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EFFECTIVE AND EFFICIENT REMOVAL OF METHYLENE BLUE DYE BY ZEOLITE ADSORBENTS

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Abstract

The application of mordenite zeolite and composite fiber as an adsorbent for the removal of aqueous methylene blue (MB) dye at room temperature was investigated. Effects of operational parameters including different contact time and different initial concentrations (C_i) of dyes on removal efficiency and adsorption amount of MB were determined. The characterization tools such as Fourier transform infrared (FT-IR), X-ray diffraction (XRD) and scanning electron microscope (SEM) were performed in order to identify the functional group, study the crystal structure and investigate the microstructure of zeolite adsorbents. Adsorption parameters were found out to be well fitted into *Langmuir* adsorption isotherm. The present work suggests that zeolite adsorbents could effectively remove MB dye. Thus, zeolites are good candidates for the removal of such organic pollutants.

Keywords: adsorbents, composite fiber, methylene blue (MB) dye, isotherm and zeolite.

Introduction

Dyes and pigments are used to apply colors for textile industry. There are nearly 800,000 tons of dyes per year in the dyeing process. In textile industry, about 10-15% of these dyes are lost during operation. Synthetic dyes are used in numerous industries such as textile, paper printing, food, pharmaceutical, leather and cosmetics. The presence of dyes can manufacture highly toxic compounds through many reactions that can cause very dangerous health problems such as allergies, tumors, and cancers in humans [Mohamed A et al, (2017)]. There are many more synthetic dyes than natural dyes. Among them, methylene blue MB ($C_{16}H_{18}ClN_3S$) is one of the most widely used dyes in some industries such as wood, linen and silk. 10 to 200 mg/L concentrations of MB are usually discharged into the environment. It is a cationic dye which is extremely resistant to be heat and light and hardly break down due to its complex structure. By exposing this dye to human, it can suffer serious damage to the eye and trouble breathing [Ahmad et al, 2019]. Even at low concentration, wastewater in organic dyes is very harmful to organisms.

There are several treatments to separate or decompose the pollutants in wastewater. The major treatments are followed in chemical precipitation/co-precipitation, membrane filtration, bio-degradation, and adsorption for heavy metals and dye [Shikha et al, (2017)]. Among these treatments, precipitation and biodegradation treatment have deficiency in high concentration level wastewater that causes fast saturation of adsorbents [Masaru et al, (2017)]. In contrast, adsorption is more economical and reliable treatment, which is one of the most effective physical processes for the decolorization of textile wastewater. Adsorption is the adhesion of atoms, ions or molecules from a gas, liquid or dissolved solid to a surface. This process creates a film of the adsorbate on the surface of the adsorbent. The mechanism of adsorption involves the adsorption of adsorbate molecules on the surface of the adsorbents through molecular interactions and

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diffusion of adsorbate molecules from the surface into the interior of the adsorbent materials either by monolayer or multilayer [Moustafa et al, (2012)]. Adsorption phenomenon depends on various factors such as pH, temperature, adsorbent dose, size and surface morphology. It also depends on the concentration and structure of adsorbate.

There are many adsorbents to remove the pollutants of wastewater. Among them, zeolites offer numerous advantages over liquid catalysts since they offer less or no corrosion, no waste or disposal problems, high thermostability and easy setup of continuous processes [Melkon et al, (2016)]. Zeolites are microporus, aluminosilicate minerals commonly used as commercial adsorbents and catalysts. Zeolites are natural or synthetic crystalline aluminosilicates with ion exchanging properties and bearing a negatively charged honeycomb framework of microspores into which molecules may be adsorbed for environmental decontamination and to catalyze chemical reactions. The main advantages of zeolites over conventional catalysts are due to the great acid strength they can have and to their great adaptability to practically all types of catalysis [N.O.Omisanya et al, (2012)]. Although zeolite powder can easily remove MB, it is difficult to separate powder from the aqueous MB solution. To overcome these problems, zeolite-composite fiber adsorbents using wet spinning method for decontamination of MB has been prepared. The treatment of such fibrous adsorbents is cheaper energy costs while membrane treatment increases energy costs through high-pressure operation although its separation efficiency is high. The advantage of fibrous adsorbents is high removal efficiency of heavy metal ions because it has small mesh structures consisting of small fiber filaments [U. Wingenfelder et al, (2005)]. In this work, zeolite adsorbents, both of powder and composite fiber, were used to remove the synthetic MB dye and investigated the removal efficiency of MB depending on contact time and initial concentration of MB.

Materials and Methods

Zeolite fibers were prepared by wet spinning process [Masaru et al, (2017)]. Zeolite concentration in the dispersion of poly ethersulfone (PES) in N methyl-2-pyrrolidone (NMP) solution was 50 wt%. Typically, 9 g of zeolite powder and 5 g of PES were dissolved in 11 ml NMP doped solution. Thus, weight ratio of PES to NMP is 1:2.333 and zeolite powder content was 50 wt % in PES in NMP solution. Then, the mixture was continuously stirred with constant speed at 50 ºC to prepare the blending solution. Blending solution containing zeolite powder was extruded through a spinneret at 3 ml/min using a high-pressure gear pump (GP Driving Unit CDS-18G-0.8; Kyowa Fine Tech. Co. Ltd). The extruded spinning solution was introduced into a water bath located at a distance of 10 cm below the nozzle. Then, the extruded spinning solution was coagulated at the room temperature in water to form zeolite fibers due to phase-transition. In the phase-transition condition, the PES and zeolites of the doped solution were both coagulated simultaneously in the water. However, NMP is not coagulated. They were kept underwater to remove the solvent from the resultant fiber. Finally, fibers were treated with excess hot water at 90 °C three times to eliminate the remaining NMP and they were stored in a wet condition at the room temperature until they are used.

Time dependence adsorption test

Time dependence adsorption test was performed in order to identify the possible rapidness of MB by adsorbents and to obtain the optimum time for complete removal of the dye (Fig. 1). Amount of 0.1 g of zeolite powders and fibers are added in 50 ml of MB solution having a concentration of 5 ppm in a rotary shaker operated at 200 rpm for 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 24, 36, 48 and 60 h at the room temperature (27 °C) .Then, the solution was filtered by using the Smith filter paper (110 mm) for the filtration of the adsorbent from the aqueous solution.

Concentration dependence adsorption test

Concentration dependence adsorption test was investigated for different concentration of MB (Fig. 2). 0.1 g of dosage were added in 50 ml of MB solution having different concentration of (1, 5, 10, 20, 30, 40 and 50 ppm) in a rotary shaker operated at 200 rpm for zeolite powders (10 h) and composite fibers (48 h).Then, the solution was filtered by using the Smith filter paper (110 mm) for the filtration of the adsorbent from the aqueous solution. The final concentration of above two adsorption tests was determined by an UV-Vis spectrometer. The removal percentage and adsorption amount q_e of MB were calculated using the following equations.

$$\text{Removal\%} = \frac{C_i - C_e}{C_i} \times 100 \qquad (1)$$

$$q_e = \frac{(C_i - C_e)V}{m} \qquad (2)$$

where

C_i = initial concentration (mg/L or ppm)

C_e = equilibrium concentrations (mg/L or ppm)

q_e = equilibrium adsorption amount of MB (mg/g)

m = mass of adsorbents (mg)

V = volume of the solution (ml)

Characterization of Adsorbents

The characterization tools such as Fourier transform infrared (FT-IR) 8400 Shimadzu spectrophotometer within the wave number from 4000 cm^{-1} to 650 cm^{-1}, X-ray diffraction (XRD) RIGAKU-RINT 2000 and scanning electron microscope (SEM) JEOL-JSM 5300 LV were performed in order to identify the functional group, study the crystal structure and investigate the microstructure of zeolite adsorbents.

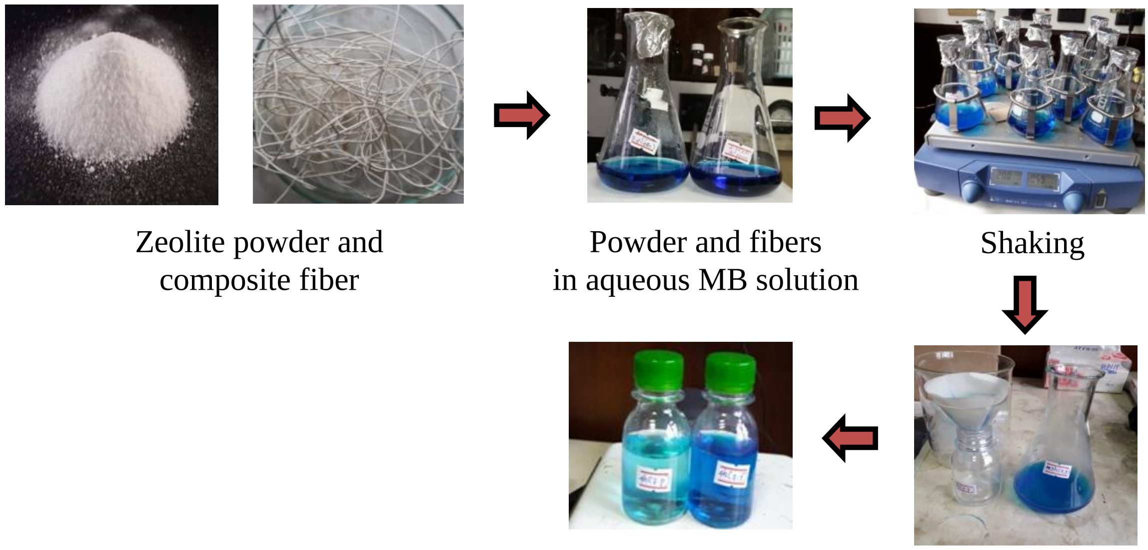

Figure 1 Photo of batch adsorption experiment for different contact times

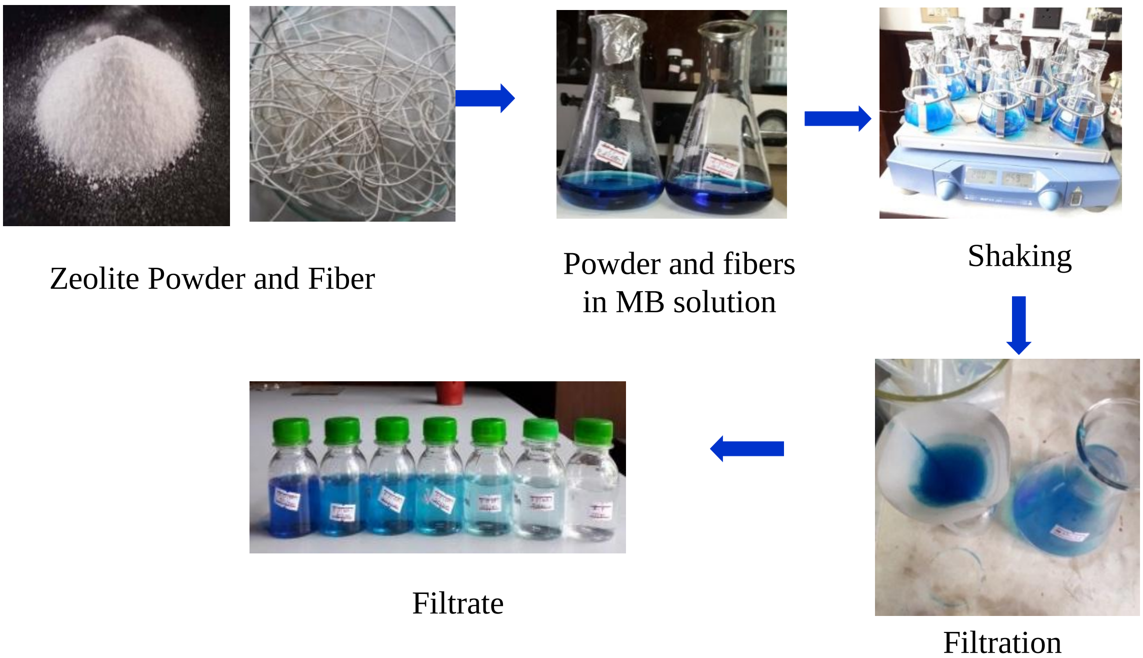

Figure 2 Photo of batch adsorption experiment for different initial concentrations

Results and Discussion

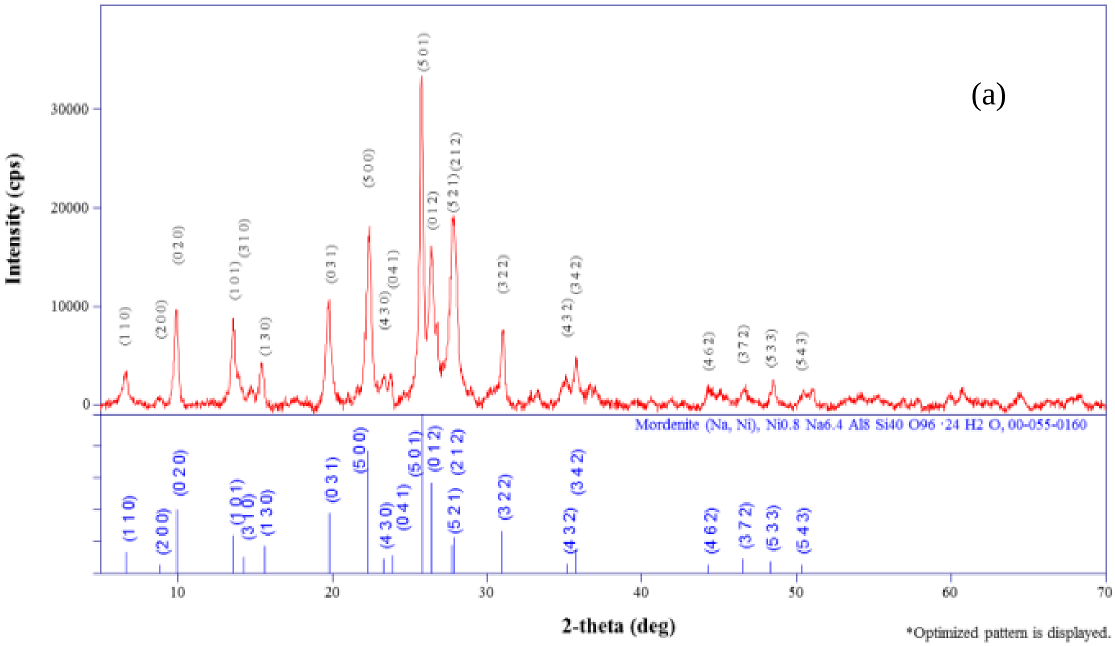

Figure 3(a) XRD spectrum of zeolite powder

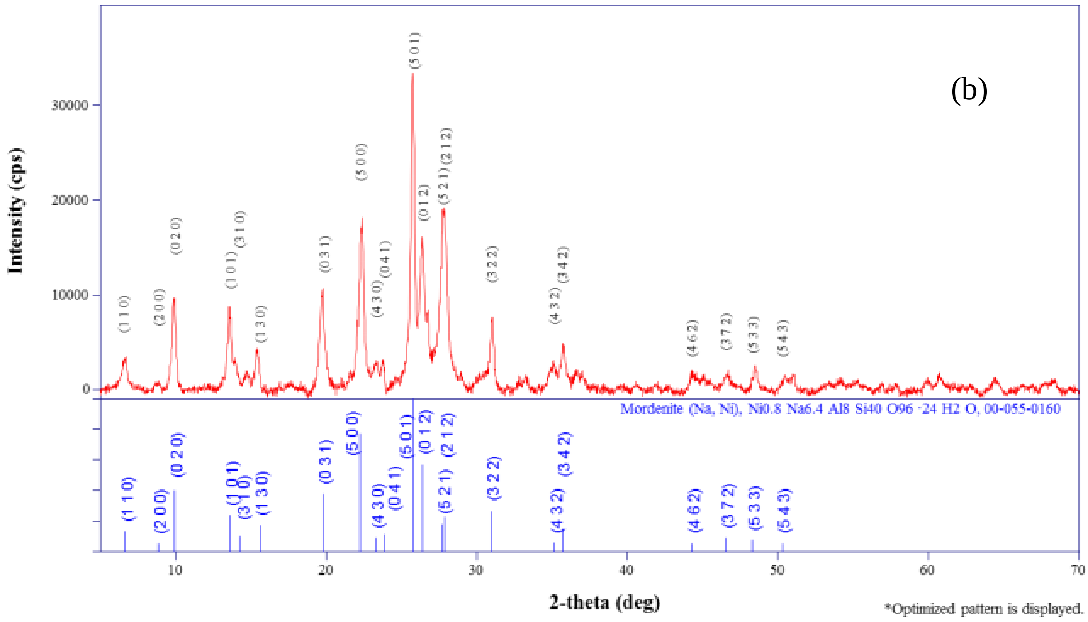

Figure 3(b) XRD spectrum of zeolite composite fiber

XRD spectrum of powder and fiber are presented in Fig.3 (a) and (b). According to the standard library file, the sharp crystalline peaks for both mordenite zeolite and the composite fibers were observed. No shift peak between the mordenite zeolite and the composite fibers was also occurred. It implies that the zeolite did not affect any changes in the crystalline structure of composite fibers.

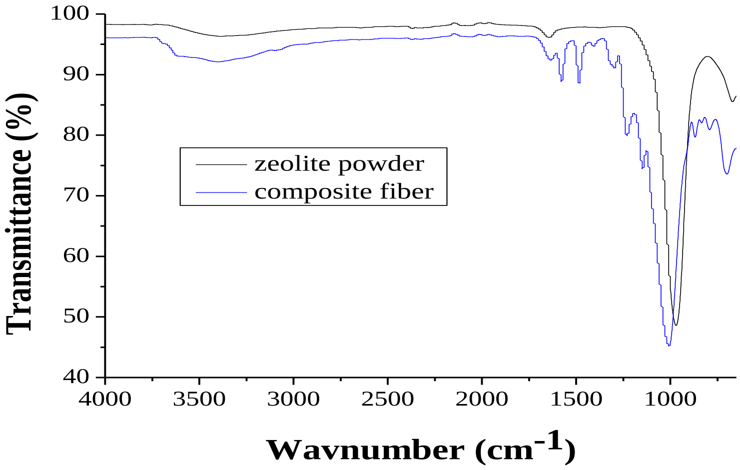

Figure 4 FT-IR spectra of zeolite powder and the composite fiber

Fig.4 shows the FT-IR spectra of zeolite powder and the composite fibers. The broad peaks at 3400 cm^{-1} in the spectra of both samples were attributed to O-H stretching vibration. For the composite fibers, the bands appeared at 1580 and 1490 cm^{-1} were assigned to the C=C stretching vibration. The peaks at 1630 and 1640 cm^{-1} in powder and fiber were due to O-H bending vibration. The peaks from 1150 to 1240 cm^{-1} were attributed to >S $(=O)_2$ stretching vibration. The intense broad peaks of Si-O and Al-O stretching vibration were observed at 1010 cm^{-1} in the zeolite fiber and at 968 cm^{-1} for composite fiber. Symmetric T-O-T vibrations (T=Si, Al) were found at the peaks 697 and 789 cm^{-1} of composite fibers [Moustafa et al, (2012)].

Fig. 5(a) is SEM micrograph of zeolite fiber with porous structure before the treatment of adsorption. In this figure, the zeolite powders were well distributed in the PES network with a sponge structure of the composite fibers. However, the pores in these fibers after the treatment of adsorption were closer than before adsorption as shown in Fig. 5(b). It implies that MB was well adsorbed by fibers. As the result, dye was successfully removed from the aqueous solution by fibers.

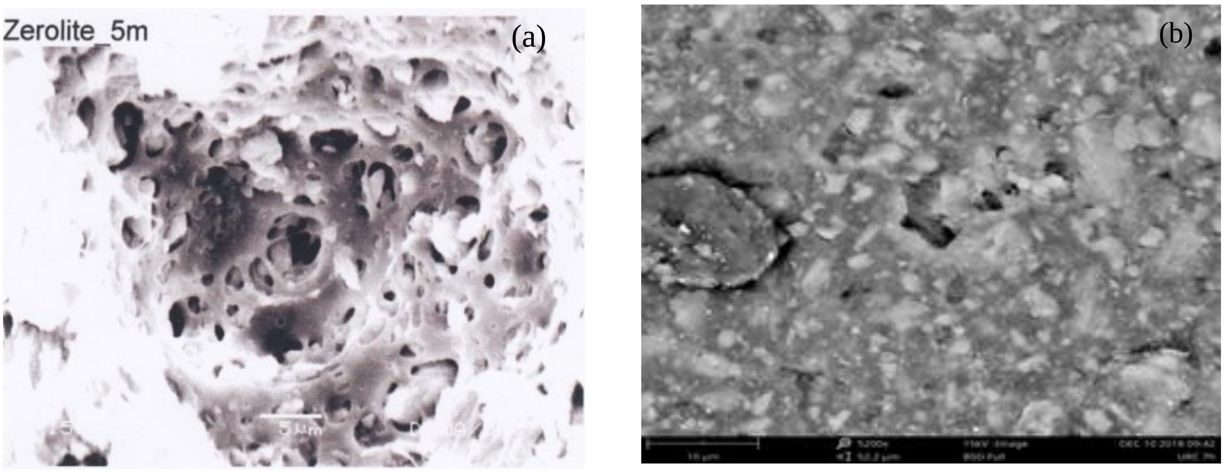

Figure 5. SEM images of zeolite composite fiber (a) before and (b) after adsorption process

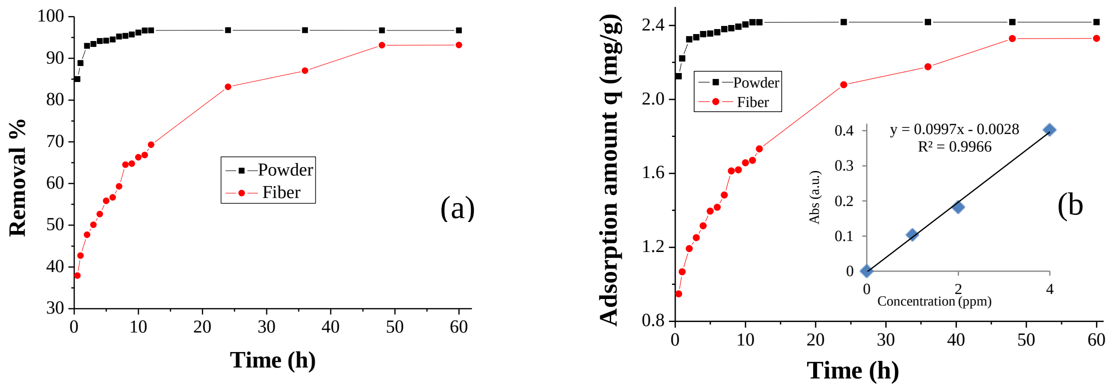

Figure 6(a) Graph showing the removal % and **(b)** adsorption amount of MB depending on different contact time (C_i=5 ppm). Inset shows calibration curve for this adsorption test.

Contact time dependence adsorption test was performed in order to study the effect of contact time on the adsorption behavior of MB by adsorbents. Fig. 6(a) shows the graph of removal percent depending on different contact time for zeolite powder and fiber on MB. The adsorption of MB to the zeolite powders was drastically increased until the contact time 10 h and then it became saturation. On the other hand, the adsorption of MB to the composite fibers were gradually increased and saturated at the contact time 48 h. As a result, zeolite powder and fiber could remove MB over 90 % for initial concentration 5 ppm of MB and dosage amount of adsorbent 0.1 g. Fig. 6(b) represents the equilibrium adsorption amount (q_e) of MB depending on different contact times of adsorption for both adsorbents. The equilibrium adsorption amounts were found out to be 2.41 mg/g and 2.33 mg/g after contact time 10 h for powder and 48 h for fiber. Thus, zeolite powder has faster adsorption capacity than fiber for C_i 5ppm of MB.

Concentration dependence adsorption experiment was carried out in order to investigate the effect of C_i on the adsorption properties of MB by both adsorbents. In this test, the experimental parameters including amount of dosage 0.1 g, volume of solution 50 ml and contact time 10 h for powder and 48 h for fibers were fixed. However, concentration of MB was varied from 1 to 50 ppm. The results were shown in Fig. 7. It was found out that adsorption capacity were dependent on concentration of MB. At low concentration of MB, the removal percent for both adsorbents were almost the same as shown in Fig. 7(a). However, a gradually decreasing in removal efficiency with increasing C_i of MB was occurred. In addition, it is remarkabe to note that powder is more effective than fibers for the removal of MB at higher concentration.

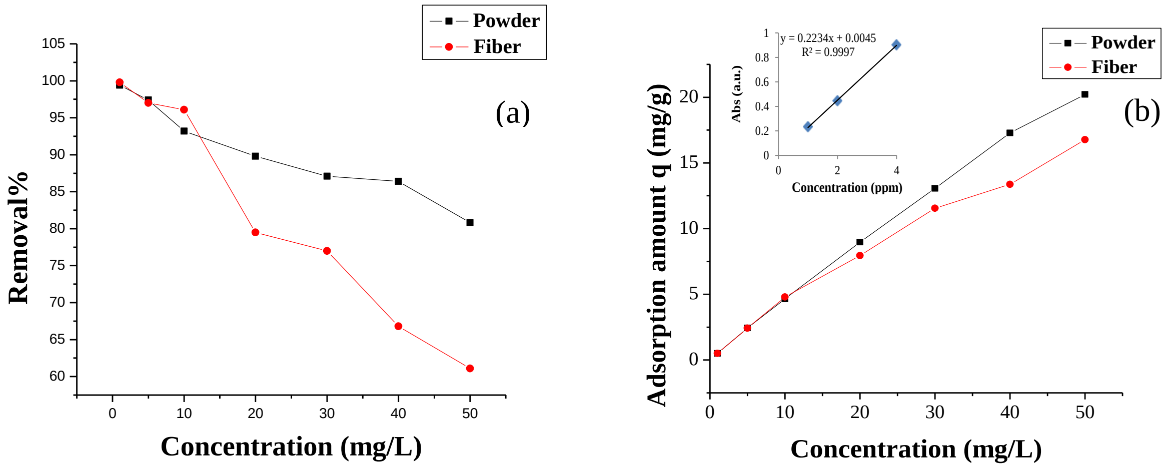

Figure 7 (a) Graph showing the removal % and **(b)** adsorption amount of MB depending on different initial concentrations Inset shows calibration curve for this adsorption test.

The adsorption amount q_e depending on different values of C_i have been conducted in order to investigate the equilibrium adsorption mechanism of dyes on adsorbents. Fig.7(b) illustrates the equilibrium adsorption amount (q_e) with different initial concentrations. Adsorption amount of MB by the powders and composite fibers were gradually increased until contact time was 10 h and 48 h. The adsorption isotherm based on experimental results has been determined. According to results, experimental adsorption isotherms of MB were well agreed with the *Langmuir* adsorption isotherm as shown in Fig.8.

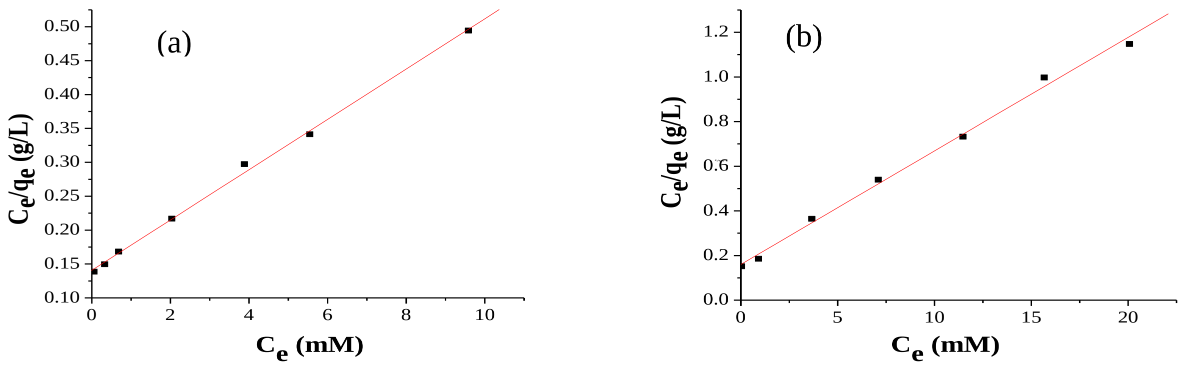

Figure 8. *Langmuir* isotherm plot for zeolite powder (a) and (b) composite fibers.

Conclusions

The adsorption behavior of MB on the adsorbents, zeolite powder and zeolite composite fibers, was investigated by doing the batch adsorption experiments. The effects of contact time and initial concentration were investigated. The contact time was firstly determined at the fixed experimental parameters including the amount of dosage 0.1 g, initial concentration 5 ppm and volume 50 ml of MB solution in order to obtain the optimum contact time for adsorption capacity. The maximum removal 96 % for powder and 91 % for fibers were obtained during the contact time 10 h and 48 h respectively. Secondly, the effect of initial concentration on adsorption behavior at the optimum contact times was studied. Both adsorbents can remove over 90 % at low concentration, 1, 5 and 10 ppm. Therefore, zeolite powder and composite fiber were effective and efficient adsorptivity for the removal of MB at low concentration. The adsorption isotherm of MB was well fitted into *Langmuir* isotherm model. Thus, zeolite based adsorbents can be applied to remove the organic pollutants.

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References

Ahmad Badeenezhad, Abooalfazl Azhdarpoor, Shima Bahrami and Saeed Yousefinejad, (2019)"Removal of methylene blue dye from aqueous solutions by natural clinoptilolite and clinoptilolite modified by iron oxide nanoparticles, molecular simulation," VOL. 45, NO. 7, 564–571.

Masaru Ohshiroa,b, Kohtaroh Nakamotoa, Takaomi Kobayashia, (2017) "Mordenite zeolite- Polyethersulfone composite fibers developed for decontamination of heavy metal ions," Journal of Environmental Chemical Engineering 5, 513–525.

Melkon Tatlier***a*** , Çiğdem Atalay-Oral***a*** **,** ***(***2016) "Crystallization of Zeolite A Coatings from Natural Zeolite," *Materials* Research. 19(6), 1469-1477.

Mohamed A. Hassaan, Ahmed El Nemr. (2017) "Health and Environmental Impacts of Dyes: Mini Review," American Journal of Environmental Science and Engineering, Vol. 1, No. 3, pp 64-67.

Moustafa E. Moustafa, Ehab A. Abdelrahman, Hisham M. Aly, (2012) "Synthesis of mordenite zeolite in absence of organic template," Advanced Powder Technology 23, 757–760.

N. O. Omisanya, C.O. Folayan, S.Y. Aku and S.S. Adefila, (2012) "Synthesis and characterization of zeolite for adsorption refrigeration application," Pelagia Research Library, Advances in Applied Science Research, 3 (6):3746-3754.

Shikha Sharma, Deepak Pathania, Pardeep Singh,(2017)"Removal of methyleneblue by adsorption onto activated carbon developed from Ficus carica bast," Arabian Journal of Chemistry 10, S1445-S1451.

U. Wingenfelder, C. Hansen, G. Furrer, R. Schulin, (2005) "Removal of heavy metals from mine waters by natural zeolites," Environ. Sci. Technol. 39, 4606–4613.