Effect of Alkaline Concentrations on the Synthesis of Volcanic Soil-Based Zeolite for Methylene Blue Removal by Fenton-Like Oxidation Process

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Abstract: This study demonstrated the potential use of volcanic ash soil (VAS) as raw materials for synthesizing zeolite without adding any templates or seeds. Here we investigated the effect of alkaline concentrations on the synthesis of VAS-based zeolite and enhanced its ability for methylene blue (MB) removal by Fenton-like process. Zeolite was directly synthesized by mixing the VAS within alkaline concentrations of 0.5 mol/L(P1), 1.5 mol/L (P2), and 3.0 mol/L (P3), respectively, followed by a simple hydrothermal procedure at 100 °C for 24 hours. The synthesized product characteristics were obtained from the Fourier transform infrared (FTIR) and X-ray diffraction (XRD) analysis, which confirmed the formation of zeolite type A and some mineral phases in the P2 and P3 samples. The mentioned samples reached equilibrium state at MB concentration of 200 mg/L with high adsorption capacity values compared to VAS. The adsorption showed a better fit to the Langmuir isotherm model ($R^2 > 0.999$), in which the maximum uptake capacities were found to be 24.03 mg/g for P2 and 14.30 mg/g for P3. Interestingly, the percentage of MB removal using P2 and P3 increased greatly from 52.81% and 32.26% to 98.92% and 98.85% by Fenton-like process, respectively.

Keywords: adsorption, catalytic, degradation, fenton-like oxidation, volcanic soil, zeolite

1. Introduction

Indonesia is known as one of the textile producers and exporters in the Asian region [1]. Textile industries mostly used synthetic dyes for coloring their textile products because of inexpensive and high thermal stability compared to natural dyes [2]. Among the various synthetic dyes used, cationic dyes are known to be more toxic than other dyes, including methylene blue (MB) [3]. Also, an aromatic ring in the MB structure makes it difficult for this compound to degrade naturally [4-7]. About 15–20% of synthetic dyes cannot bond strongly with fabric fibers and lost to water during the washing process. It is estimated that 280,000 tons of dye are discharged annually from the textile industry [8]. This wastewater contains dyes with a concentration range of 10-200 mg/L [9-12].

Several treatment methods have been used to eliminate organic pollutant contamination from water [11]. Among them are electrochemistry, membrane filtration, bioremediation, coagulation, and adsorption [13-17]. Each of the techniques mentioned has advantages and disadvantages, but the most important criteria are the cost of wastewater treatment required. So far, adsorption is considered the cheapest and easiest methods for the treatment of organic pollutants, which has high effectiveness depending on the sorbents. Unfortunately, the limitation of adsorption method is transferring pollutants from aqueous solution to adsorbents. The advanced oxidation process (AOP) can be combined with the

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adsorption method to overcome this drawback. AOP is a method of degrading organic matter through a radical attack. However, the existence of multifunctional material is not abundant in soil environments.

Zeolites are known as porous materials and contain negative charges on their surface. Due to these properties, zeolites are widely used as adsorbents and catalysts in the industry [18]. The pore on zeolite structures can adsorb small organic molecules, while the negative charge on the surface can bind cations. Because zeolites have low catalytic properties to degrade organic matter, zeolites were usually composed with metal oxides such as TiO_2, AgO, and CuO [19]. Generally, zeolite/metal oxide composites were made by synthesizing metal oxides in the presence of zeolite as a host or vice versa [20].

Here, we reported the use of volcanic ash soil (VAS) as a raw material for zeolite synthesis, which can degrade organic matter using AOP through Fenton-like reaction. The main components of VAS are SiO_2, Al_2O_3, and Fe_2O_3, which are potentially used as a precursor for synthesizing zeolite materials [21]. In this work, we evaluated the effect of alkaline concentrations on the synthesis of zeolite and its ability to adsorb and degrade MB from aqueous solution using AOP through Fenton-like reaction.

2. Materials and methods
2.1. Materials
Volcanic ash soil (VAS) sample were collected from the area around the Chemistry Department of IPB University, Dramaga, Indonesia. The sample was dried, mashed, and filtered using a standard sieve of 100 mesh without further purification. Zeolite A as reference material was purchased from Toso Chemical. Methylene blue ($C_{16}H_{18}ClN_3S$), sodium hydroxide (NaOH), and hydrogen peroxide (H_2O_2) were purchased from Nacalai Tesque Chemical.

2.2. Synthesis of zeolite
Zeolite was synthesized through a simple hydrothermal route under different alkaline concentration. Firstly, about 10 g of VAS were weighed and put in a polypropylene bottle containing 80 mL of NaOH solution. The concentration NaOH used were 0.5, 1.5, and 3.0 mol/L with solid ratio was 1:8. The mixture was stirred for 30 min at normal temperature (30°C). Secondly, the mixtures were heated using a dried oven at 100°C for one day and washed several times with distilled water to obtain the products at neutral *p*H. Finally, the products were dried using a dried oven at 100°C for 12 h. The characteristic of obtained products were determined using ED-XRF (PANalytical Epsilon 3^{XLE}), FT-IR spectroscopy (Perkin Elmer Spectrum One), and X-ray diffraction (a Rigaku Ultima IV X-ray diffractometer).

2.3. Adsorption equilbrium studies
The equilibrium state of MB adsorption was studied by shaking 50 mg of adsorbent in 10 mL of MB solution with concentrations of 25, 50, 75, 100, 150, 200, 250, and 300 mg/L. The mixtures was allowed for 24 h at room temperature. Afterward, the final MB concentration was measured using a visible spectrophotometer (Biochrom Libra S11) and the uptake capacity value was determined through Equation 1.

$$q_e = \frac{(C_0 - C_e)}{m} x V \tag{1}$$

where q_e, m, *V*, C_0, and C_e refer to the uptake capacity value (mg/g), adsorbent mass (g), the volume of MB solution (L), initial MB concentration (mg/L), and final MB concentration after equilibrium state (mg/L), respectively. In order to understand the adsorption properties of MB onto zeolite prepared from VAS, two isotherm models were investigated (Langmuir and Freundlich models). The linear form of both isotherm models is given by Equations 2 and 3.

$$\text{Langmuir equation model} \quad : \quad \frac{C_e}{q_e} = \frac{1}{bq_{max}} + \frac{C_e}{q_{max}} \qquad (2)$$

$$\text{Freundlich equation model} \quad : \quad \log q_e = \log K_f + \frac{1}{n_f} \log C_e \qquad (3)$$

where q_{max} is the maximum value of adsorption capacity (mg/g), b refers to the Langmuir constant (L/mg), K_f and n_f are the Freundlich constant (L/g) and the adsorption intensity (g/L), respectively.

2.4. Degradation of Methylene Blue

About 10 mL of MB solution (200 ppm) was mixed with 50 mg of samples and shaked for a while. Afterward, 1 mL of 2.5 mol/L H_2O_2 was added and allowed for 24 h. The final MB concentration was measured by using visible spectrophotometer. The effect of degradation time was also investigated for 1.5, 6, 12, and 24 h. From Equation 4, the percentage of dye removal (% Deg) was calculated.

$$\% \, \text{Deg} = \frac{C_e - C_t}{C_e} \, x \, 100 \qquad (4)$$

where C_e is the concentration of MB after equilibrium adsorption (mg/g) and C_t is the MB concentration after adsorption at a certain time (mg/g).

3. Results and discussions

3.1. Materials characterization

The result of XRF analysis showed that VAS contained SiO_2 (42.622%), Al_2O_3 (38.195%), Fe_2O_3 (14.129%), CaO (1.456%), K_2O (0.147%), P_2O_5 (1.699%), TiO_2 (1.132%), MnO (0.239%), ZrO_2 (0.144%). Figure 1 shows the XRD pattern of the VAS and synthesizes product samples. As seen, VAS was clearly dominated by amorphous quartz as the major phase that appeared on the sample. The VAS pattern was similar characteristics to the Bali pumice sample in our previous study [22]. When VAS was treated under the alkaline condition and followed by the hydrothermal process, the amorphous content decreased. Amorphous aluminosilicate materials such as VAS or pumice dissolved easily under alkaline conditions even at low concentrations and room temperature [23]. In the present study, we used alkaline concentrations of 0.5, 1.5, and 3.0 mol/L to prepare zeolite from VAS without purification.

As shown in the XRD patterns, the appearance of zeolite A and sodalite phases occurred at 1.5 and 3.0 mol/L NaOH with similar characteristic peaks of zeolite A commercial. The typical zeolite A patterns appeared at 2θ degree = 7.35°, 10.33°, 12.63°, 16.27°, 21.83°, 24.15°, 27.27°, 30.11°, 32.69°, and 34.35°. For sodalite, the peak appeared at 14.00°. Meanwhile, the low-intensity peaks appear at 13.8°, 18.14°, 21.5°, 23.9°, 26.56°, 29.9°, and 34.08° for the sample treated by 0.5 mol/L alkaline concentration. The appearance of a low-intensity peak indicates a phase change from the amorphous phase into crystalline materials. The intensity of peak for the sample treated with higher alkaline concentration accelerates the zeolite formation phase. Increasing the alkaline concentration accelerated the dissolution, nucleation, and zeolite crystal growth. Figure 1 shows that the intensity of zeolite A and sodalite peaks on the P3 sample was higher than the P2 sample. Therefore, the alkaline concentration plays a role in controlling zeolite crystallization and its quantities.

According to Ayele *et al.* [24], the use of 3.0 mol/L NaOH produced high crystallinity on the synthesis of zeolite A. Here the ratio Si/Al of zeolite A was found to be 1.14, with a similar result to the literature [24]. On the other hand, other mineral phases were also formed in P2 and P3 samples, such as hematite.
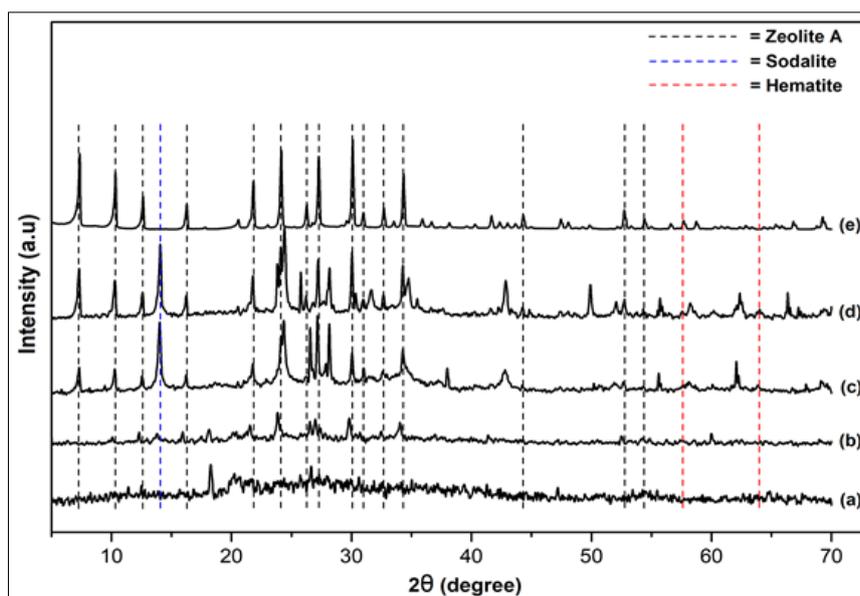
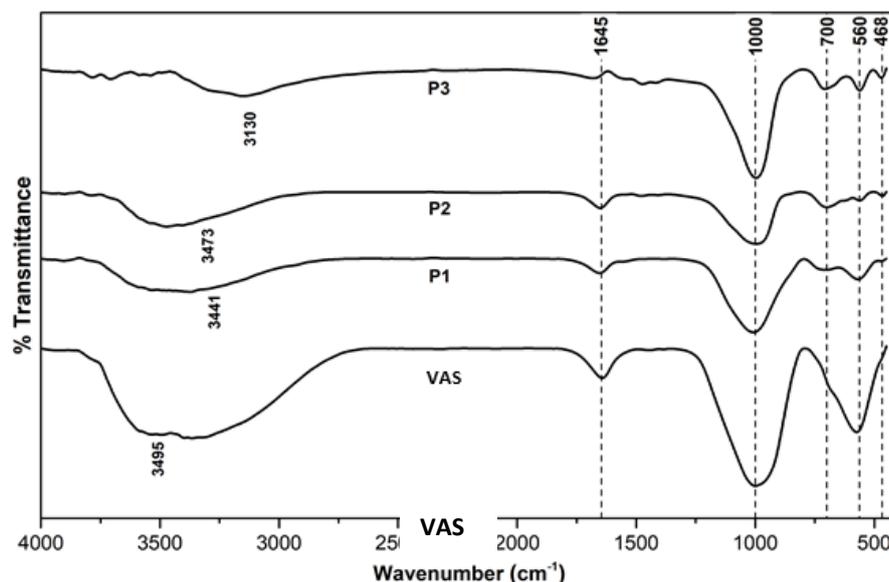**Figure 1.** XRD patterns of (a) VAS, (b) P1, (c) P2, (d) P3, and (e) zeolite A

Figure 2. FTIR spectra of VAS, P1, P2, and P3

The FTIR spectra of VAS before and after the treatment process were scanned from 485-4,000cm^{-1} and displayed in Figure 2. It can be seen that VAS has several absorption peaks at 560, 1000, 1645, and 3495 cm^{-1}. The spectrum obtained is similar to the basic FTIR characteristic of allophane reported by Shukla *et al.* [25]. In general, the peaks observed at 560 cm^{-1} and 1000 cm^{-1} were assigned to the vibration peaks of Si-O bond from silicate chains (a three-dimensional silica phase). Two peaks that appeared at regions of 1645cm^{-1} and 3495cm^{-1} were associated with the water molecule (H-O-H bending) and the functional group of O-H stretching, respectively. In the treated sample, the absorption peak intensity of 560cm^{-1} decreased due to amorphous silicate dissolution, resulting in structural rearrangement accompanied by the appearance of absorption peaks at 468cm^{-1} and 700cm^{-1}. The appereance of these two peaks might be caused the formation of zeolite frameworks after the hydrothermal process, in which the position peaks at 468cm^{-1} and 700cm^{-1} were attributed to the Al-O bond and the Si-O-Al bending vibration, respectively. In the P2 and P3 samples, the peak at 560cm^{-1} was assigned as double four-ring (D4R) of zeolite A.
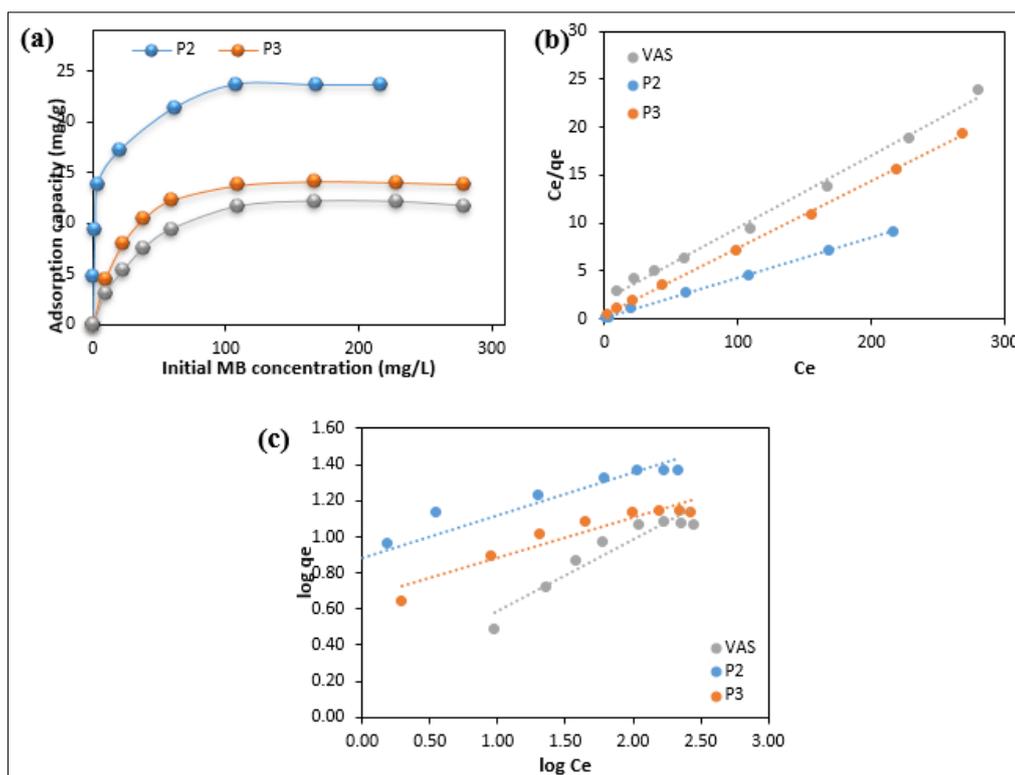
Figure 3. (a) Adsorption capacity of adsorbent, (b) Langmuir isotherm model, and (c) Freundlich isotherm model

3.2. Adsorption equilibrium studies

The adsorption equilibrium provides physicochemical data to optimize the efficiency of the adsorption process. The adsorption process was allowed for 24 h to reach the equilibrium condition. Here we did not try the adsorption ability of P1 due to the absence of zeolite formation. According to the characterization results, zeolite was only formed in the P2 and P3 samples. The Figure 3a shows the uptake capacity of VAS, P2, and P3 samples to remove MB from an aqueous solution. As seen in Figure 3a, the VAS sample has capability of adsorbing MB directly, although with a lower uptake capacity than the P2 and P3 samples. These might be related to amorphous aluminosilicates material contain silanol groups in their surfaces. The uptake capacity of VAS increased from 3.12 mg/g to 11.63 mg/g with increasing the MB concentrations from 25 to 150 mg/L and reached constant at 150–300 mg/L.

Compared to the VAS sample, the P2 sample showed a high adsorption capacity than VAS and P3 samples. It is due to negative charges of zeolite and also some of the remaining amorphous aluminosilicates. At MB concentrations of 25 to 200 mg/L, the adsorption capacity of the P2 sample increased significantly from 4.73 mg/g to 23.64 mg/g and reached constant at 200–300 mg/L. Meanwhile, the amount of MB adsorbed on the P3 sample lower than the P2 sample. The adsorption capacity of P3 increased from 4.44 mg/g to 13.73 mg/g with increasing MB concentrations from 25 to 150 mg/L and reached constant at 150–300 mg/L. The amorphous aluminosilicate materials contributed to the MB adsorption on the P2 sample than the P3 sample. The XRD pattern shows that the P3 sample contains more zeolite than the P2 sample.

In this study, we only used two isotherm models to understand the distribution of MB molecules from aqueous solution to adsorbents, namely the Langmuir and Freundlich isotherm models. The Langmuir model followed the assumption of homogeneous and monolayer adsorption, while the Freundlich model assumed heterogeneous and multilayer adsorption. Table 1 shows several parameter values of the Langmuir and Freundlich models. Based on the isotherm data, the adsorption of MB molecules onto the VAS, P2, and P3 showed excellent fitting with the Langmuir isotherm model compared to the Freundlich isotherm model. This shows that the monolayer of adsorption of methylene

blue molecules occured on the zeolite surface (Figure 3b and 3c). VAS, P2, and P3's maximum uptake capacity values were found to be 13.368 mg/g, 24.038 mg/g, and 14.306 mg/g, respectively.

Table 1. Parameters of Langmuir and Freundlich isotherm models

Adsorbent	Temperature (ºC)	pH	Langmuir model			Freundlich Model		
			R^2	q_{max} (mg/g)	b (L/mg)	R^2	1/n	K_f (mg/g)(L/g)^n
VAS	30	6	0.995	13.368	0.034	0.918	0.390	1.568
P2	30	6	0.999	24.038	0.242	0.882	0.237	7.594
P3	30	6	0.999	14.306	0.171	0.904	0.224	4.567

3.3. Degradation of Methylene Blue

A Fenton-like oxidation process was carried out after the equilibrium adsorption to degrade the MB molecules adsorbed on adsorbent surfaces. As a part of AOP, the Fenton-like process was selected due to its effectiveness in degrading a wide variety of organic pollutants with low processing costs. Iron oxide contents play a role as Fe^{3+} ion sources to form $[Fe^{III}OOH]^{2+}$ intermediate as the first step reaction in the presence of H_2O_2. The intermediate might be possible to bond with organic compounds or break up at the Fe-O bond to generate Fe^{2+} and hydroperoxyl radical (•OOH). It might be also break up at the O-O bond by generating the ferryl ion ($[Fe^{IV}O]^{2+}$) and hydroxyl radical (•OH). The hydroxyl radicals as a quite reactive species then preferentially attack the benzene ring of MB to form the final mineralization products [26]. This process is called a Fenton-like process.
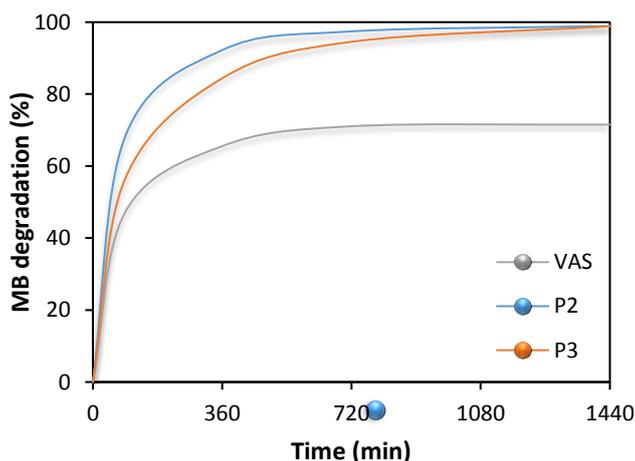
$$Fe^{3+} + H_2O_2 \rightarrow [Fe^{III}OOH]^{2+} + H^+ \qquad (4)$$

$$[Fe^{III}OOH]^{2+} \rightarrow Fe^{2+} + •OOH \qquad (5)$$

$$[Fe^{III}OOH]^{2+} \rightarrow [Fe^{IV}O]^{2+} + •OH \qquad (6)$$

Figure 4. The percentage of MB degradation for 24 hours

As seen in Figure 4, the catalytic properties of P2 and P3 were higher than VAS. The percentages of MB removal increased highly from 68.23% to 97.43% for P2 and 56.51% to 94.53% for P3 with increasing degradation time from 90–720 min. At 720–1440 min, the rate of MB removal using P2 and P3 increased slightly, in which the percentage values were 98.92% and 98.85%, respectively. This may be related to the formation of some iron oxide minerals (e.g. hematite) in the P2 and P3 samples during

the hydrothermal process. Increasing Fe(III) dose would be enhanced the formation of Fe(III)-H_2O_2 complexes and accelerated the formation of •OH as a quite reactive radical to degrade the adsorbed organic compounds. Meanwhile, the percentage of MB removal using VAS also increased from 56.51% to 71.07% with increasing degradation time from 90–720 min, but the percentage value only increased to be 71.53% at 1440 min. Overall, the percentage of MB removal was successfully enhanced by the Fenton-like process, as seen in Figure 5.
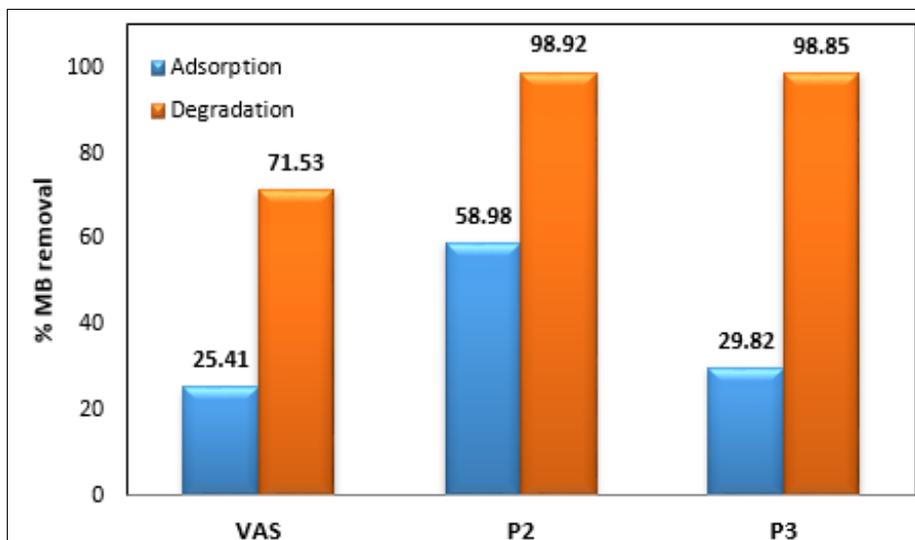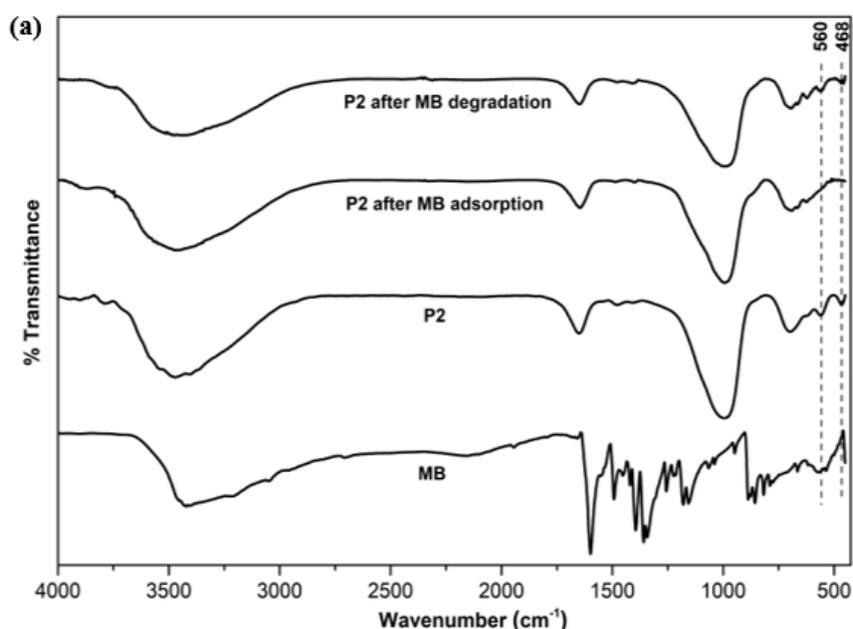

Figure 5. Adsorption and degradation of 200 mg/L MB solution for 24 h

To ensure MB molecules had been adsorbed and degraded, the functional groups of P2 and P3 were characterized by FTIR spectroscopy (Figure 6). Based on the FTIR results, the absorption peaks of adsorbents (P2 and P3) at 560 cm^{-1} and 468 cm^{-1} were disappeared as a consequence of MB adsorption on the adsorbent surface. This might be due to MB molecules covered the surface of adsorbents and caused the peak of the double four-ring (D4R) at 560 cm^{-1} disappeared. However, these two peaks reappeared after the degradation process, which showed that the MB adsorbed has been degraded.
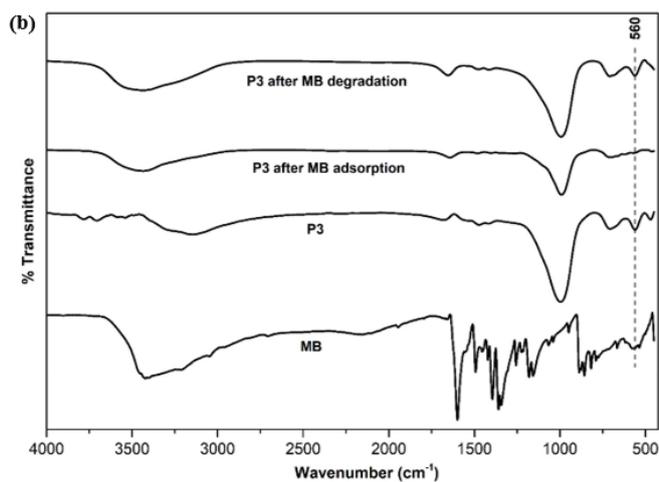
Figure 6. FTIR spectra of MB after adsorption and degradation using (a) P2 and (b) P3

4. Conclusions

In this research, we have reported the potential use of VAS as a raw material for preparing zeolite A without the addition of any templates or seeds. We also enhanced its ability to remove MB from aqueous solution by combining adsorption and AOP methods through a Fenton-like reaction. VAS alone mixed with alkaline concentrations of 1.5 (P2) and 3.0 mol/L (P3) was able to form zeolite, which was revealed by FTIR and XRD analysis. Increasing the alkalinity accelerated the dissolution of amorphous quartz as well as the growth of zeolite crystals. The adsorption was more favorable to the Langmuir isotherm model compared to the Freundlich model. This means the interaction between each adsorbent and MB molecules followed the assumption of homogeneous and monolayer adsorption. The maximum uptake capacities of VAS, P2, and P3 were 13.36, 24.03, and 14.30 mg/g, respectively. Although P2 and P3 only adsorbed as much as 58.98% and 29.83% of MB concentration (200 mg/L) at equilibrium state, the AOP process through Fenton-like reaction enhanced the percentage of MB removal to be 98.92% and 98.85%, respectively.

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