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Research Article

Influence of Mixing Time and Mass Ratio of Precursor on Preparation of Magnetic Biochar Derived from Cassava Peel (*Manihot utilissima*)

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Abstract: The use of magnetic biochar to overcome aquatic environmental problem has received interesting attention in recent years. Several methods in preparing magnetic biochar have been applied including impregnation-pyrolysis, chemical co-precipitation, and reductive co-precipitation. In case of co-precipitation method, the obtained magnetic biochar is relatively stable and easy to handle, that make it important to study. The purpose of this work is to study the influence of mixing time and mass ratio of precursor on preparation of magnetic biochar using this method. The cassava peel (*Manihot utilissima*) was used as feedstock for biochar preparation. The magnetic biochar which is characterised using FTIR, XRD, and SEM-EDX analysis was successfully prepared and applied as an adsorbent for MB. The optimum mixing time of precursor was identified at 60 minutes and maximum mass ratio was achieved at 1:1 of biochar:Fe_3O_4. Importantly, it can be known that MB adsorption successfully improved with the increase of mixing time, up to the optimum adsorption capacity at 60 minutes of precursor mixing time. Furthermore, at the mass ratio of 1:1 magnetic biochar displayed the highest adsorption capacity. The parameter in preparation method developed in this work can be used as an additional information in the magnetic biochar preparation.

Keywords: Magnetic Biochar, Methylene Blue, Adsorption

Introduction

Biochar provides an attractive prospect for the removal of organic contaminant in aqueous system. It is one of the low-cost sorbent materials generated by pyrolysis process in limited oxygen condition [1]. It can be produced from various feedstock biomaterial including forest residues, household and agricultural waste. Due to its unique properties including porous structure, surface area and functional group, it can efficiently adsorb various organic contaminant [2]. The adsorption of some organic contaminant in water, such as pesticide [3], chlorophenol [4], and methylene blue [5] have been reported. However, the separation process of biochar from an aqueous media usually needs filtration and centrifugation, that make a limitation in its application especially for large scale waste water treatment [6]. In this case, biochar can be modified using another material to produce more effective adsorbent.

The using of magnetic material to overcome aquatic environmental problem has received interesting attention in recent years. This material can be combined with another material and also applied to adsorb contaminant. Modification using magnetic material can be an interesting option to improve the performance of biochar, especially in its separation step after adsorption process [6]. In previous study, it has been reported that magnetic biochar not only simplified the separation process, but also significantly improved the adsorption capacity [7].

Preparation of magnetic biochar is an interesting factor to study, some methods have been conducted to prepare magnetic biochar including impregnation-pyrolysis, chemical co-precipitation, and reductive co-precipitation. Impregnation-pyrolysis means that magnetic biochar is prepared by firstly

mixing the biomass with precursor solution, and the resulted solution undergoes pyrolysis in an anoxic environment for heating treatment. In case of chemical co-precipitation, magnetic biochar was prepared by dispersing biochar in the magnetic precursor solution, which then followed by dropping alkaline solution. The reductive co-precipitation is conducted by using reducing agent to the mixed solution of biochar and iron salt, the Fe^{3+}/Fe^{2+} is reduced to zero-valent iron (ZVI) and placed on biochar surface [8, 9].

Focusing on co-precipitation method, the preparation step is easy to handle and the obtained magnetic biochar is relatively stable, that make it interesting to study [8]. To the best author's knowledge there are very few publications that report the optimum condition on magnetic biochar preparation using this method. For this reason, the aim of this work is to study the influence of mixing time and mass ratio of precursor on this method. The cassava peel (*Manihot utilissima*) was used as feedstock for biochar preparation. Cassava peel is an interesting renewable carbon-rich biomaterial that also economical source for adsorbent production [10]. However, to well increase the use of this biomaterial, there is a need to observe more the adsorption process to achieve the highest organic dye removal rate. Hence, the purpose of this work is also to display the potential of cassava peel used as feedstock for magnetic biochar.

Methods

Materials

Cassava peels was collected from Yogyakarta region, Indonesia. $FeCl_3.6H_2O$ (99.5%), $FeSO_4.7H_2O$ (99.5%), NaOH (≥97%), and methylene blue were purchased from Merck. All reagent and chemicals were used as received.

Adsorbent Preparation

In order to eliminate the impurities, waste of cassava peel was washed and kept under direct sunlight. Then, the sample was heated in a furnace with temperature of 300 °C for one hour. The resulted biochar was crushed and sieved, which then followed by treating process using H_3PO_4 14%. A mixed solution of $FeCl_3.6H_2O$ (7.8 g, 28 mmol) and $FeSO_4.7H_2O$ (3.9 g, 14 mmol) was diluted in aquadest. Then, the solution was mixed with biochar and stirred for 30 minutes at a temperature of 70 °C. NaOH was added dropwise to precipitate the iron oxide. The stirring process was kept with 4 variations of time including 30, 60, 90 and 120 minutes. After separation, the obtained solid sample was washed several times using aquadest and dried in an oven for 3 hours at a temperature of 100 °C. In case of mass ratio of precursor, biochar and Fe_3O_4 were used in the variation of 1:0, 1:0.50, 1:0.75, and 1:1 of biochar:Fe_3O_4, with the similar steps on mixing time variations.

Adsorbent Characterisation

The functional group of biochar was analysed by Fourier Transform Infrared Spectroscopy (Perkin Elmer, FTIR Spectrometer). The sample was observed by scanning electron microscopy-energy dispersive X-ray (SEM-EDX) using JEOL JSM 6510 LA to identify its morphological structure and elemental composition. The crystal structure of the sample is identified by X-ray diffraction (XRD, Bruker D2 Phaser).

Adsorption Experiment

In order to assess the performance of biochar and magnetic biochar in variation of mixing time and mass ratio of precursor, adsorption experiments were conducted using UV-Vis Spectroscopy. Biochar and magnetic biochar were added in MB solution and mixed using shaker at 250 rpm for one hour. The MB concentration was monitored at 663 nm of wavelength and adsorption capacity (q_e) was calculated using the equation 1.

$$q_e = \frac{(Co - Ce)\,V}{m} \quad \ldots\ldots\ldots\ldots \quad (1)$$

q_e : Amount of MB adsorbed onto adsorbent (mg/g)
Co : MB concentration at initial time (mg/L)
Ce : MB concentration at final time (mg/L)
V : Solution volume (L)
m : Adsorbent mass (g)

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Results and Discussion

1. FTIR spectroscopy

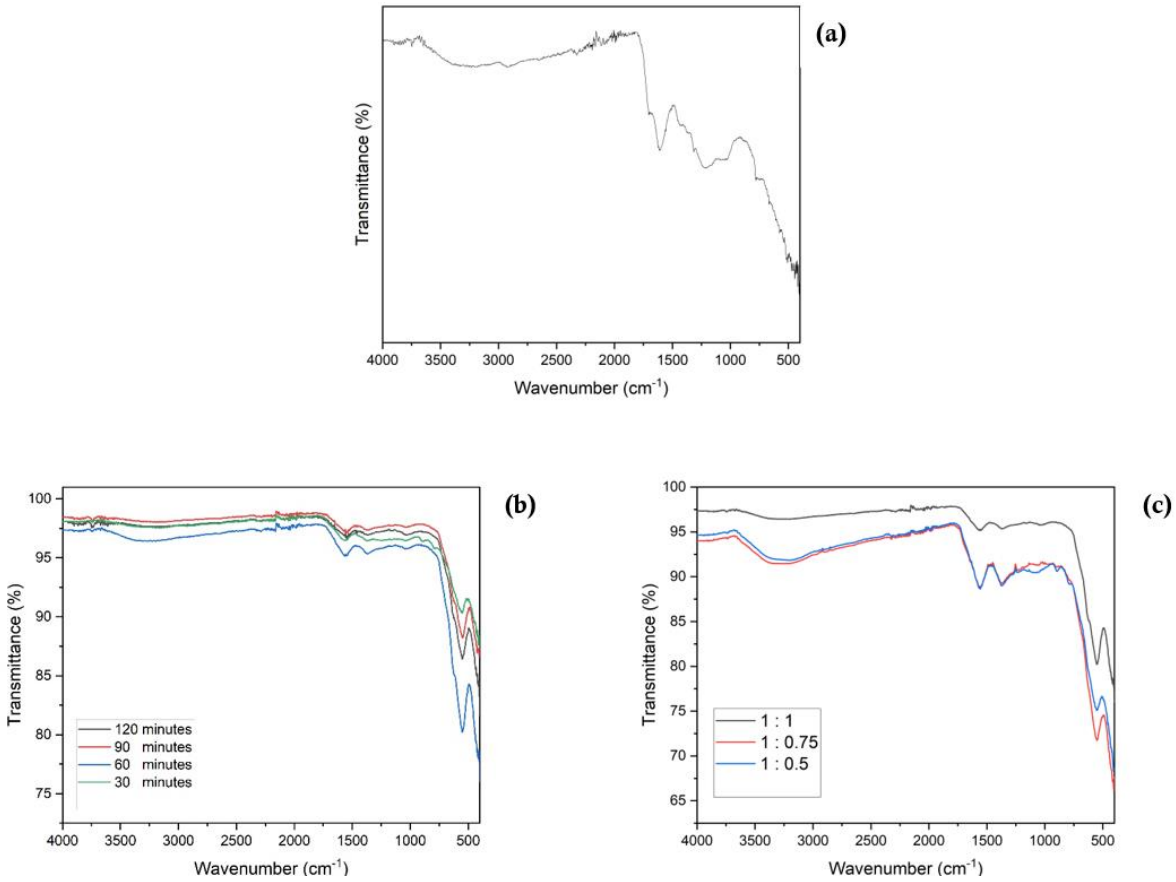

Figure 1. FTIR spectra of (a) biochar, (b) magnetic biochar in the mixing time variation of precursor and (c) magnetic biochar in the mass ratio variation of biochar : Fe_3O_4

FTIR spectra for the biochar, magnetic biochar with mixing time variation and magnetic biochar in the variation of mass ratio of biochar:Fe_3O_4 were presented in Figure 1. As can be seen in Figure 1.a, FTIR spectra of biochar samples show the characteristic peaks of biochar material at around 3256, 1554, and 1034 cm^{-1} which correspond to -OH, C=C, and C-O, respectively. After magnetization (Figure 1.b), the characteristic peaks at around 552 cm^{-1} appear in the corresponding spectra, which is assigned to the stretching vibrational mode of the Fe-O bonds [11, 12]. It is indicating the presence of iron oxides on biochar and will be confirmed with result obtained from XRD analysis in the next section. Interestingly, it can be seen that the spectra of magnetic biochar with mixing time of 60 minutes have the greatest adsorption of Fe-O groups, which is indicate the most effective mixing time of precursor. In addition, as can be known in Figure 1.c, the broad band at 3256 cm^{-1} was mainly assigned to the stretching vibration of O-H. The peaks at 1554 and 1034 cm^{-1} were related to the vibration of C=C and C-O, respectively. The presence of Fe-O bonds is assigned to the characteristic peaks of at around 552 cm^{-1}[11, 12]. It can be seen that the spectra of biochar:Fe_3O_4 with mass ratio of 1 :1 has the greatest adsorption of Fe-O groups, which is indicate that the most effective of mass ratio used in this study.

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2. SEM-EDX Observation

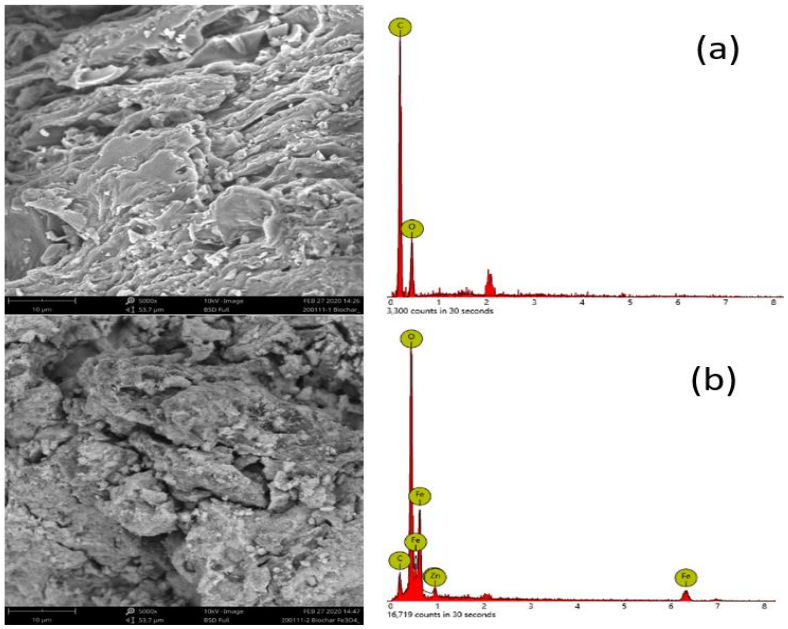

Figure 2. SEM micrographs and EDX spectra of (a) biochar and (b) magnetic biochar

The micrographs given in Figure 2 show the differences of the biochar and magnetic biochar surface morphology. It can be seen that the surface of biochar is depicted porous structure with irregular pores. On the other hand, magnetic biochar has an irregular form also with agglomeration in its structure. EDX mapping as presented in Figure 2 indicates the presence of C and O for biochar, which then C, O, Fe, and Zn for magnetic biochar. It can be identified that the biochar consists mainly C (70.22%) and O (29.78%). Compared to biochar, the magnetic biochar shows that the percentage of carbon has decreased to be 16.69% and oxygen has increased to be 58.21%. The presence of Fe in magnetic biochar was detected in percentage of 23.94%, with trace amount of the Zn element in the amount of 1.17%. The presence of iron and improvement of oxygen percentage can prove the formation of iron oxide in the magnetic biochar [13, 14] and will be confirmed using XRD analysis in the next section.

3. XRD Analysis

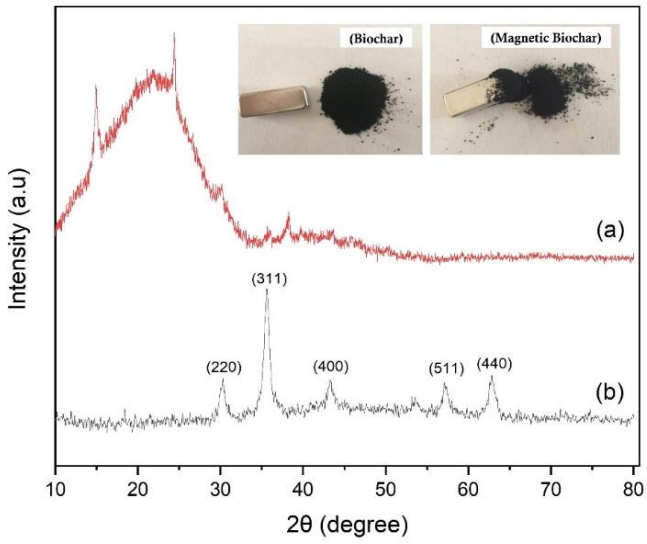

Figure 3. XRD patterns of (a) biochar and (b) magnetic biochar

Figure 3 shows the XRD pattern of biochar and magnetic biochar. The XRD patterns of biochar and magnetic biochar present that the crystal structure and intensity of XRD diffraction peaks significantly altered. There were main peaks in the magnetic biochar diffraction pattern (2θ: 30.30, 35.44°, 43.59°, 57.99°, and 62.62°). These peaks correlate to the four indexed planes (220), (311), (400), (511), and (440) of maghemite, which is correspond to the characteristic peaks of Fe_3O_4 (magnetite) [15, 16]. This result confirms that the main crystalline in magnetic biochar is magnetite and Fe_3O_4 was successfully loaded to the biochar. Furthermore, it is also can be seen that magnetic biochar can be attracted by external magnet as shown in Figure 3 inset.

4. Adsorption Experiment

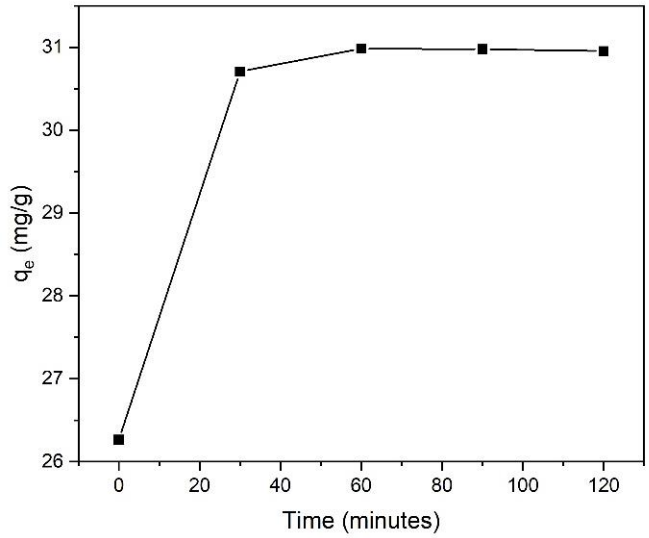

Figure 4. The MB adsorption in the mixing time variation of magnetic biochar precursor

This research was studied the MB adsorption in the mixing time variation of precursor to get an additional information of the best mixing time used in magnetic biochar preparation. It can be seen in Figure 4 that MB adsorption successfully improved as the increase of mixing time, up to the optimum adsorption capacity at 60 minutes of precursor mixing time. This is related to the results of the FTIR analysis where 60 minutes is the best mixing time as indicated by the highest Fe-O adsorption. In this case, Fe–O bond and $-N^+(CH_3)_2$ of MB cations were responsible for the electrostatic attraction onto adsorbent [17], hence MB adsorption is significantly influenced by Fe-O amount.

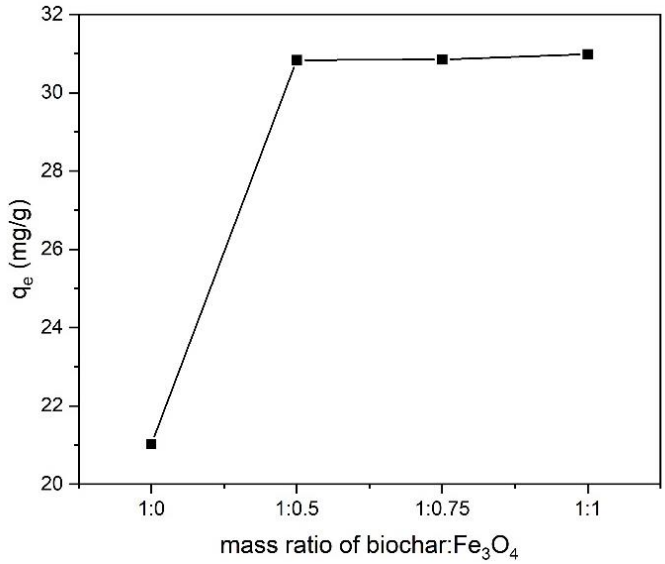

Figure 5. The MB adsorption in mass ratio variation of magnetic biochar precursor

In addition, this research was also studied the MB adsorption in variation of mass ratio of precursor to get the best amount of precursor used in magnetic biochar preparation. Figure 5 represents the adsorption capacity of MB from aqueous solution when the mass ratio of biochar:Fe_3O_4 was 1:0, 1:0.5, 1:0.75, and 1:1. It can be seen that the adsorption capacity of MB on the magnetic biochar increased as the improving of Fe_3O_4. Based on this result, it is can be known that at the mass ratio of 1:1, magnetic biochar displayed the highest adsorption capacity of 30,98 mg/g for MB. This is also related to the results of the FTIR analysis where mass ratio of 1 :1 has the greatest adsorption of Fe-O groups.

Conclusion

This report studied the influence of mixing time and mass ratio of precursor on magnetic biochar preparation. The magnetic biochar which is characterised using FTIR, XRD, and SEM-EDX analysis was successfully prepared from cassava peel which then applied as an adsorbent for MB. The optimum mixing time of precursor is identified at 60 minutes and maximum mass ratio was achieved at 1:1 of biochar:Fe_3O_4. Importantly, the modification using Fe_3O_4 successfully increased the adsorption capacity of biochar both in MB adsorption result of mixing time and mass ratio variation. It can be known that MB adsorption successfully improved with the increase of mixing time, up to the optimum adsorption capacity at 60 minutes of precursor mixing time. Furthermore, at the mass ratio of 1:1, magnetic biochar displayed the highest adsorption capacity.

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