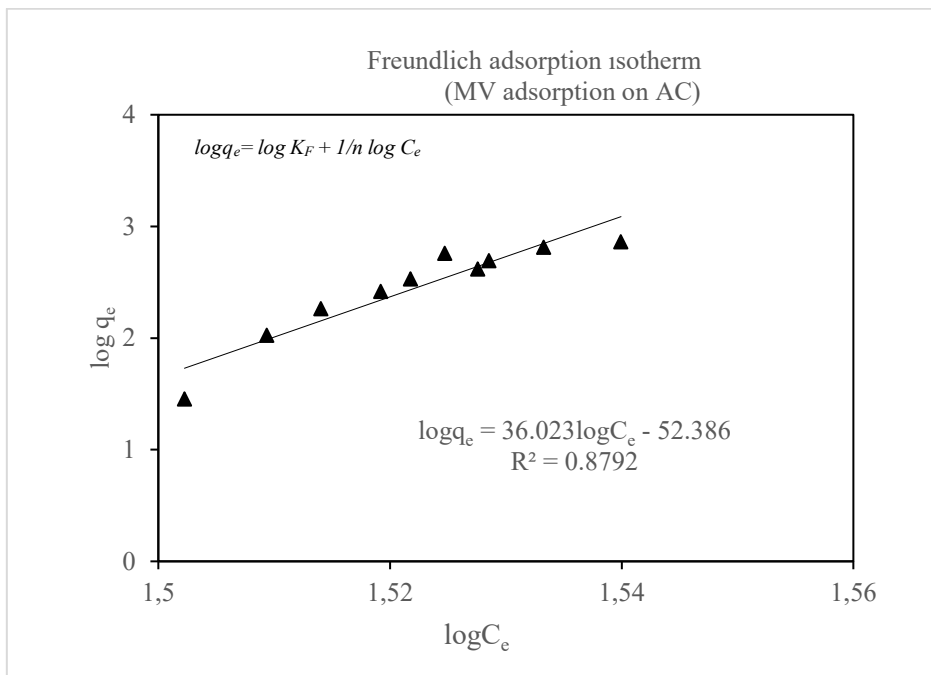


Figure 5. Freundlich isotherm for MV dye adsorption on AC

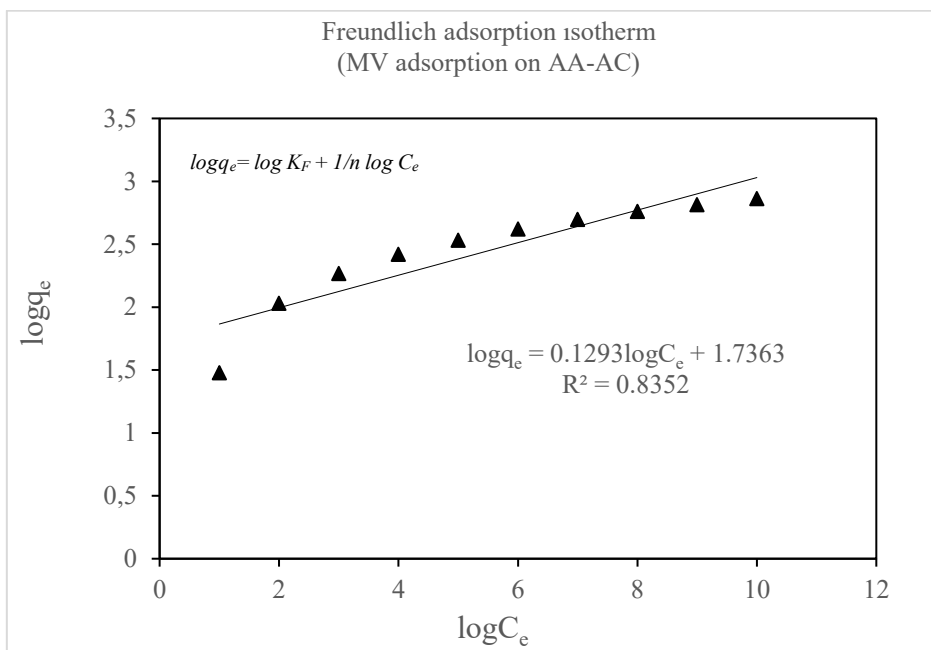


Figure 6. Freundlich isotherm for MV dye adsorption on AA-AC

The linear Temkin equation is given in Eq. 5 [10]:

$$q_e = \frac{RT}{b} \ln A + \frac{RT}{b} \ln C_e \quad (5)$$

where R is the universal gas constant ($J \text{ mol}^{-1} \text{ K}^{-1}$), T is temperature (K), A is Temkin isotherm equilibrium binding constant ($L \cdot g^{-1}$), b is Temkin isotherm constant.

For the Temkin adsorption isotherm, the linear q_e versus $\ln C_e$ plot was drawn and the Temkin adsorption isotherm parameters, A and b were obtained from the slope and the intersection point of this linear plot, respectively, and the results were given in Table 3.

The Temkin isotherms for AC and AA-AC are shown in Figs. 7 and 8.

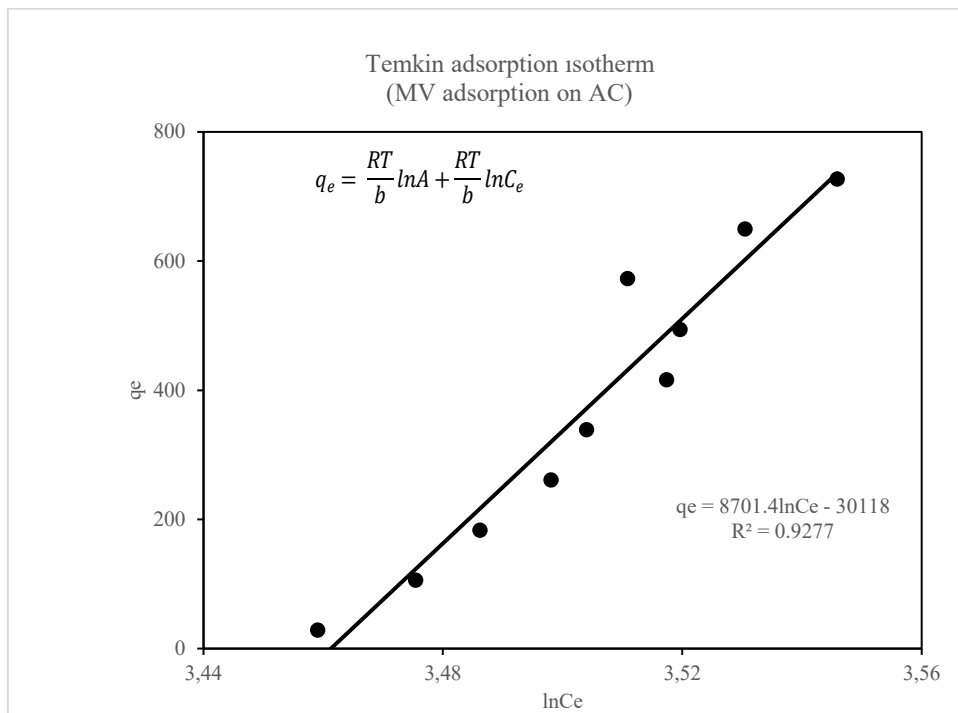


Figure 7. Temkin isotherm for MV dye adsorption on AC

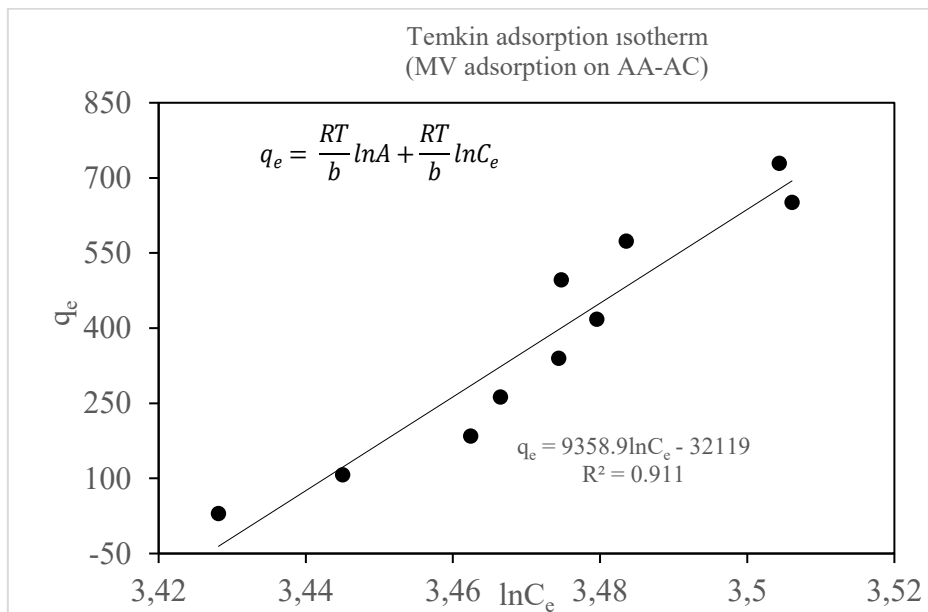


Figure 8. Temkin isotherm for MV dye adsorption on AA-AC

Table 3. Graphically determined parameters for Freundlich and Temkin isotherm models based on experimental studies

Isotherm		AC	AA-AC
Freundlich	logK _F (L.mg ⁻¹)	-52.4	1.7
	n	0.028	7.74
	R ²	0.879	0.835
Temkin	lnA	-3.46	-3.43
	b	0.28	0.26
	R ²	0.928	0.911

Table 4. Adsorption kinetics parameters for MV adsorption on AC and AA-AC

Kinetic Model	Parameters	AC	AA-AC
Pseudo 1 st	k_1	0.0012	0.0002
	R^2	0.068	0.008
Pseudo 2 nd	k_2	0.0023	0.0448
	R^2	0.798	0.993
WM ID	k_3	0.746	0.0539
	C	29.852	39.812
	R^2	0.0958	0.0093

According to the regression coefficients of these two isotherms, it was concluded that the experimental adsorption data fit well the Temkin isotherm model (Table 3).

Adsorption kinetics studies

Adsorption kinetics is used to show what kind of mechanism plays a role during the adsorption of the adsorbed substance onto the adsorbent surface. To determine the kinetics of MV removal from synthetic waste water solutions via AC and AA-AC, the pseudo-first [11], pseudo second order [12] and Webber-Morris intraparticle diffusion models (WM ID) [13] were tested by fitting the experimental data as shown in Eqs. 5, 6 and 7, respectively.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (5)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (6)$$

$$q_t = k_3 t^{\frac{1}{2}} + C \quad (7)$$

In the equations, q_t and q_e (mg. g⁻¹) are the amounts of MV adsorbed at various t times and equilibrium, k_1 (min⁻¹), k_2 (g.mg⁻¹. min⁻¹) and k_3 (mg.g⁻¹. min^{-1/2}) are the pseudo-first-order, pseudo-second-order and intraparticle diffusion model rate constants, respectively. C in Eq. 7 is the intercept related to the thickness of the boundary layer. The kinetic parameters for the adsorption of MV on AC and AA-AC adsorbents are given in Table 4.

Comparing the correlation coefficients of the three kinetic models, it is seen that the kinetics of MV adsorption onto AC and AA-AC followed the pseudo-second-order model.

CONCLUSION

The aim of this study was to develop a biopolymer-impregnated activated carbon adsorbent for the treatment of synthetic waste water containing

methyl violet dye by the adsorption technique. The plot of the adsorption isotherms showed that the Temkin model better represents the adsorption of methyl violet on AA-AC adsorbent. The kinetic studies proved that the adsorption of MV on AA-AC adsorbent fits the pseudo-second-order kinetic model with good correlation. The maximum MV removal yield with AA-AC adsorbent was obtained at 180 min as 55%.

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