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International
Journal
Of Modern Engineering Research (IJMER)

Adsorption of Methylene Blue From Aqueous Solution with Vermicompost Produced Using Banana Peel

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ABSTRACT: *The removal of Methylene blue as a synthetic dye from aquatic system was investigated by using vermicompost. The dye concentration, contact time and pH of the solution carried out in the adsorption studies. Batch adsorption experimental data were suitable for the Langmuir isotherm and a very good fit to the second order kinetic model (pH=10). The maximum adsorption capacity calculated 256.66 mg g-1 . Vermicompost and the dye loaded vermicompost were characterized by SEM and FTIR. It was found that the vermicompost is stable without losing their activity.*

Keywords : *Vermicompost, adsorption, environment, FTIR, SEM.*

I. INTRODUCTION

There are more than 100,000 different dye structures have been synthesized for the [1] industrial applications. These dyes can be divided into different groups, such as anionic, cationic, and nonionic [2]. The cationic dyes are especially used in our daily life. However, these dyes are extremely toxic, hazardous, non-biodegradable and mutagenic agents for the body. These dyes cause irritation, itching, scaling for human body. The existence of organic dyes in wastewater has a negative effect on the aquatic organisms because they reduces the penetration of sunlight [3–4]. They can threat aquatic life by giving rise to failure in brain and central nervous system as well as the function of kidneys, reproductive system [5, 6]. Vermicompost is formed by a mixture of organic matter, by earthworm action in a 3 or 6 month period[7]. Vermicompost can be obtained from different sources such as cattle and pig manure with soil and municipal solid waste [8-10]. There are three main methods, as physical, chemical, and biological for the removal of dyes from aquatic environment [11-15]. In our work, the adsorption behavior of vermicompost that was produced from domestic waste especially banana peel with soil by the worms was studied on methylene blue adsorption in aqueous solutions by a batch technique. In this study, vermicompost as an alternative adsorbent material for removing of dyes such as methylene blue from aquatic environment.

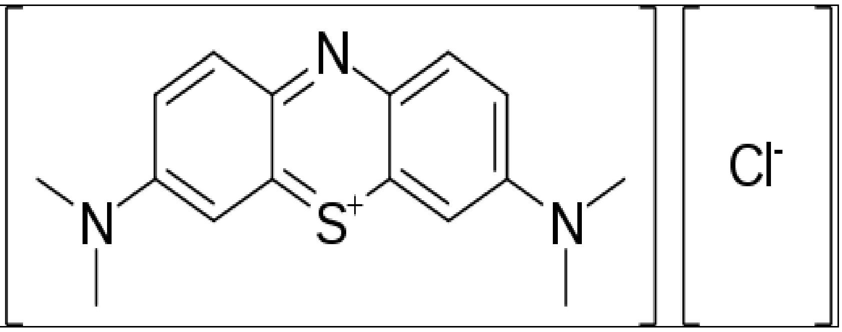
II. MATERIAL AND METHODS

2.1.Materials

Methylene blue was purchased from (Carlo Erba Reagent). It is a cationic dyestuff (chemical formula $C_{16}H_{18}CIN_3S$, dye purity >90%). This dye was commercial product and used without purification. The characteristics of this dye are presented in Table 1

Table 1. Chemical Structure of Methylene blue [16]

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	

2.2. Experimental studies

Adsorption studies were performed in 100 mL Erlenmeyer Flasks. Methylene blue solution (30 mL) added 0.1 g vermicompost. All the adsorption experiments were performed at 25°C via batch method. The solution was shaken by a mechanical shaker (VWR) at the constant agitation time (150 rpm) during 5 hours. Then the supernatant was centrifuged at 4000 rpm and 10 minutes in a centrifuge (Hettich Zentrifugen) after the batch tests. The absorbance of dye was measured at maximum wavelength (λ_{max}:665 nm) by UV–VIS Spectrophotometer (Shimadzu UV 1208). For the contact time experiments, the dye concentrations were varied from 100 to 500 mg/L. The incubation time was tested in a time from 10 to 180 min. All experiments were repeated twice. The adsorption amount of Methylene blue dye was calculated as follows, Eq. 1:

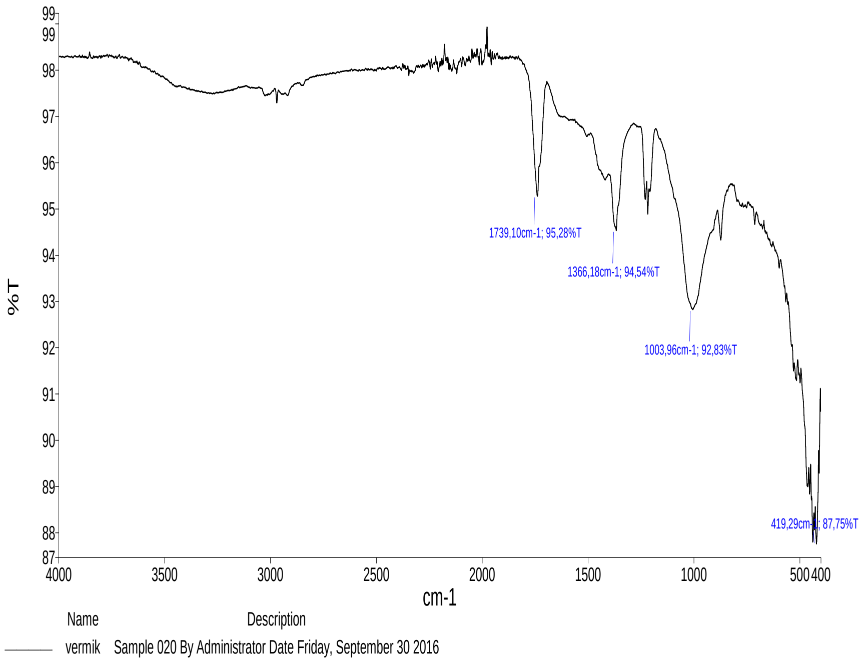
$$\text{Amount of adsorption } (Q) = \frac{(C_o - C_t)V}{m} \qquad (1)$$

C_o is the initial dye concentration (mg/L) whereas C_t is the dye concentration after adsorption, V dye volume (mL), m adsorbent mass (g) [17-19].

III. RESULTS AND DISCUSSION

3.1.Functional groups

Fig 1 presented the FTIR spectra of vermicompost before and after dye adsorption. Comparing the two spectra, it is seen that after the adsorption of methylene blue, new peaks appear in the spectra Fig 1. (b), of vermicompost. These findings implied that methylene blue is adsorbed by vermicompost.



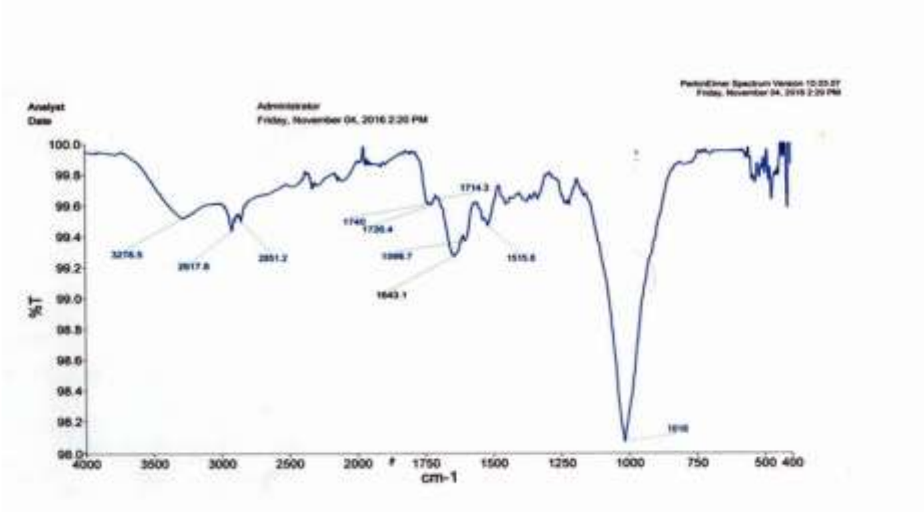


Figure 1. FTIR spectra of vermicompost before (a) and after dye adsorption (b)

3.2.SEM Images

SEM fotos of unloaded and dye loaded adsorbent presented Fig 2. After the methylene blue adsorption onto vermicompost, as seen in Fig 2. b, a large number of pores are filled with large amount of dyes.

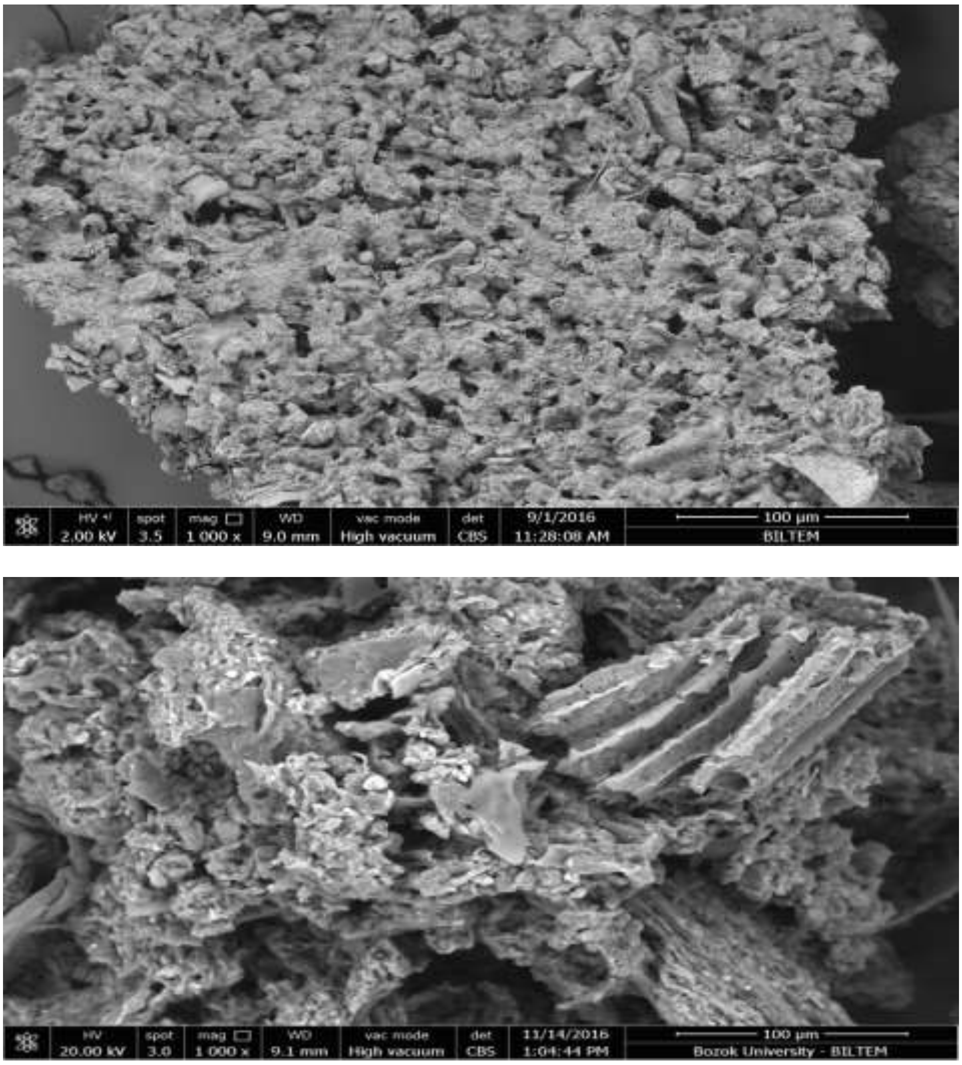


Figure 2. SEM fotos of unloaded (a) and dye loaded (b) vermicompost.

3.3. Effect of time on adsorption

The influence of contact time on the dye adsorption was studied in the range of 0-180 min (Fig 3.). The initial dye concentration effect on the adsorption of dye was examined in the range of 100-500 mg L^{-1} . As seen in figure 3, when initial dye concentration is increased, adsorption rate is increased due to mass transfer driving force becoming larger, thus, resulting in adsorption of methylene blue. Similar result was observed for the adsorption of methylene blue from aquatic solution by prepared activated carbon from coconut husk [20]. The time for reaching the adsorption equilibrium about is 1 hour. Also, as shown in Figure 3 equilibrium reach time is not effected by initial dye concentration.

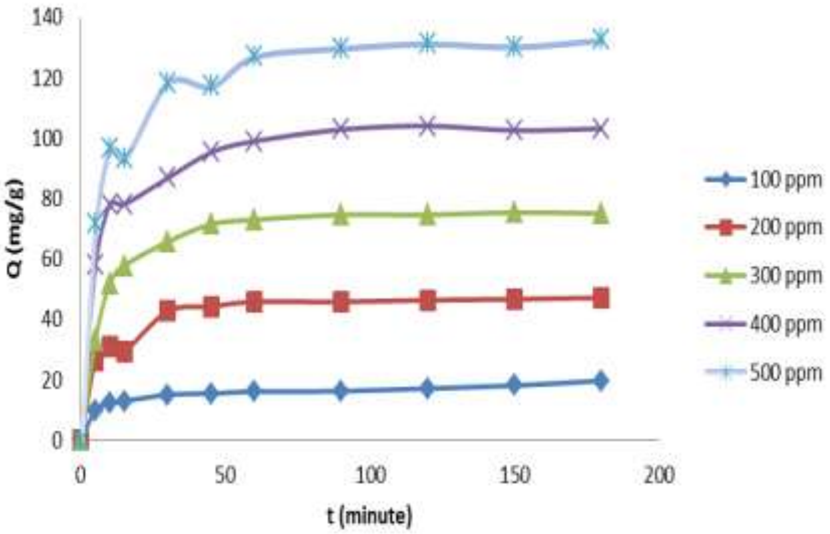


Figure 3. Variation of specific adsorption with time for various initial dye concentrations (W=0.1 g, pH=10, V=30 mL, T= 25 ^{0}C)

3.4. Effect of initial dye concentration

Fig 4 describes that effect of initial dye concentration on methylene blue removal. As shown in Figure 4, when initial dye concentration is increased, adsorption amount of methylene blue is increased until 800 mg/L. After that, adsorption amount of methylene blue was not change with increasing initial dye concentration because of saturation of functional group into vermicompost. In addition to, as seen in figure 4, it seems that it is almost 100% of the removal rate in the wide concentration range. In this situation, it has been observed that the vermicompost produced from the banana peels can be used as an adsorbent in the removal of methylene blue at a wide concentration range.

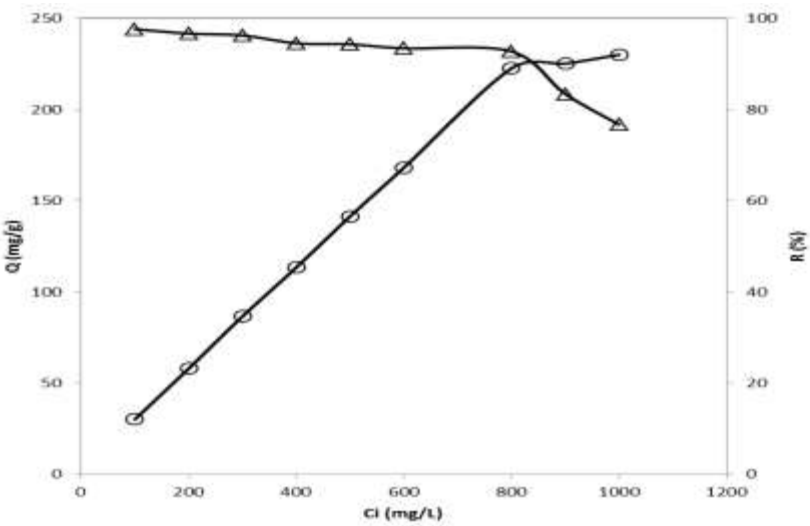


Figure 4. Effect of initial dye concentration

3.5.Adsorption isotherms

Langmuir model equation is given by Eq 2 [21]:

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

C_e :The equilibrium concentration of adsorbate in solution after adsorption (mg/L)
q_e :The equilibrium solid phase concentration (mg/g)
K_L (L/g) and a_L (L/mg): Langmuir constants.
However, the Freundlich isotherm can be expressed by Eq. 3:

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

K_F (L/g): The adsorption capacity at unit concentration
1/n:Adsorption intensity.
Dubinin-Radushkevich isotherm is used for understand of adsorption type. Free energy (E) can be computed by the equation as given below [22-26].

$$E = \left[\frac{1}{\sqrt{2B_{DR}}}\right] \qquad (4)$$

B_{DR} :The isotherm constant. The parameter ε can be correlated as:

$$\varepsilon = RT\ln\left[1 + \frac{1}{C_e}\right] \qquad (5)$$

R: The gas constant (8.314 J/mol K)
T: Temperature (K)
C_e :Equilibrium concentration (mg/L)

Ɛ value is calculated equation 5. $Ɛ^2$ plot against ln Qe was drawn for the D-R isotherm and B_{DR} was calculated from slop of graphic. After that, E value was calculated using equation 4. In this study, isotherm parameters of methylene blue adsorption onto vermicompost obtained from equilibrium models was given Table 2. Adsorption of methylene blue on vermicompost were suitable for the Langmuir isotherm (pH=10) because of higher R^2. This means that the surface is homogeneous. Also, it is described that adsorption is monolayer and all the adsorption sites of vermicompost are identical. The maximum adsorption capacity was found to be 256.66 mg g^{-1}. Adsorption capacity of different adsorbents in literature was given in Table 3. When found adsorption capacity is compared with given values in literatures, found adsorption capacity in this study is much higher than that of given adsorbent in the literatures. It can be offered that vermicompost as an alternative adsorbent material for removing of dyes such as methylene blue from aquatic environment. Adsorption of methylene blue onto vermicompost has been determined that physical adsorption according to D-R Isotherm [34].

Table 2. Isotherm parameters

Langmuir	Parameter (unit)	Value
	K_L (L/g)	11.627
	a_L (L/mg)	0.0453
	Qmax (mg/g)	256.666
	R^2	0.9946
Freundlich Isotherm	n_F	1.831
	K_F	18.378
	R^2	0.8768
Dubinin-Radushkevich	q_m	375.177
	E	0.707
	R^2	0.8315

Table 3. Comparision of adsorption capacity of Methylene blue on vermicompost in literature

Adsorbent	Dye	Q_{max} (mg/g)	References
Biochars (produced by pyrolyzing vermicompost)	Congo red 300 ^{0}C 500 ^{0}C 700 ^{0}C Methylene blue 300 ^{0}C 500 ^{0}C	 11.63 20.00 31.28 174.22 36.11	[27]

	700 ^{0}C	27.35	
Micro-organisms based compost	Malachite green	150.8	[28]
Vermicompost (at column)	Crystal violet Methylene blue	0.78 5.47	[29]
Wheat straw (WS) was modified using phytic acid	Methylene blue	205.4	[30]
Citrus limetta peel	Methylene blue	227.3	[31]
Cucumber peels	Methylene blue	111.1	[32]
Coconut coir dust	Methylene blue 30 ^{0}C 40 ^{0}C 50 ^{0}C 60 ^{0}C	 29.50 21.14 20.41 20.16	[33]
Vermicompost derived banana peel with soil	25 ^{0}C	256.66	This study

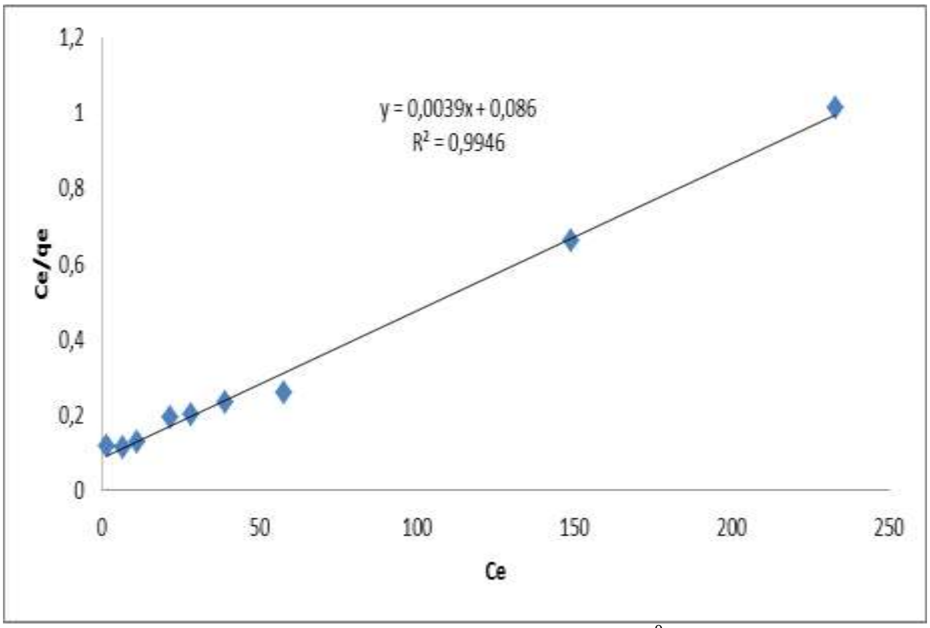


Figure 5. Langmuir Isotherm (pH=10; T=25 ^{0}C; t=5 h)

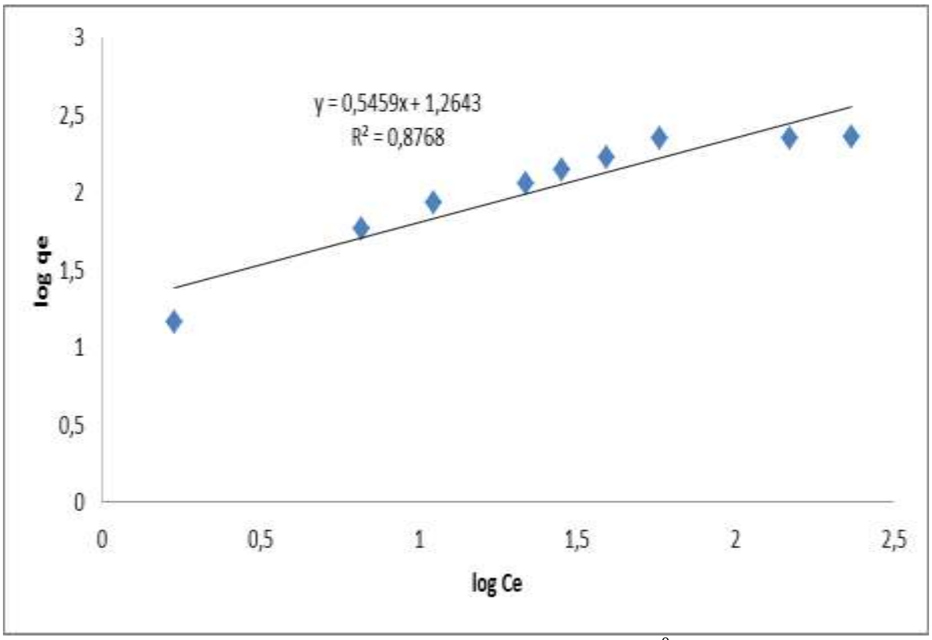


Figure 6. Freundlich Isotherm (pH=10; T=25 ^{0}C; t=5 h)

3.6.Kinetic of dye adsorption

The kinetic rate equations can be written as:

$$\log \frac{(q_e - q_t)}{q_e} = -\frac{k_{1,ad}t}{2.303} \qquad (6)$$

q_e and q_t: The amount of adsorbed on the vermicompost (mg/g) at equilibrium
t : (min): Time
k_1 (1/min): The rate constant of pseudo-first-order kinetics.
The pseudo second order equation is:

$$\frac{t}{q_t} = \left[\frac{1}{k_{2,ad}q_{eq}^2}\right] + \frac{1}{q_{eq}}t \qquad (7)$$

k_2 (g/mg•min): The rate constant[35].

Second order rate equation can be written as:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + kt \qquad (8)$$

k (g/mg•min): The rate constant.

The Weber's intraparticle diffusion model is given as:

$$qt=k_{id}t_{1/2}+C \qquad (9)$$

where k_{id} is the intraparticle diffusion rate constant (mg.g^{-1} h$^{-1/2}$) and C (mg.g^{-1}) is a constant that gives idea about the thickness of the boundary layer. If the qt vs. $t^{1/2}$ plot is a straight line, then the adsorption process is only controlled by intraparticle diffusion [36-38]. Fig7 shows that the intraparticle diffusion for methylene blue on vermicompost. The parameters of these three models are given in Table 4-5-6. According to the Table 4-5, adsorption of methylene blue on vermicompost is more fitted pseudo second order kinetic model than pseudo first order kinetic model and intraparticle diffusion, due to high R^2 values. Also, found experiment of qe values are very near calculated of qe values.

Table 4. Values of Pseudo First Order Kinetic Model

Initial Dye Concentration (mg/L)	qe (mg g^{-1}) (experiment)	qe (mg g^{-1}) (calculated)	k_1 (min^{-1})	R^2
100	16.086	3.475	0.0345	0.3998
200	45.788	8.515	0.0271	0.1224
300	72.961	11.694	0.0278	0.1007
400	98.943	10.819	0.00644	0.0065
500	127.008	12.217	0.00368	0.0017

Table 5. Values Of Pseudo Second Order Kinetic Model

Initial Dye Concentration (mg/L)	qe (mg g^{-1}) (experiment)	qe (mg g^{-1}) (calculated)	k_2 (g mg^{-1}min^{-1})	R^2
100	16.086	27.322	0.00159	0.8435
200	45.788	48.076	0.00478	0.9987
300	72.961	76.923	0.0130	0.9993
400	98.943	105.263	0.00256	0.9992
500	127.008	135.135	0.00180	0.9991

Table 6. Values Of Weber-Morris

Initial Dye Concentration (mg/L)	k_p (g mg^{-1}min$^{-1/2}$)	R^2
100	3.9623	0.9892
200	10.153	0.9762
300	16.108	0.9946
400	24.905	0.9982
500	30.825	0.9987

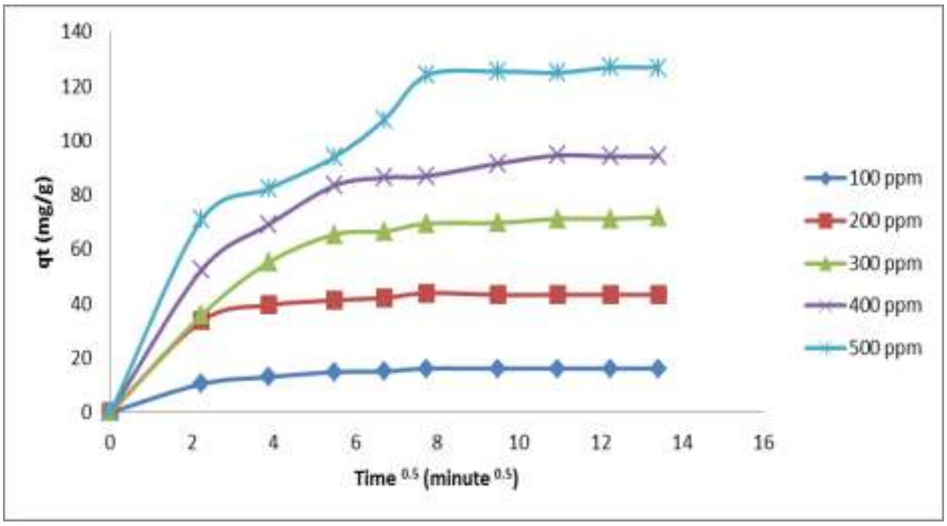


Figure 7. The intraparticle diffusion for methylene blue on vermicompost

3.7. Reusability

The exapriment was repeat five times (Fig 8). The experiments did five times. It was shown that the adsorption capacity of vermicompost did not change. This results shows that vermicompost are reusable adsorbent for the removal of Methylene Blue.

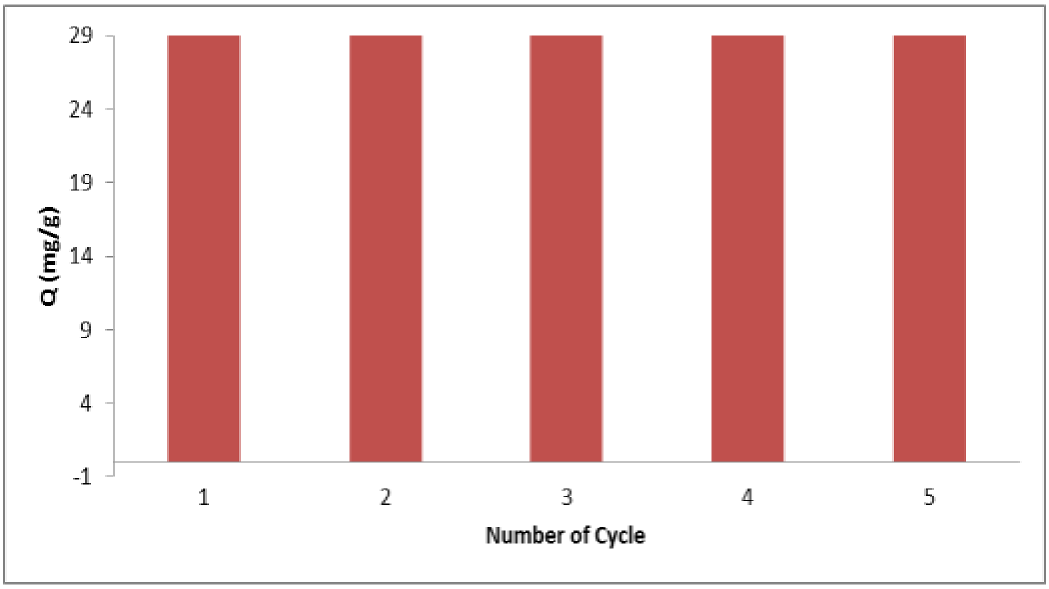


Figure 8. Methylene Blue adsorption capacity of vermicompost after adsorption/desorption cycle (Ci=100 ppm, T=25 ^{0}C, t=5 h pH=10)

IV. CONCLUSION

The adsorption of a methylene blue onto vermicompost was investigated. The SEM and FTIR shown the interactions between vermicompost surface and dyes. The experiments did five times the regeneration of vermicompost never losing their activity.

Batch adsorption experimental data were suitable for the Langmuir isotherm and second order kinetic model (pH=10). It has high capacity (256.66 mg g^{-1}).

ACKNOWLEDGEMENTS

Editor thank to Bozok University Scientific Research and Project Department (BAP) Project number: 6601-FEB/17-64.

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Halil Kayaalp. "Adsorption of Methylene Blue From Aqueous Solution with Vermicompost Produced Using Banana Peel." International Journal of Modern Engineering Research (IJMER) 7.7 (2017): 64-73.