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Vermicompost as a Potential Adsorbent for the Adsorption of Methylene Blue Dye from Aqueous Solutions

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Abstract: Vermicompost (VC) as a low cost and waste-derived material was used as an adsorbent to remove textile dye effluents from the wastewater. Methylene blue (MB) was selected as a representative of dye effluents and its adsorption to VC was investigated. The effect of parameters such as pH, adsorption time, and the initial concentration of MB were determined via lab-scale batch experiments. The highest adsorption capacity of VC was reached when the pH of the solution was 4. The equilibrium was maintained after 90 minutes of operation since the removal percentage of MB was stabilized at 99%. The pseudo-second-order kinetic model described the most appropriate adsorption kinetic behavior. Both Langmuir (R^2=0.9891) and Freundlich isotherms (R^2=0.9895) fitted very well to the experimental data. Based on these results, vermicompost can be evaluated as an alternative adsorbent for the removal of dye effluents.

Keywords: Adsorption, Isotherms, Kinetics, Methylene Blue, Vermicompost.

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INTRODUCTION

Composting and vermicomposting are two biological processes to convert organic wastes such as sewage sludge, municipal solid waste, etc. into soil amendments (1). Composting is homogenization of mixed organic wastes by means of thermophilic process at a temperature range of 45 to 65 °C, while vermicomposting is the stabilizing the organic wastes or compost by the digestion of earthworms and micro-organisms at 35 °C (1,2). The final products after two processes have nutrients for the soil, humic acid, and metals together with high moisture contents; compost with 40 to 60 wt.% and vermicompost with 70 to 90 wt.% respectively (3).

Converting organic wastes into vermicompost is perceived as environmentally and economically sustainable since the product could be used as a promoter for plant growth and soil amendment. However, there are reports in the literature criticizing the usage of compost and vermicompost as soil amendments since they may have pathogens and heavy metals which are hazardous for the human. Although vermicomposting reduce somewhat human pathogens, regulations by the governments limit the usage of compost and vermicompost due to their hazardous nature to human health (4). This situation influenced the researchers to investigate alternative usage areas for compost and vermicompost different from agricultural purposes. Vermicompost has gained attention to be used as an adsorbent to remove organic and inorganic contaminants in the wastewater and studies showed that due to its high surface area and functional groups existing naturally, making vermicompost an effective adsorbent (5). Especially the humic substances in the organic fraction of vermicompost provide the high surface area with high porosity, high density of negative charges, and noticeable cationic exchange capacity.

Adsorption is a widely known technique applied to wastewater to remove organic and inorganic contaminants. Activated carbon is one of the most promising adsorbents according to the studies in the literature (6). However, its high cost limits its applicability therefore investigation of alternative adsorbents with low cost and appropriate characteristics is crucial. In this regard, compost, clays, chitosan, peats, biochar, etc. were utilized and a variety of contaminants tested in order to extract their potential as an effective adsorbent (7). Vermicompost, on the other hand, has proper physical and chemical properties to be evaluated as an absorbent, and its low cost attracts researchers to investigate its adsorption capability. Currently, vermicompost's price is around 20 TRY/kg and according to a recent report, its annual production rate was about 20,000 tonnes in 2017, in Turkey (8).

Early studies focused on the metal removal from the wastewater and the results were promising. Vermicompost produced from cattle manure was utilized in a glass column to determine its adsorption capability on Cu, Ni and Zn, and it was proven that higher adsorption rates were achieved compared to various adsorbents such as sewage sludge, apple residues, peat moss etc. (5). Zhu et al. reported that high removal efficiencies of Pb and Cd from wastewater stream were possible when cow manure and its vermicompost were used as adsorbent. They also determined that the performance of vermicompost was better and mainly the functional groups such as aliphatic alcohols, aromatic acids, carbonates, and phosphates contributed to the efficient removal of the metals (9). Pesticide methylparathion removal from water stream via adsorption onto vermicompost was studied as well and the results suggested that experimental data fitted to the Langmuir linear model yielding 0.17 mg/g of maximum adsorption capacity (10).

Apart from the metals and pesticide, dye effluents such as congo red, crystal violet, etc. were also adsorbed onto vermicompost and results looked promising (11,12). However, there is still more work to be carried out to figure out the optimum conditions for the process. Especially for Turkey, producing a versatile, low cost, and highly efficient adsorbent is important, as textile and leather industrial wastewater contains great amounts of dye effluents. In addition, only around 0.38% of 34.500 tonnes of MSW produced in Turkey is composted annually, according to TUIK (13). Since compost can be used for vermicompost production, Turkey has a great potential to reach vast production figures if alternative routes for vermicompost utilization could be established. In this study, vermicompost was evaluated as a potential adsorbent for methylene blue adsorption as a model dye effluent. As a cationic dye, methylene blue could be contained in the textile and leather industrial wastewater since it is used in silk and wool dyeing processes. The high concentration of methylene blue is regarded as hazardous, and avoiding its leakage to soil and rivers is crucial (14).

The primary aim of this study was to examine the influences of the adsorption conditions such as the initial concentration of MB, pH of media on the adsorption capacity of MB onto VC. In addition, kinetic models (the first and second-pseudo-order, Intraparticular and Elovich models) and four isotherm models (Langmuir, Freundlich, Temkin and Dubinin-Radushkevich) were utilized to determine their compatibility with the experimental data.

MATERIALS AND METHODS

Materials

Sodium chloride, hydrochloric acid, sodium hydroxide, and methylene blue were purchased from Sigma Aldrich. Bidistilled water was used in the whole experimental process. Vermicompost (VC) was purchased from a local producer from İzmir, and it was produced from sewage sludge compost and sawdust. Initially, vermicompost was dried and sieved to yield a particle size of 0.125<Dp<0.600 [mm] for homogenization of the sample. Vermicompost sample was oxidized in a furnace at 500 °C for 6 hours and its ash content was determined as 31.05 wt.%.

Sorption Experiments

Methylene Blue (MB) solutions at various pH values were prepared and 10 mL of specified concentration of MB solutions were poured into an erlenmeyer flask along with 0.1 g of VC sample. The sorption experiments were carried out in an incubator shaker operating at 100 rpm and 25 °C temperature. After the sorption experiments were completed, the solutions in the Erlenmeyer flasks were pulled out and centrifuged at 400 rpm for 1 minute. The initial and the supernatant concentrations were read with the help of UV-Vis spectrophotometer (Perkin Elmer, Lambda 365) at λ max: 664 nm. Adsorption capacity (AC) and removal yield (R%) were determined according to equations 1 and 2, respectively.

$$AC=\frac{(C_i-C_e)*V}{m} \tag{1}$$

$$R\ \%=\frac{(C_i-C_e)*100}{C_i} \tag{2}$$

C_i and C_e represent the initial and equilibrium concentration of the solution (mgL^{-1}), respectively. m denotes the mass of VC (g).

Determination of pHpzc

Slightly modified potentiometric titration method of Mohan et al. 2014 (15) was utilized to determine the point of zero charge. Briefly, 0.1 g of VC was added to 10 mL of 0,1 M NaCl solutions having pH values in the range of 2 to 12. The solutions were placed into the shaking water bath for 24 hours. After that, supernatant pH values were measured and a plot consisting of pH of initial solutions versus pH of final solutions was obtained.

Adsorption Kinetics

Batch kinetics were assessed with the help of appropriate kinetic models so that the adsorption rates and mechanism could be defined. In this research, the pseudo-first order (Eq. 3) (16), the pseudo-second-order (Eq. 4) (17), Intraparticular (Eq. 5) (18) and Elovich kinetic models (Eq. 6) (19) were applied to experimental data. The coefficient of determination (R^2) was calculated for each kinetic model to determine the best fit model.

$$\log\left(q_e - q_t\right) = \log q_e - \frac{k_p}{2.303} t \tag{3}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{4}$$

$$q_t = k_p t^{0.5} + c \tag{5}$$

$$q_t = \frac{1}{\beta} ln(\alpha\beta) + \frac{1}{\beta} ln\, t \tag{6}$$

Where q_e is the equilibrium adsorption capacity (mg/g), k_1 is pseudo-first-order constant (min^{-1}), k_2 is the pseudo-second-order constant (g/mg.min), β is the Elovich equation exponent (g/mg), k_p is diffusion constant.

Isotherm Models

In order to appraise the adsorption behavior, four isotherm kinetic models were utilized. Table 1 represents the Langmuir (20), Freundlich (21), Temkin (22), and Dubinin-Radushkevich (D-R)(23) isotherm models.

Table 1. Applied Isotherm Models with their equations and units.

Models	Equations	Units
Langmuir	$\frac{C_e}{q_e} = \frac{1}{q_{max} K_L} + \frac{C_e}{q_{max}}$	q_e: adsorbed amount (mgg^{-1}) C_e: adsorbed equilibrium (mgL^{-1}) K_L: Langmuir constant related to sorption energy (Lmg^{-1}) q_{max}: maximum adsorption capacity (mgg^{-1}) related to monolayer coverage
Freundlich	$ln q_e = ln(K_F) + \frac{1}{n} \ln C_e$	C_e: adsorbed equilibrium (mgL^{-1}) K_F: Freundlich constant (mgg^{-1})(Lmg^{-1})^n 1/n: intensity of adsorption
Temkin	$q_e = B ln a_T + B ln C_e$ $B = \frac{RT}{b_T}$	C_e: adsorbed equilibrium (mgL^{-1}) a_T: equilibrium bond constant B,b_T: Temkin constants
Dubinin-Radushkevich	$ln q e = ln q_m - \beta \varepsilon^2$ $\varepsilon = RT\, ln(1 + \frac{1}{C_e})$ $E = \frac{1}{\sqrt{2\beta}}$	C_e: adsorbed equilibrium (mgL^{-1}) q_m: maximum adsorption capacity (mgL^{-1}) ε: Polanyi potential β: activity coefficient (mol^2J^{-2}) R: gas constant (8.314 $kJmol^{-1}K^{-1}$) E: mean adsorption Energy ($kJmol^{-1}$)

RESULTS AND DISCUSSION

Effect of pH on methylene blue removal mechanisms

The impact of pH on the MB sorption was investigated with batch experiments performed in a pH range of 2-10 and the outcomes were shown in the Figure 1. The maximum MB removal was achieved when pH of the solution was 4. Therefore, all adsorption experiments were executed at pH 4.

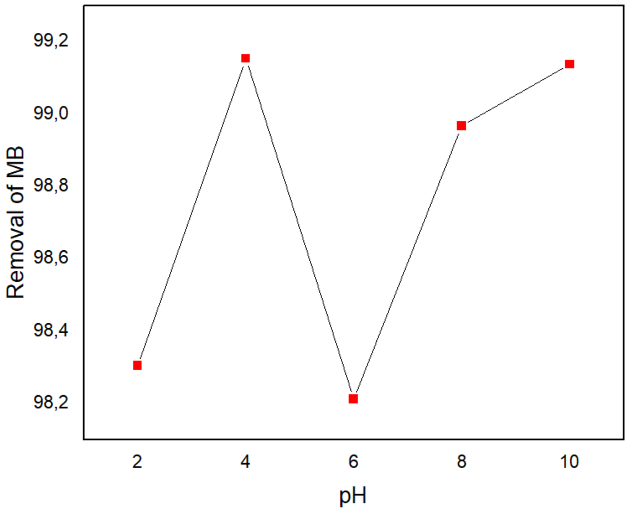

Figure 1. pH effect on the removal of MB.

Moreover, the point of zero charge (pHpzc) was measured as 8.51 as shown in Figure 2. At this pH, the surface charge of VC is zero. When pH<pHpzc, the surface of vermicompost has positive charge. In the opposite cases, the functional groups of vermicompost are negatively charged. MB is a cationic dye as it is known. Furthermore, the pKa of MB is 3.8; the cationic species of MB are dominant in the solutions above the value of pKa (24). The electrostatic adherence has occurred between the adsorbent and adsorbate at pH 4.

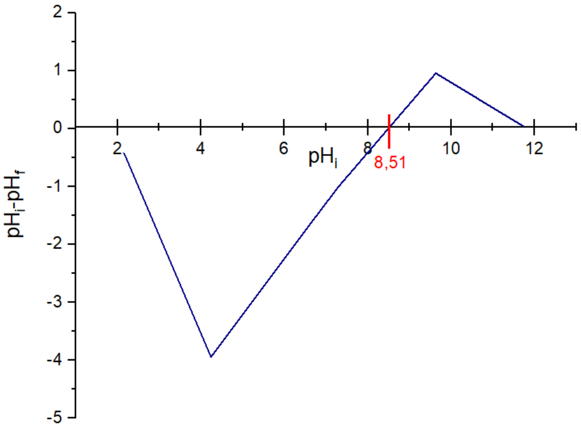

Figure 2. The point of zero charge of VC.

Effect of time and initial concentration of MB

The impact of time on MB adsorption onto VC was shown in Figure 3. Methylene blue adsorption onto VC was so rapid that adsorption equilibrium could be achieved within 60 minutes. As the vacant sites on the surface of VC were occupied with methylene blue, adsorption process happened very slowly by virtue of the small number of vacant sites and 99% removal of MB was achieved at 90 min. Besides, adsorption capacity enhanced with the higher initial concentration of MB, this phenomenon indicated in Figure 4. Initial concentration raises mass transfer between the adsorbate and the adsorbent owing to the driving force.

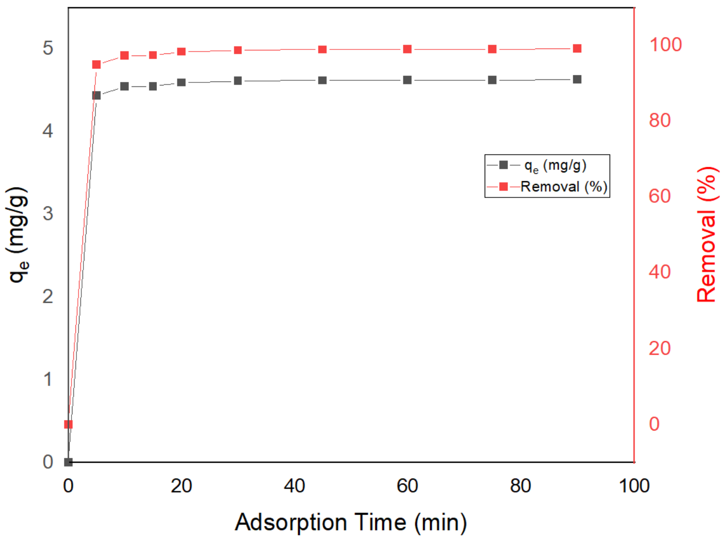

Figure 3. The effect of time on MB adsorption onto VC.

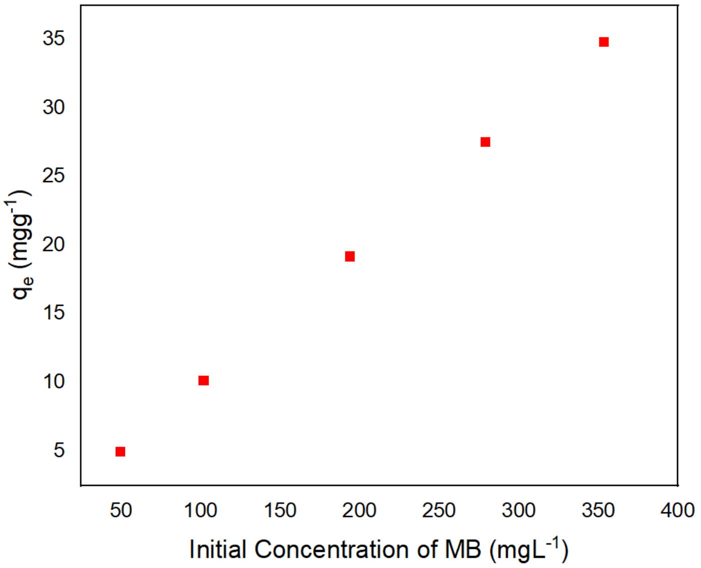

Figure 4. The effect of initial concentration on the adsorption capacity of MB onto VC.

Kinetic isotherm models

It can be deduced from Table 2 that chemisorption occurred according to the pseudo-second-order model. The first step of sorption was so fast owing to the large number of active sites of VC. With the increasing adsorption time, vacant sites of the surface were gradually decreased. As a result, all active surface was totally filled the adsorbate and adsorption process reached the equilibrium (25). The coefficients of determination of the kinetic models applied as shown in Figure 5 indicating that the pseudo-second-order model had the finest linear fit to the experimental data. Also, adsorption onto the VC comprised of two stages represented a multilinearity. Within the 5 min, the rapid MB adsorption took place. Then, the adsorption process has slightly risen. The boundary layer diffusion constitutes the first step, and the second stage was ascribed to the intraparticle diffusion (26).

Table 2. Kinetic parameters of applied kinetic models for MB adsorption onto VC at 298 K.

Models	**Model parameter**	**VC**
Pseudo-first-order kinetics	qe	0.6760
	k_1	0.0914
	R^2	0.7571
Pseudo-second-order kinetics	qe	4.63
	k_2	1.58
	R^2	1.0
Intraparticular	K_p	0.3846
	C_1	1.9457
	R^2	0.5208
Elovich	α	1.104
	β	3.758
	R^2	0.6887

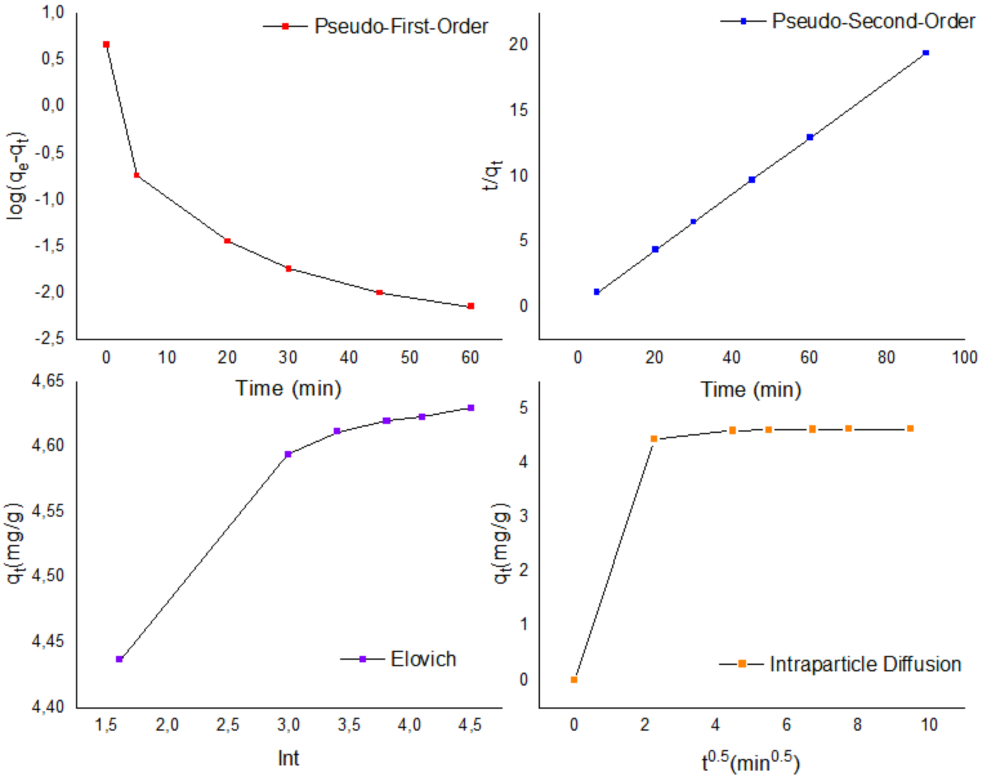

Figure 5. Applied kinetic models on the MB's adsorption onto the VC a) pseudo-first-order b) pseudo-second-order c) Elovich d) Intraparticle diffusion.

Adsorption isotherm models results

The calculated parameters for isotherm models applied in this research are summarized in Table 3. Furthermore, a plot was drawn by using nonlinear regression analysis showing the conformity of the isotherm models to experimental data in Figure 6. It can be said that both Langmuir and Freundlich isotherm models were excellent-fitted to empirical data. In fact, the coefficients of determination were so close to each other in all models. The Freundlich isotherm gave an idea that adsorption happened on the heterogeneous surface. Besides, there were no equal binding sites (27).

Table 3. The parameters of applied isotherm models for MB adsorption onto VC at 298 K.

Models	**Model parameter**	**VC**
Langmuir	qe(calculated)	34.7900
	qmax	58.4795
	K_L	0.2070
	R^2	0.9891
Freundlich	n	1.3077
	K_F	9.5410
	R^2	0.9895
Temkin	B	10.0620
	a_T	3.1760
	b_T	246.3545
	R^2	0.9832
Dubinin-Radushkevich	Qm	23.8456
	$\beta x10^7$	2.0000
	E	1581.1390
	R^2	0.9430

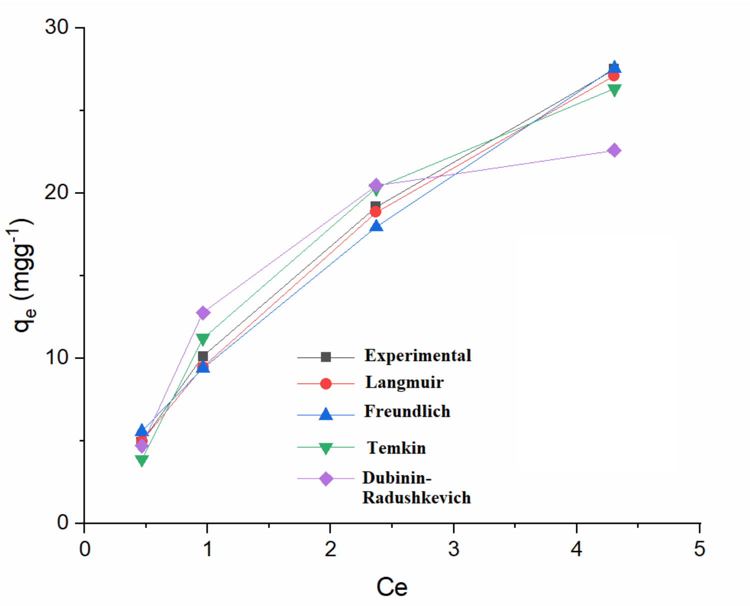

Figure 6. Adsorption isotherms of MB onto VC.

FTIR Analyses of the Adsorbent

FTIR analyses of raw vermicompost and vermicompost after MB adsorption were carried out and resulting spectra are shown in Figure 7. Raw vermicompost's broad peak seen at 3368 cm^{-1} is corresponding to the -OH band of hydroxyl groups which could belong to phenolic compounds. Furthermore, it can be inferred from the literature survey of vermicompost, N-H stretching band from amides and amines are observed in the range of 3300-3500 cm^{-1} (28). The sharp peak at 1634 cm^{-1} is attributed to -OH band. The intense peak at 1031 cm^{-1} may be assigned to stretching C-O group of polysaccharides. When the FTIR spectrum of vermicompost after MB adsorption was examined, the specific peak was detected at 1593 cm^{-1} corresponds to the C=C due to the aromatic rings. The two lower signal peaks were observed at 1323 cm^{-1} and 1384 cm^{-1} owing to the C–N stretching vibrations and -OH functional groups, respectively (29). Also, the symmetrical stretching C-H of CH_2 band appeared at 2928 cm^{-1} (28). The dramatic decrease on the magnitude of -OH peaks after the adsorption of MB onto VC could be evaluated to the chemisorption since the hydroxyl groups were neutralized.

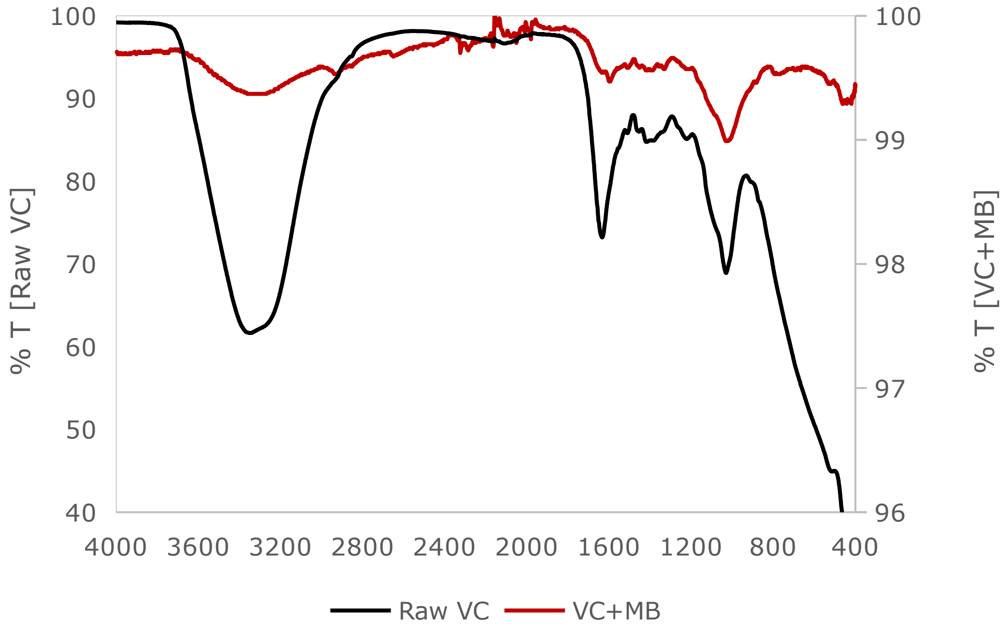

Figure 7. FTIR spectrum of Raw VC and MB adsorbed VC.

CONCLUSION

Vermicompost was evaluated as a cost-effective adsorbent in order to MB sorption from aqueous solution. The various kinetic models were applied to identify the reaction mechanism and the pseudo-second order kinetic model was matched with the experimental data, yielding the highest coefficient of determination (R^2=1.0). The nonlinear regression results of the isotherms pointed out that Langmuir model fitted the empirical results better than the other isotherm models. The maximum adsorption capacity value was calculated as 58.48 mgg^{-1} via the Langmuir isotherm. Furthermore, before and after the adsorption process, VC's functional groups were observed by FTIR. These results indicated the mechanism of the adsorption process between the VC and MB. Last but not the least, VC is a good candidate for the removal of MB.

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