

Methyl violet dye removal investigation on submicron particle size rubber powder obtained from scrap tyre functionalized with agar-agar

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In this study, submicron particle size rubber powder adsorbent obtained from scrap tyre functionalized with agar-agar (RP-AA) was used to remove methyl violet (MV) dye from synthetic wastewater. The effects of different reaction parameters such as initial MV concentration, contact time and solution temperature on the adsorption of MV onto RP-AA at constant adsorbent dose and pH were investigated. To explain the adsorption character of MV adsorption on RP-AA some kinetic models and adsorption isotherms were applied.

Keywords: Scrap tyre; Methyl violet dye; Agar-agar; Kinetic studies; Adsorption isotherms

INTRODUCTION

Methyl violet dye is mostly used in textile and paint industries. It is toxic and mutagenic, and because of this, it is harmful for the aquatic environment [1]. In industry, adsorption process is mostly used to treat the wastewater. Adsorption process is the process of separating chemical substances that cause pollution such as toxicity, color and odor, which are difficult to purify using classical purification, by adhering to the surface of a solid material (adsorbent) with chemical and physical bonds. The adsorption process is affected by pH, temperature and surface area of the adsorbent used [2]. Lots of adsorbents such as activated carbon, date seed, wood, zeolite, some waste sources, such as scrap tyre, have been used to remove dye from wastewater [3]. Agar-agar-functionalized activated carbon was used successfully to remove Pb^{2+} ion from wastewater [4]. This paper results demonstrated that agar-agar functionalization of adsorbent was useful to remove dye from wastewater.

In the present work, dye removal from a synthetic methyl violet solution with rubber powder obtained from scrap tyre functionalized with agar-agar adsorbent (RP-AA) was investigated. The adsorbent was characterized *via* FTIR-ATR spectral analysis to confirm the presence of agar-agar on rubber powder. RP-AA adsorbent was used to remove MV from synthetic wastewater solution and three kinetic isotherm models were applied.

EXPERIMENTAL

Methyl violet dye ($C_{24}H_{27}N_3ClH$) and agar-agar were purchased from Merck and Sigma-Aldrich, respectively (Fig. 1). Submicron particle size rubber powder ($<300 \mu$) was obtained from scrap tyre waste. 5 g of rubber powder surface was functionalized with 3.75 g of agar-agar in 50 ml of hot water by mixing at 85 °C for 24 h. After functionalization, RP-AA was washed three times with cold water to remove non-adsorbed agar-agar from the medium and dried in vacuum oven at 100 °C. Thermo Fischer Scientific Nicolet 10 model FTIR-ATR spectrophotometer, Sigma 3-18K model ultracentrifuge device, Shimadzu Uvmini-1240 UV Visible spectrophotometer and Daihan Scientific Multi-Heat Mixer were used.

A calibration curve was obtained as $A=0,1215C+0,0379$, $R^2=0.993$ from the absorbance values at wavelength 578 nm of 2-4-6-8-10 mg/L dye solutions prepared by diluting MV from 1000 mg/L stock solution in pure water.

Methyl violet was removed from synthetic waste water by adsorption on RP-AA. In all measurements, the amount of adsorbent was kept constant as 80 mg at pH 7 and the mixing speed was kept constant as 300 rpm. In 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) of MV dye adsorbed on RP and RP-AA from synthetic waste aqueous media were examined (Fig. 1).

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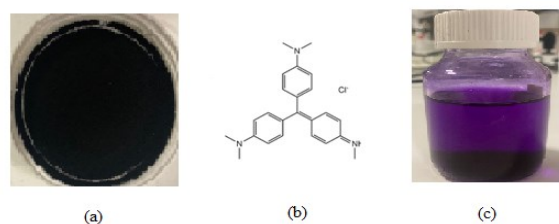


Figure 1. Picture of rubber powder (a), methyl violet dye (b), wastewater including methyl violet solution and adsorbent (c)

The adsorption capacity of RP-AA adsorbent, the amount of MV adsorbed at equilibrium, was calculated using Eq. 1:

$$q_e = \frac{(C_o - C_e).V}{w} \quad (1)$$

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 RP-AA adsorbent.

The dye removal percent yield (RY, %) of the adsorbent was calculated using Eq. 2 [1]:

$$\%RY = \frac{(C_o - C_e)}{C_o} . 100 \quad (2)$$

RESULTS AND DISCUSSION

FTIR-ATR analysis was carried out to determine the structure and functional group of agar-agar-modified scrap tyre rubber powder adsorbent and the FTIR-ATR spectra of RP and RP-AA are given in Figure 2.

Comparing the FTIR spectra of RP and RP-AA, the intensity of some peaks decreased, some new peaks were formed and some peaks were shifted.

Agar-agar-modified rubber powder showed characteristic bands at 3310 cm^{-1} (O–H stretching vibration of hydroxyl group of agar-agar) and 1147 (new sharp peak), 1075 , 994 , 930 cm^{-1} (C–O and C–C stretching vibrations of pyranose ring common to all polysaccharides)[5]. In order to investigate the contact time of the dye adsorption on adsorbents and to determine the optimum retention time of adsorption capacity, the adsorption removal efficiencies of RP-AA were examined for 30-60-90-120-150-180-210-240 min from the solution containing 50 mg/L dye. After the determined time passed, the batches were centrifuged for 10 min, the adsorption values of the solutions were taken with a UV-VIS spectrophotometer, C_e values were found from the calibration curve according to their absorbance at 578 nm, and adsorption capacity of adsorbent, q_e and dye removal yield percent (RY, %)

of RP-AA adsorbent were calculated according to Eqs.1 and 2, respectively, and results are given in Table 1. Time effect on ce , q_e , RY parameters of MV dye removal with RP-AA is shown in Fig. 3.

The average dye removal efficiency was determined as 37.5 ± 0.20 % for dye removal with RP-AA. It is seen that time did not affect the dye removal with RP-AA adsorbent.

The temperature effect on percent dye removal of RP and RP-AA adsorbents was studied within the temperature range of 20-25-30-35-40-45-50 °C in a 50 mg/L MV solution for 150 min.

Dye removal percent yield and adsorption capacity of adsorbents at equilibrium did not change significantly with increased temperature and it was obtained as average $37.2\% \pm 0.23$.

Adsorption isotherms and kinetics

The adsorption isotherm shows the correlation between the adsorption capacity at equilibrium, q_e and the equilibrium concentration of adsorbate, C_e . Langmuir [6], Freundlich [7] and Temkin [8] adsorption isotherms were applied to MV adsorption on RP-AA. To plot adsorption isotherms, initial MV concentrations were used as 50-100-150-200-250-300-350-400-450-500 mg/L for 150 min at room temperature on the RP-AA adsorbent. The results are given in Table 3.

The Temkin isotherm adsorption model equation is expressed as follows [8]:

$$q_e = B \ln A + B \ln C_e \quad (3)$$

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

For 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. The results are given in Table 4.

The Temkin isotherm corresponding to MV adsorption on RP-AA is plotted in Fig 4.

The regression coefficients of Langmuir, Freundlich and Temkin adsorption isotherms for RP-AA were determined as 0.44, 0.78 and 0.96, respectively. The experimental adsorption data fit well with the Temkin isotherm model for RP-AA since it had a higher correlation value than Freundlich and Langmuir isotherms.

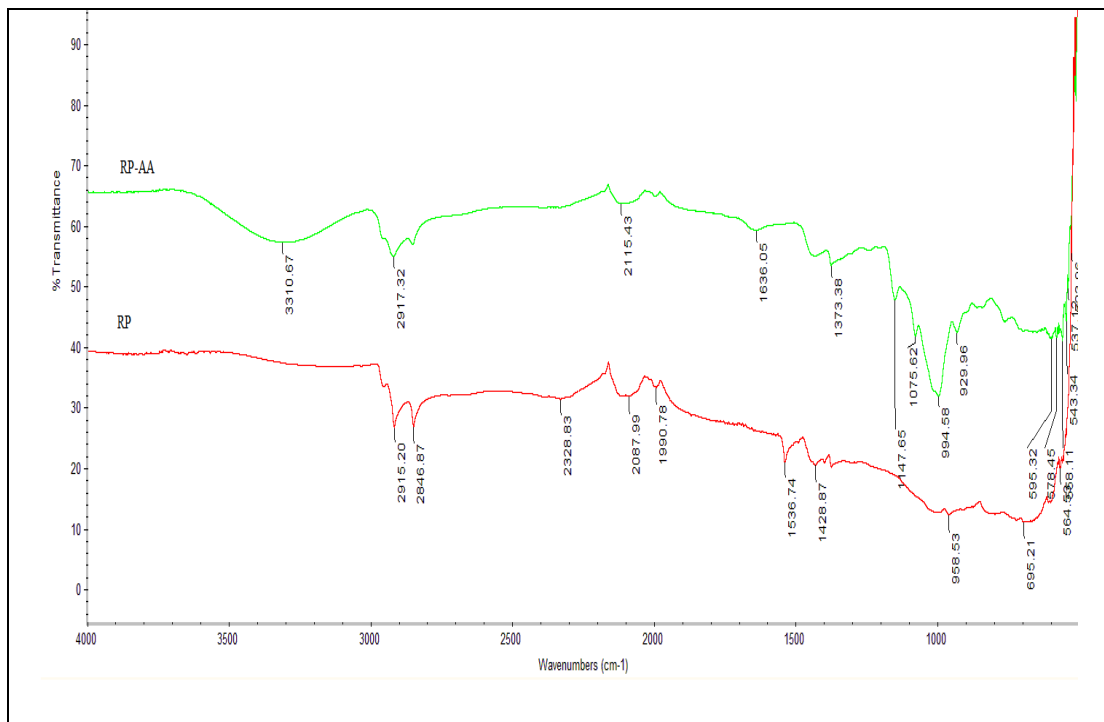


Figure 2. FTIR-ATR spectra of RP and RP-AA adsorbents

Table 1. MV dye solution concentration at the equilibrium stage, dye removal yield percent and adsorption capacity values of RP-AA adsorbents: effect of contact time.

t (min)	A	C _e (mg/L)	RY (%)	q _e (mg/g)
30	3.83	31.19	37.61	29.38
60	3.81	31.07	37.85	29.57
0	3.82	31.15	37.69	29.44
120	3.84	31.32	37.35	29.18
150	3.84	31.30	37.39	29.21
180	3.83	31.19	37.63	29.39
210	3.84	31.32	37.36	29.19
240	3.85	31.36	37.29	29.13

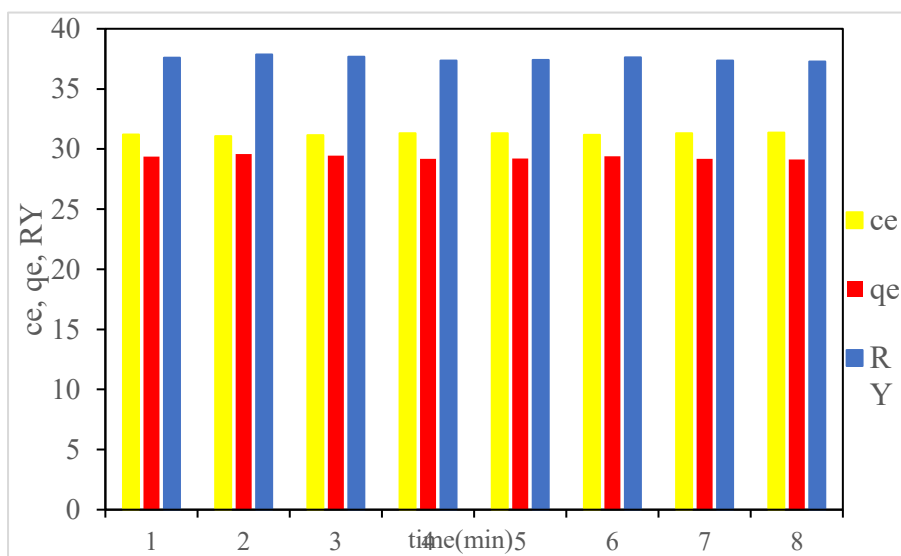


Figure 3. Changes of ce , qe and RY parameters of MV dye adsorption on RP-AA vs. time (1.30-2.60-3.90-4.120-5.150-6.180-7.210-8.240 min)

Table 2. Adsorption of MV on RP-AA adsorbent: temperature effect

T (°C)	A	C _e (mg/L)	RY (%)	q _e (mg/g)
20	3.87	31.52	36.97	28.88
25	3.85	31.39	37.22	29.08
30	3.84	31.28	37.44	29.25
35	3.86	31.46	37.06	28.96
40	3.87	31.53	36.94	28.86
45	3.85	31.41	37.18	29.05
50	3.83	31.22	37.56	29.35

Table 3. Adsorption of MV on RP-AA adsorbent: concentration effect

C _{MV} (mg/L)	A	C _e (mg/L)	RY (%)	q _e (mg/g)	lnC _e
50	3.87	31.57	36.85	28.79	3.45
100	3.91	31.90	68.09	106.39	3.46
150	3.96	32.16	78.56	184.12	3.47
200	3.91	31.88	84.06	262.68	3.46
250	3.98	32.46	87.01	339.90	3.48
300	4.00	32.65	89.12	417.74	3.49
350	4.04	32.91	90.59	495.46	3.49
400	4.05	33.03	91.74	573.39	3.50
450	4.09	33.32	92.59	651.06	3.51
500	4.10	33.49	93.30	728.93	3.51

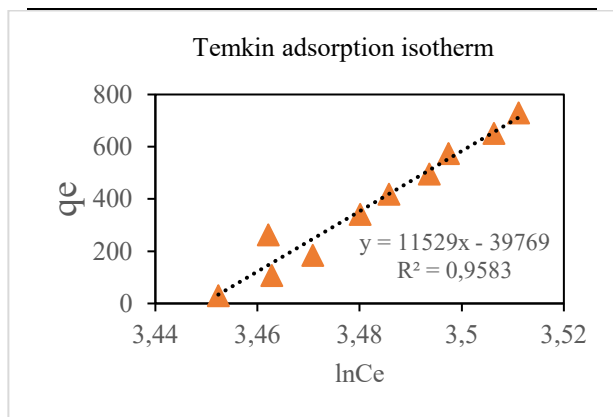


Figure 4. Temkin isotherm corresponding to MV dye adsorption on RP-AA

Adsorption kinetics reveals the adsorbed amount as a function of time and gives information about the adsorption speed, mechanism and adsorbent quality. The pseudo-first [9], pseudo-second order [10] and Webber-Morris intraparticle diffusion models (W-M

ID) [11] were applied for MV dye adsorption on RP-AA and kinetic parameters for the adsorption of MV on RP-AA adsorbent are given in Table 5. The kinetic model plots are given in Fig. 5.

Table 4. Parameters obtained from Freundlich and Temkin isotherms of MV adsorption on RP-AA adsorbent

Isotherm	RP-AA adsorbent	
Freundlich	K _F	3.4.10 ⁻⁶⁵
	n	0.023
	R ²	0.79
Temkin	B	11529
	lnA	-3.45
	b	0.21
	R ²	0.96

Table 5. Adsorption kinetic parameters corresponding to MV adsorption on RP-AA

Kinetic Model	Parameters	RP-AA
Pseudo 1 st	k ₁	-7.10 ⁻⁵
	R ²	0.49
Pseudo 2 nd	k ₂	1.2.10 ⁻³
	R ²	0.99
W-M ID	k ₃	-0.03
	C	29.66
	R ²	0.47

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

CONCLUSION

In this manuscript, the effects of time, temperature and concentration on the methyl violet removal from synthetic wastewater with agar-agar functionalized rubber powder obtained from scrap tyres were investigated. It was concluded that time and temperature did not affect the dye removal efficiency of the RP-AA adsorbent. The adsorption data and kinetic models were fitted into Langmuir, Freundlich and Temkin isotherms. The Temkin adsorption isotherm and pseudo-second-order kinetic model were found to have the highest regression value and, hence, the best fit. It could be concluded that submicron particle size rubber powder adsorbent obtained from scrap tyre modified with agar-agar is a potential and active biosorbent for removal of methyl violet dye from its aqueous solution and industrial wastewater treatment.

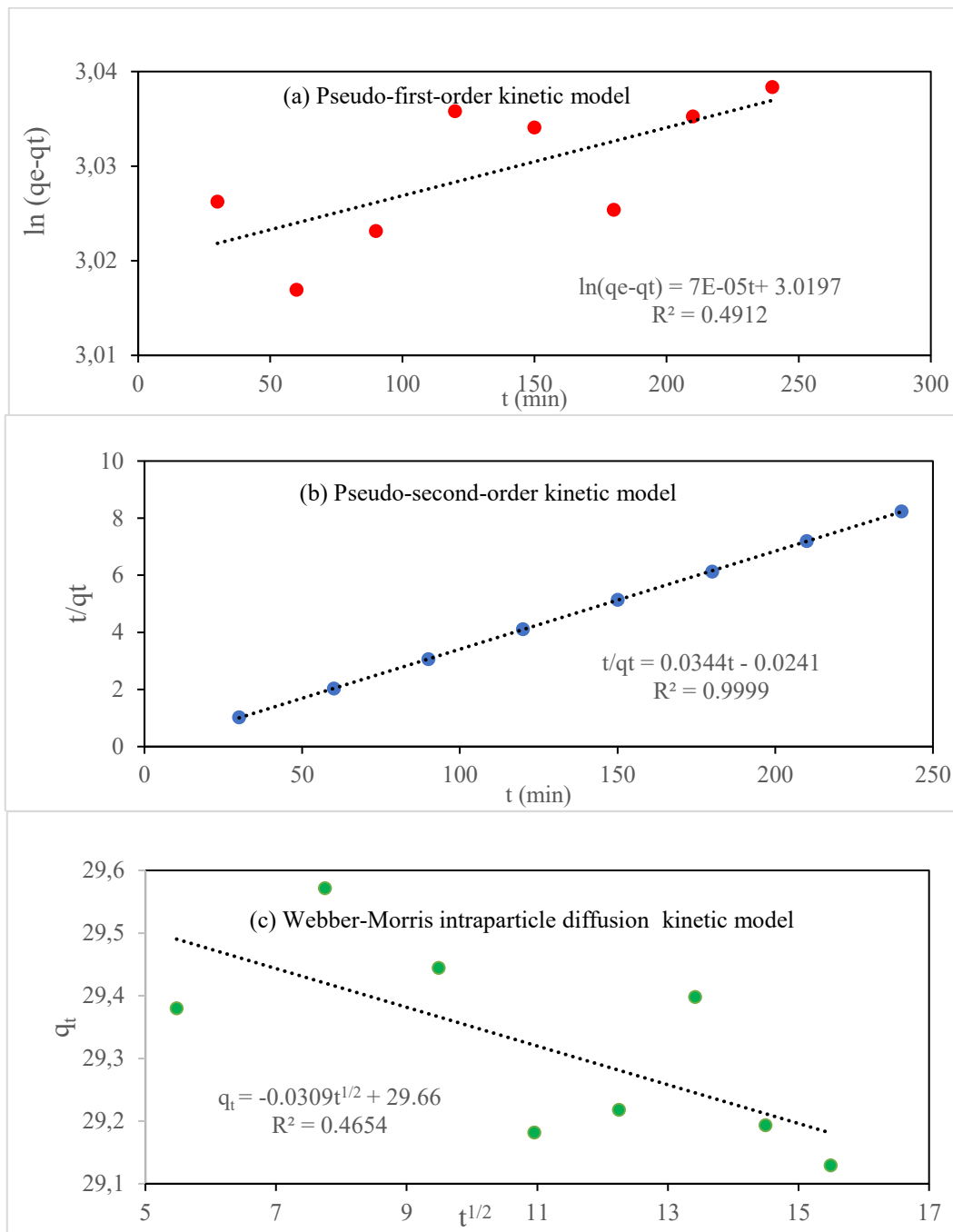


Figure 5. Kinetic studies: (a) pseudo-first-order, (b) pseudo-second-order, and (c) Weber-Morris intraparticle diffusion kinetic plots for the adsorption of MV onto RP-AA

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