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FAST ADSORPTION OF METHYLENE BLUE BY FILTER COFFEE WASTE

ABSTRACT

In this study, removal of a cationic dye methylene blue by filter coffee grounds as a potential waste was investigated. Systematically, the effect of initial dye concentration, pH and contact time on the adsorption efficiency were determined. Isotherm and kinetic models were studied. Langmuir and Freundlich model were calculated for adsorption of methylene blue. Langmuir model is better fit than Freundlich model (R^2=0.9892). The maximum adsorption capacity of filter coffee waste were 312.515 mg/g. Scanning electron microscope (SEM) images were used to record the surface characteristics and morphological features of filter coffee waste. This study emphases that filter coffee waste can effectively remove methylene blue from aqueous solution.

Keywords: Adsorption, Methylene Blue, Isotherm, Kinetic, SEM

1. INTRODUCTION

Annually, about 1.6 million tons of dyes (reactive, disperse, organic and direct) are produced. Substantial numbers of dyes are used in the textile, printing, leather, paper, food and cosmetic industries [1, 2 and 3]. These dyes are stable, toxic and pour biodegradable in the environment. Many industries waste water treatment plants do not remove the dyes efficiently. They have become a major contaminant of water bodies. It causes various diseases such as teratogenic, carcinogenic, and mutagenic disorders. It damage to human organs due to their toxic effects [4]. Also, wastewater with dye discharged into the aqueous environment without treatment, prevents the passage of sunlight slowing the rate of photosynthesis. This reduces the dissolved oxygen value which negatively affects the ecosystem [5 and 6]. There are many methods for treatment of this waste water such as flocculation, coagulation, adsorption, ultrafiltration, reverse osmosis, electrochemical treatments and photo catalytic oxidation [7, 8, 9, 10, 11 and 12]. Adsorption is one of the most effective methods for treatment of dye wastewater [13]. Although color removal may be obtained with active carbon, it is very expensive. Naturally, cheap, abundant and effective adsorbents have been used for the removal of dyes in recent years [14]. In recent years, researchers were studied large number of adsorbents such as chitin [15], coal gangue [16], almond shell residues [17], sunflower seed hull [18], cucumis sativus peel [19] modified spent tea leaves [20], powdered orange waste [21] for removal of waste water with dyes. Agricultural wastes are the most common raw materials being studied for removal of pollutants from waste water. The spent coffee waste obtained from the treatment of coffee with hot water. In 2011, in the whole world 4.0 million tons spent coffee waste was produces (U.S. Department of Agriculture (USDA)) [22]. There are a few studies that coffee waste can be used as an adsorbent for the removal of pollutants from aqueous solutions [23]. In

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this study the aim was to remove cationic dye pollutants from synthetic wastewater using filter coffee waste as an adsorbent with the batch method. For this purpose, the adsorption capacity of a potential waste product of filters coffee waste for cationic dye methylene blue was studied with the adsorption. The surface morphology studies analyses with SEM. Additionally, the contact time of adsorption, dye concentration and pH parameters were studied to find equilibrium and kinetic parameters.

2. RESEARCH SIGNIFICANCE

The importance of this study is the adsorption of methylene blue using filter coffee waste as an adsorbent, remove of a cationic dye and bringing coffee waste to the economy.

3. MATERIAL AND METHODS

3.1. Filter Coffee Waste

Filter coffee waste was provided a local coffee shop in Turkey. This waste was washed with distilled water to remove color and dirt and dried 50°C for 24 hours in an oven. Figure 1 shows washing step for filter coffee in laboratory.

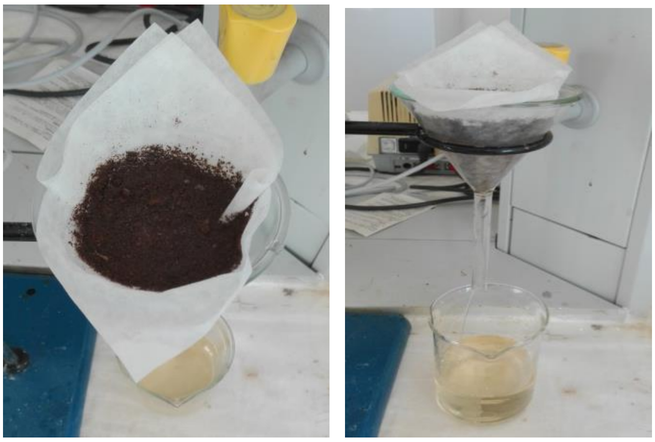
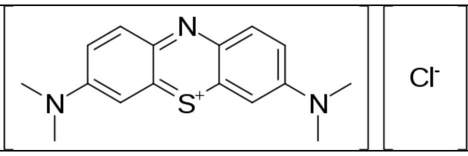


Figure 1. Washing step for filter coffee in laboratory

3.2. Adsorbate

Methylene blue was purchased from Carlo Erba Reagent. It is a cationic dyestuff (chemical formula $C_{16}H_{18}CIN_3S$, dye purity >90%). Table 1 is presented the characteristics of this dye.

Table 1. Chemical structure and characteristics of methylene blue [24]

Methylene Blue	
Molecular Weight (g/mol)	319.85
Color	Blue
λ_{max} (nm)	665
Dye purity	<90%
Chemical formula	$C_{16}H_{18}CIN_3S$
Structure	

3.3. Surface Morphology Studies

Before observing the SEM, all the samples were fixed on coated with gold and aluminum stubs.

3.4. Bach Adsorption Studies

Adsorption batch experiments were performed 250mL erlenmeyer. The pH was adjusted with 0.1 M HCl or 0.1 M NaOH. The adsorption amount of Methylene blue dye was calculated as follows, Equation 1:

$$\text{Amount of adsorption } (Q) = \frac{(C_o - C_t)V}{m} \qquad (1)$$

C_o : The initial dye concentration (mg/L)
C_t : The dye concentration after adsorption,
V: Dye volume (mL)
m: Adsorbent mass (g) [25].

4. RESULTS AND DISCUSSION

The SEM micrographs of filter coffee waste before and after methylene blue dye adsorption processes are given in Figure. 2-3. When Figure 2 is examined, it appears the no pores in filter coffee waste. After dye adsorption is examined, it appears to be a layered structure.

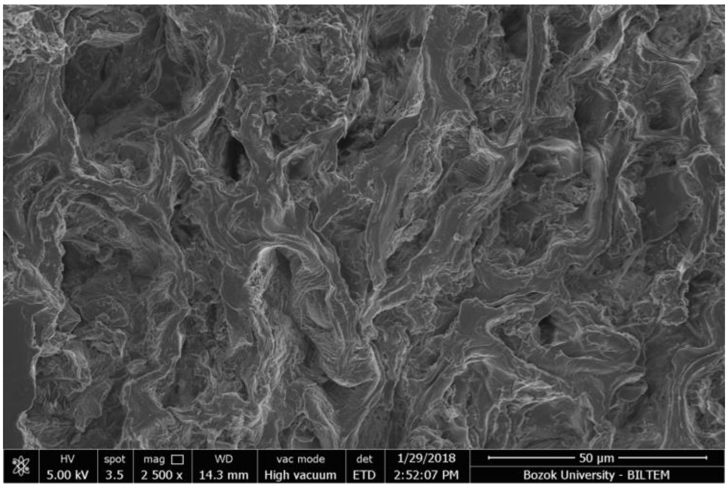


Figure 2. Filter coffee without dye

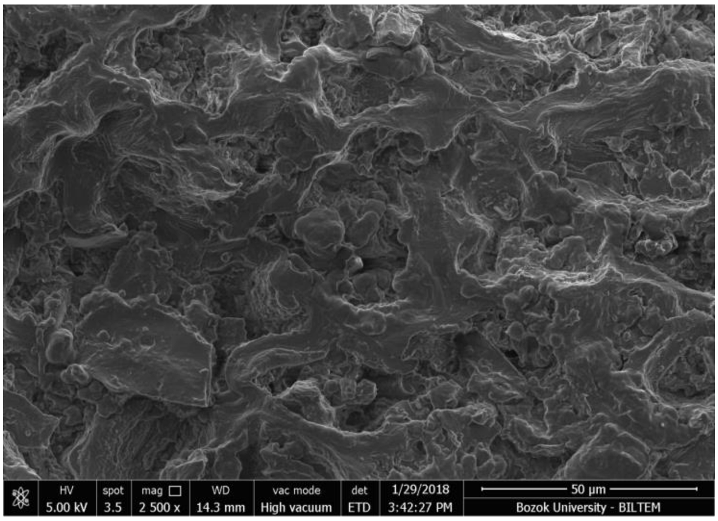


Figure 3. Filter coffee with dye

4.1. Effect of pH

The initial pH value is the most important factor give information about surface characteristic of adsorbent. Effect of pH is given in Figure 4. The effect of pH on the filter coffee waste of methylene blue was researched by varying the initial pH value from 2.6 to 10.0 while fixing the dye concentration at 100 mg/L, temperature at 25°C and adsorbent concentration at 0.3 g/100 mL. Figure 3 is shown that in an increase in adsorption capacity of the adsorbent, together with increased dye removal [26]. As the adsorbent surface begins to gain negative load, the initial pH value is increased. According to the results obtained, optimum pH was chosen as 10.0 considering the removal efficiency of methylene blue.

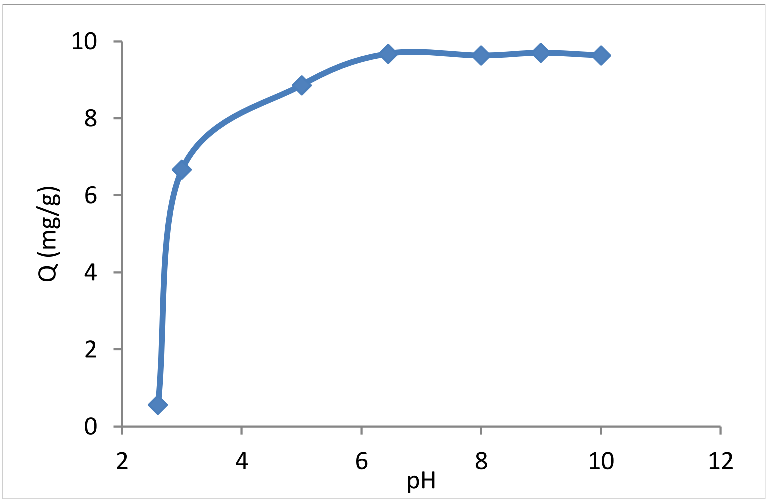


Figure 4. pH effect ($T=25^0C$, Adsorbent:0.3g, t=24h, $C_i=100$ mg/L)

4.2. Effect of Initial Dye Concentration

With the purpose of investigating the effects of initial concentration of the methylene blue, adsorption experiments were completed with pH 10, 0.3 g adsorbent dosage and temperature 25°C with dye concentrations from 100 to 4000 mg/L. Figure 5 is shown that effect of initial dye concentration. It reached equilibrium at 3500 mg/L.

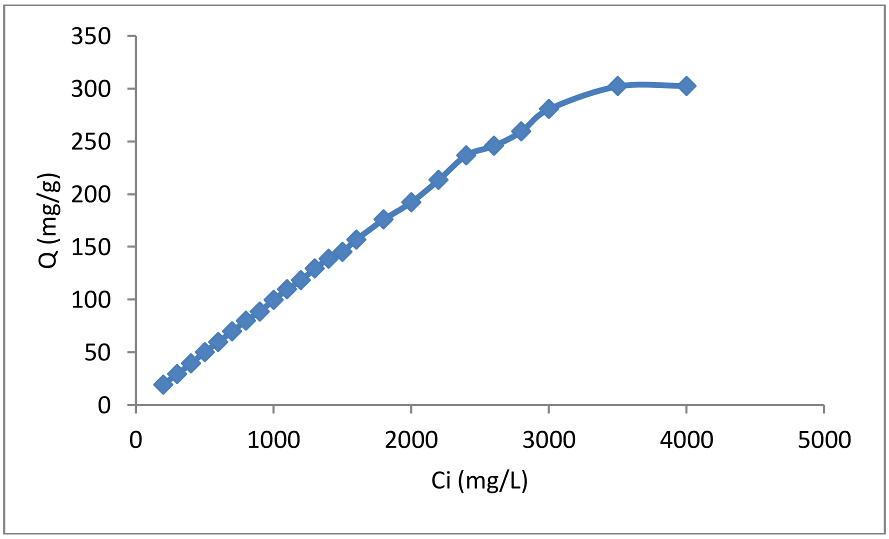


Figure 5. Effect of initial dye concentration

4.3. Effect of Contact Time on Adsorption

Figure 6 shows the effect of time of methylene blue onto filter coffee waste. The results described that there are two stages of adsorption. The first step is fast adsorption and then slows adsorption. Similar results found that Lou et al., (2019) [27].

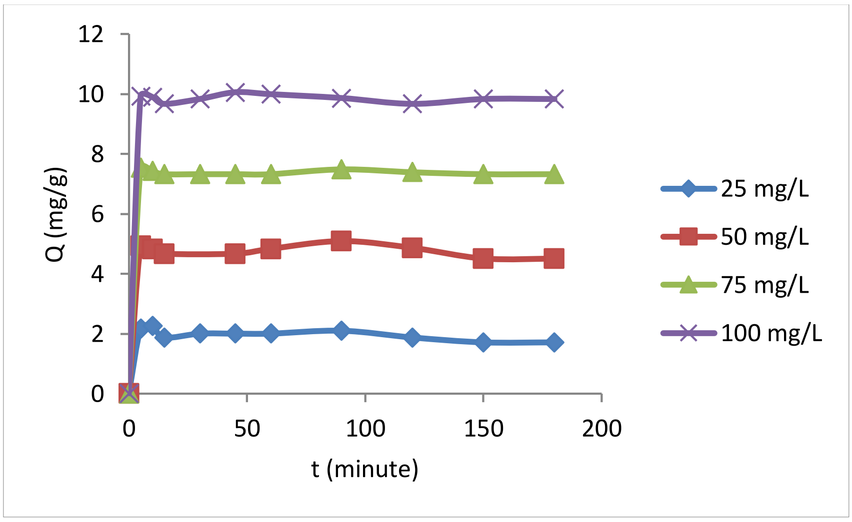


Figure 6. Effect of time

4.4. Isotherm Studies

Adsorption isotherms are used to explain the relationship between adsorbent and adsorbate under fixed equilibrium conditions, in addition to being used to calculate the maximum adsorption capacity. This study calculated the two-parameter isotherms of Langmuir and Freundlich. Table 2 is given that comparison of adsorption capacity from literature. Langmuir model which describes the monolayer adsorption of dye molecules on a homogenous surface with a limited number of identical sites is given by Equation 2 [28]:

$$\frac{C_e}{q_e} = \frac{1}{K_L} + (\frac{a_L}{K_L})C_e \quad (2)$$

where; C_e is the equilibrium concentration of adsorbate in solution after adsorption (mg/L), q_e is the equilibrium solid phase concentration (mg/g), as well as K_L (L/g) and a_L (L/mg) are the Langmuir constants. However, the Freundlich isotherm supposes a heterogeneous surface with a no uniform distribution and can be expressed by Equation 3:

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \quad (3)$$

where K_F (L/g) is the adsorption capacity at unit concentration and 1/n is adsorption intensity [29].

Table 2. Comparison of adsorption capacity

Adsorbent	Dye	Adsorption capacity (mg/g)	References
Degreased Coffee Beans	Malachite Green	55.3	[25]
Magnetic Green Coffee	Methylene Blue	66.2	[30]
Coffee Residues	Methylene Blue	4.68	[31]
Coffee Residues	Methylene Blue	112	[32]
Filter Coffee	Methylene Blue	312.515	This study

Table 3. Langmuir Constants

Adsorbent	Dye	K_L (L/g)	a_L (L/mg)	Qmax (mg/g)	R^2	References
Filter Coffee	Methylene Blue	9.813	0.0032	312.515	0.9892	This Study

Table 4. Freundlich Isotherm Constant

Adsorbent	Dye	n_F	K_F	R^2
Filter Coffee	Methylene Blue	2.991	41.9083	0.5953

Langmuir and Freundlich isotherm models given in Figure 7.

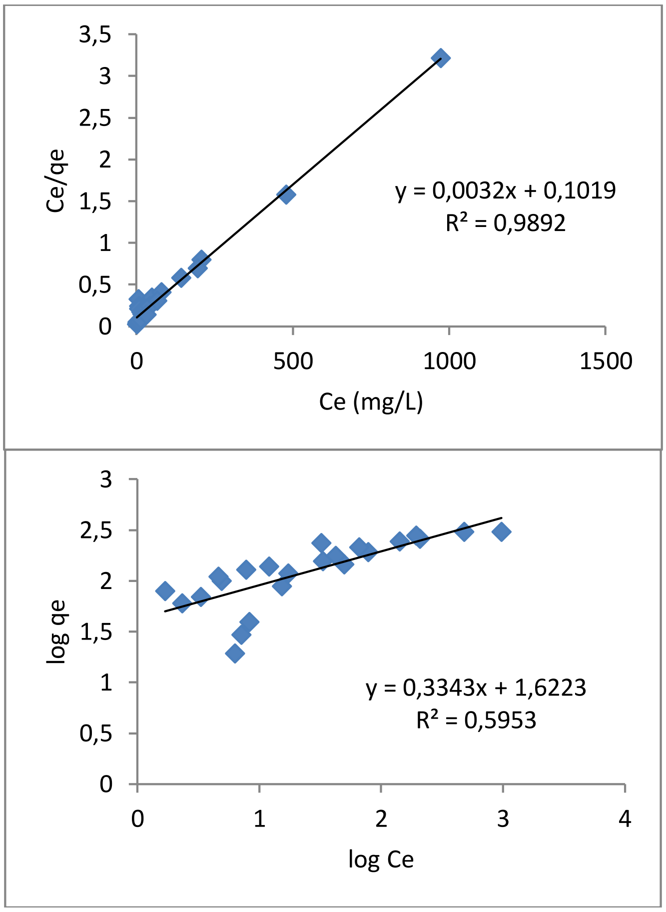


Figure 7. Langmuir and Freundlich Isotherms

4.5. Kinetic of Adsorption

Pseudo first order, pseudo second order and intraparticle diffusion models were tested for removal of methylene blue onto filter coffee waste (Table 5). The correlation coefficient (R^2) calculated for pseudo second order model and the values were higher than the other models. Pseudo second order kinetic model by:

$$\frac{t}{q_t}=\left[\frac{1}{k_{2,ad}q_{eq}^2}\right]+\frac{1}{q_{eq}}t \tag{4}$$

k_2 (g/mg•min) is the rate constant for the pseudo-second-order kinetics [33].

Table 5. Pseudo second order kinetic coefficient

Initial Dye Concentration (mg/L)	q_e	$k_{2,ad}$	R^2
25	1.737	0.145	0.9926
50	4.574	0.129	0.9966
75	7.347	0.946	0.9999
100	9.803	0.481	0.9999

Table 6. Intraparticle diffusion constants

Initial Dye Concentration (mg/L)	k_{id} (mg g^{-1} $dk^{-1/2}$)	R^2
25	0.9707	1
50	2.2043	1
75	3.3758	1
100	4.4404	1

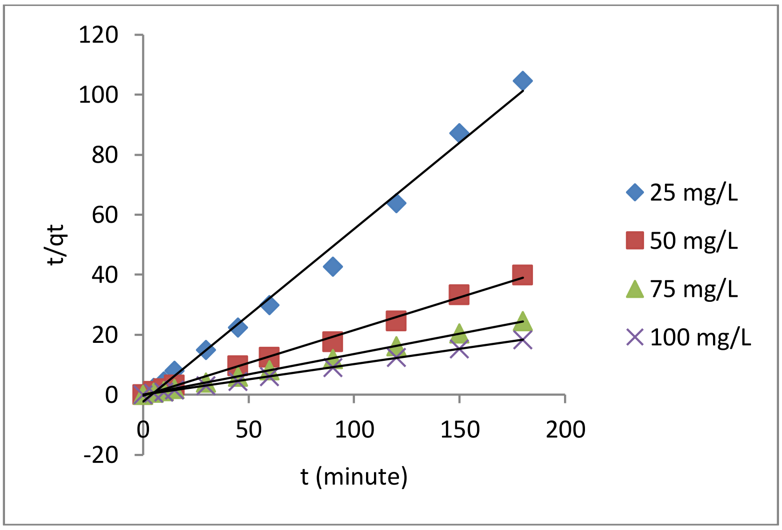


Figure 8. Pseudo second order kinetic model

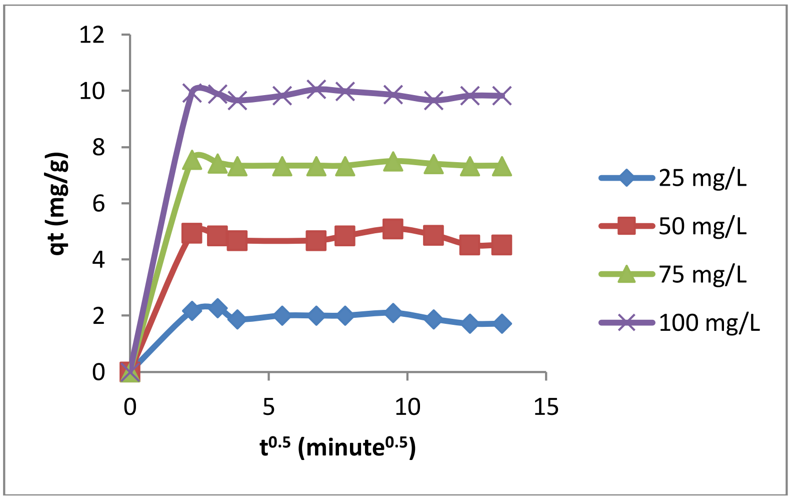


Figure 9. Intraparticle diffusion plot at different concentration for MB adsorption onto filter coffee waste

5. CONCLUSION

In this research, filter coffee waste was evaluated for removal of a cationic textile dye methylene blue. The effect of initial dye concentration, pH and contact time on the adsorption efficiency was studied. Langmuir model is better fit than Freundlich model (R^2=0.9892). The maximum adsorption capacity of filter coffee waste was 312.515 mg/g. Scanning Electron Microscope (SEM) images were used to record the surface characteristics and morphological features of filter coffee waste. The filter coffee waste can use of removal of methylene blue from aqueous solution.

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