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Improving Adsorption Performance of Water Hyacinth-Derived Activated Biochar via Controlling the Activating Agents and Pyrolysis Temperature

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Biochar, a carbon material, has become an attractive material for various applications due to its intriguing properties. The characteristics and adsorption performance of biochar depended on synthesis conditions. Hence, this work aimed to study the influence of activating agents and pyrolysis temperature on the structure and adsorption performance of biochar. The activated biochar (AB) was prepared by treatment of raw water hyacinth (an agricultural waste) with different activating agents including $ZnNO_3$, $FeCl_3$, $NiCl_2$, KOH and HNO_3 before treatment at high temperature under N_2 atmosphere. The obtained AB samples were characterized by XRD, SEM, Raman, and BET. The activating agents strongly affected on the structure of the AB and methylene blue adsorption performance. The $ZnNO_3$-activated biochar exhibited highest MB removal, compared to the KOH-, $FeCl_3$-, $NiCl_2$-, and HNO_3-activated biochar. In addition, it was found that the pyrolysis temperature significantly enhanced the adsorption performance. The MB removal increased from 21.4 % to 99.4 % corresponding to the increasing of the temperature from 500 to 800 °C. Moreover, the highest MB adsorption capacity was 59.6 mg g^{-1} for Zn-BC-800.

1. Introduction

Biochar (BC) was produced for biomass or agricultural wastes via thermal treatment. It is a carbon-rich containing material, low cost, and environmentally friendly (Álvarez et al., 2015). Thus, BC has become a crucial material for environmental applications (Das et al., 2020). However, activity of biochar was relatively low due to limited functional groups, low surface area, and poor porous structure (Lee et al., 2018). In order to improve those properties, the activation process was conducted using various methods to produce activated BC (Panwar and Pawar, 2020). It was reported that the physicochemical properties of activated BC could be improved by using different activation processes. For example, Shao et al., applied physical activation method to prepare activated biochar from corncob, showed that the BET surface area significantly increased from 56.1 (without activation) to 755.3 m^2/g (with CO_2 activation) (Shao et al., 2018). They also demonstrated that CO_2 molecules reacted with carbon of the biochar resulting in the formation of microporous structure.

Compared to physical activation method, chemical activation not only enhanced porous structure but also generated multi-functional groups and removed impurities. Thus, the chemical activation method is widely applied to synthesize activated BC for desired applications. For instance, He and co-workers reported the chemical activation of rice husk-derived biochar using $ZnCl_2$, the activated BC exhibited high surface area of 1442 m^2/g and contained 99 % mesoporous (He et al., 2013). The acidity of activated BC can be generated by phosphoric acid activation, which served as active sites for catalytic hydrolysis of starch and dehydration of fructose (Cao et al., 2018). Liu et al. demonstrated that KOH-activated BC increased surface area and introduced to oxygen-containing functional groups, resulting in enhancing the adsorption capacity on tetracycline (Liu et al., 2012). It was recognized that the applying of different activating agents for preparing activated BC

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has strongly affected its textural properties and adsorption performance. However, the activated BC was prepared from various biomass sources at different conditions, which leads to the difficulty in the selection of a suitable activator.

To determine the suitable activating agent for preparing a desire material, the effect of activating agents have to study. Ludwinowicz and Jarnoiec (2015) investigated the influence of activating agents (i.e. KOH, CO_2, NH_3, $ZnCl_2$) on CO_2 adsorption of activated BC derived commercial carbon, showing that KOH-activated carbon has the highest CO_2 uptake (6.9 $mmol^{-1}$ at 1 bar), compared to the others. Safitri and co-workers observed that H_3PO_4-activated BC derived rice husk exhibited better adsorption performance than KOH-activated BC (Safitri et al., 2017). Another report showed that the alkali treated biochar was effective than that was treated by acidic agent (Liu et al., 2012). The previous reports indicated that each single activating agent could act on a specific biomass source. The influence of various chemical agents on the adsorption capacity have become attractive studies. Herein, we aim to study the effect of activating agents on the methylene blue adsorption of activated BC. Various chemical activating agents including alkali (KOH), acid (HNO_3), and metal salts ($Zn(NO_3)_2$, $NiCl_2$, and $FeCl_3$) have been used to activated biochar derived from Water hyacinth. The activated BC was evaluated the methylene blue adsorption in aqueous solution. In addition, the pyrolysis temperature of the material and kinetic studies were also reported.

2. Experimental

2.1 Synthesis of Water hyacinth-derived biochar samples using different chemical agents

All chemicals were purchased and used directly, without any further purification.

Activation procedure was carried out analogous previous literatures, here water hyacinth was used as precursor. Typically, 10 g water hyacinth was added into 200 mL solution of chemical activating agents such as KOH, HNO_3, $Zn(NO_3)_2$, $NiCl_2$, and $FeCl_3$ (0.25 M). The mixture was stirred for 24 h at room temperature, then filtered to collect the solids. The obtained solids were dried at 100 °C overnight, before the pyrolysis process. The dried solids were placed in the crucible inside the oven. The N_2 gas was purged into the over with the flow rate of 40 mL min^{-1} in 30 min before heating. The sample was calcined at 600 °C with heating rate of 5 °C min^{-1} and keep at desire temperature in 5 h. The sample inside the oven was cooled to room temperature, then immersed in 200 ml HCl 15 % for 6 h. The black powder was washed by water several times until pH reached neutral, and dried at 100 °C for 12 h. the resulted powder was named as K-BC-600, Fe-BC, HNO_3-BC, $NiCl_2$-BC, and $Zn(NO_3)_2$-BC, corresponding to the activating agent of KOH, $FeCl_3$, HNO_3, $NiCl_2$ and $Zn(NO_3)_2$.

2.2 Characterization

The BET surface area was calculated based on N2 adsorption/desorption analysis, which was performed on a Micromeritics ASAP 2020. Raman spectroscopy (Raman Labram 300, Jobin Yon) was used to determine carbon structure of the synthesized samples under excitation of 532 nm.

2.3 Adsorption studies

Methylene blue (MB) was chosen as an adsorbate for evaluating the adsorption ability of the synthesized samples. 0.05 g activated biochar was added into 100 mL MB solution (50 mg/L). The solution was shacked at room temperature for 2 h. After 2 h, 1 mL liquid was withdrawn from the solution and diluted into 10 times before UV-Vis analysis. The concentration of MB after dilution was determined at 668 nm. The removal and adsorption capacity (q) were calculated as Eq (1) and (2):

$$Removal\ (\%) = \frac{Co - Ct}{Ct} * 100\ \% \qquad (1)$$

$$q\ (\%) = \frac{V(Co - Ct)}{w} \qquad (2)$$

where Co and Ct are initial and final concentration of MB in solution, w is amount of activated BC used.

3. Results and discussion

3.1 Effect of activating agents on the MB adsorption of the activated BC samples

The adsorption efficiency of the activated BC samples was showed in Figure 1. It can be seen that the chemical activating agents strongly affected the removal MB in the aqueous solution. The removal efficiency was not significant difference between the Fe-BC, Ni-BC, and H-BC with the BC sample (without activation), which was only around 12-16 %. The K-BC sample showed better efficiency with 56.9 %. Interestingly, the Zn-BC exhibited the best performance with 75.0 % removal of MB. In addition, the adsorption capacity was also calculated to be

56.5, 35.7, 16,6, 16.5, and 12.1 mg g^{-1} for $Zn(NO_3)_2$, KOH, $FeCl_3$, $NiCl_2$, HNO_3. These results indicate that the chemical activating agents effected on the MB adsorption efficiency of the synthesized samples was in the following order: $Zn(NO_3)_2$ > KOH > $FeCl_3$ > $NiCl_2$ > HNO_3, which is the first time observation. Ludwinowicz and Jarnoiec (2015) reported that the KOH-activated carbon was better than that used $ZnCl_2$, NH_3, and H_2O. While Safitri et al. (2017) showed that acid-treated biochar exhibited higher removal than alkali-treated biochar.

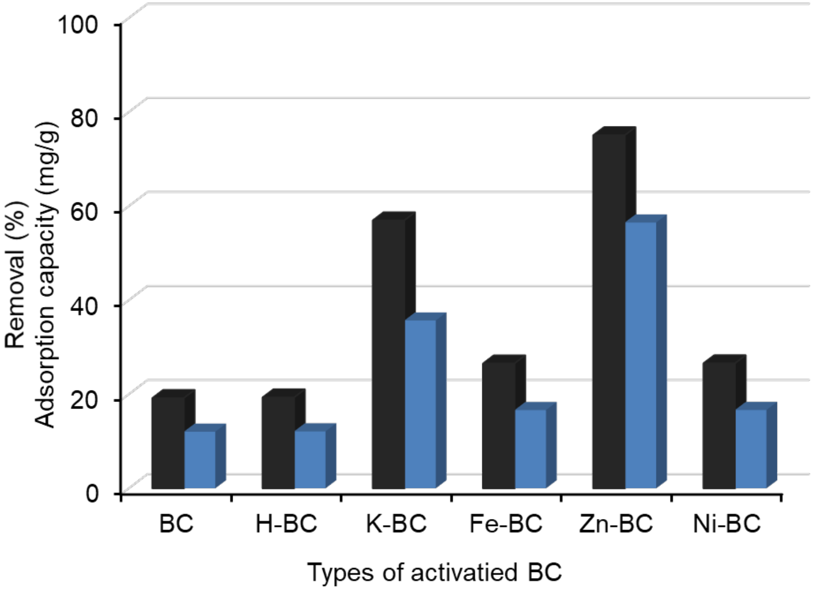

Figure 1: Illustration of removal efficiency and adsorption capacity of MB on the activated BC

It was reported that the activating agents changed the textural properties of the synthesized materials, resulting in the difference in the adsorption performance. It was reported that the porous structure contributed to the adsorption activity. The porous properties of the activated biochar samples were showed in the Table 1. However, the removal efficiency has no relationship between the porous property and adsorption ability of the activated biochar samples. The BET surface area of H-BC was highest with 606.5 m^2 g^{-1}, compared to Ni-BC of 433.5 m^2 g^{-1}, Fe-BC of 461.9 m^2 g^{-1}, Zn-BC of 500.3 m^2 g^{-1}, and K-BC of 590.1 m^2 g^{-1}, which did not consist with the adsorption performance. Therefore, we suggest that the adsorption performance of the activated biochar could be governed by the physical interaction between MB and the material (Dutta et al., 2021).

Table 1: Porous characteristics of the synthesized activated biochar samples

Samples	BET surface area (m^2 g^{-1})	Pore diameter (nm)
Zn-BC	500.3	1.99
Fe-BC	461.9	3.51
Ni-BC	433.5	2.06
K-BC	590.1	2.31
H-BC	606.5	3.08

The π-π interaction between MB and biochar was considered as important factor to enhance the adsorption capacity. Raman spectroscopy was performed to evaluate the graphitic structure of the activated biochar samples. As shown in Figure 2, Raman spectra of the synthesized activated biochar revealed the G (1596 cm^{-1}) and D (1350 cm^{-1}) band, corresponding to C(sp^2) carbon and defects (Primo et al., 2012). The calculation of I_D/I_G ratio showed that the I_D/I_G of Zn-BC sample is 0.95, which is lower than that of Fe-BC (0.99), Ni-BC (1.00), H-BC (1.01), and K-BC (1.00). The low I_D/I_G ratio indicated more π bonding on the structure of the biochar, which resulted in the improving of MB adsorption. Based on the observations, we suppose that the MB adsorption capacity on the activated biochar sample was contributed to both surface area and π-π interaction.

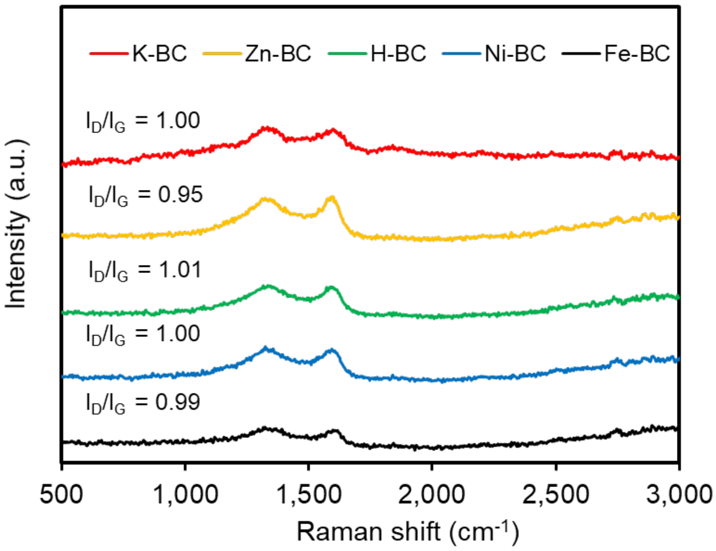

Figure 2: Raman spectra of the activated biochar.

3.2 Effect of pyrolysis temperature on the MB adsorption

The effect of pyrolysis temperature on the adsorption ability of the activated biochar was investigated. The activated biochar was synthesized from 500 to 800 °C using $Zn(NO_3)_2$ as activating agent. Figure 3 shows that increase in the pyrolysis temperature leaded to significant improvement of the MB removal. Only 24.1 % MB was removed in 2 h using Zn-BC-500, this value sharply increased to 94.94.5 and 99.5 % for Zn-BC-700 and Zn-BC-800. In addition, a high adsorption capacity 56.5 and 59.6 mg g^{-1} was observed using Zn-BC-700 and Zn-BC-800 as absorbents. The adsorption capacity was This observation was similar with the previous reports (Mahdi et al., 2017). Ding et al. (2016) studied the influence of synthesized temperatures on the MB adsorption, showing that increase in the synthesized temperature leaded to enhancing the adsorption.

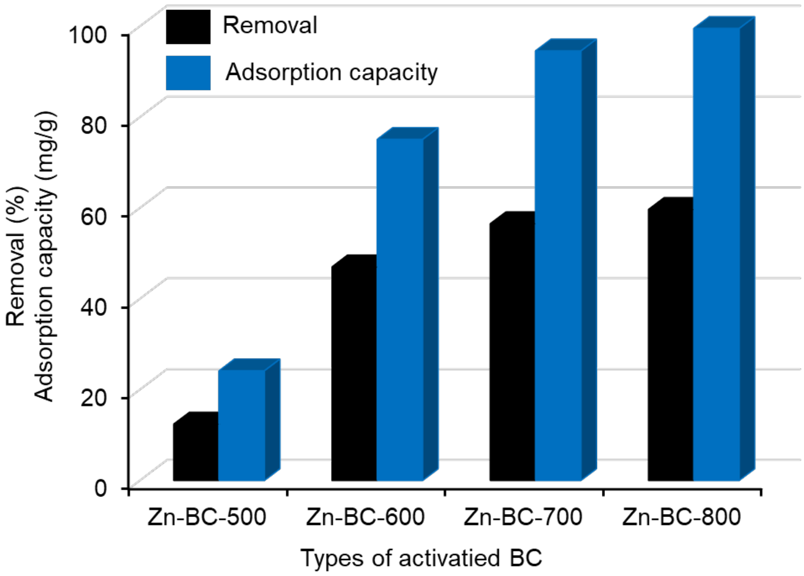

Figure 3: Illustration of effect of pyrolysis temperature by removal efficiency and adsorption capacity of the activated BC on MB.

3.3 Effect of contact time on MB adsorption ability of activated biochar

Figure 4 showed that the adsorption process of MB by activated BC was extremely fast in the first of 20 min, then reached the equilibrium state at 120 min for all MB concentrations. Dural et al. (2011) reported that the MB absorbed on activated carbon derived from *Posidonia oceanica* (L.) has the equilibrium time of 60 min (2011). Another report showed the contact time of MB adsorption on carbon-based material was 100 min (Sharma, 2010). At the equilibrium time, the MB removal obtained to be 89.0, 89.5, 68.8, 54.6, and 50.3 % for the MB concentration of 70, 90, 110, 130, 150 mg/L. In addition, the maximum capacity adsorption of MB on the Zn-BC-700 was calculated to be 163.3 mg/g, which was comparable with the previous reported (Yao et al., 2010).

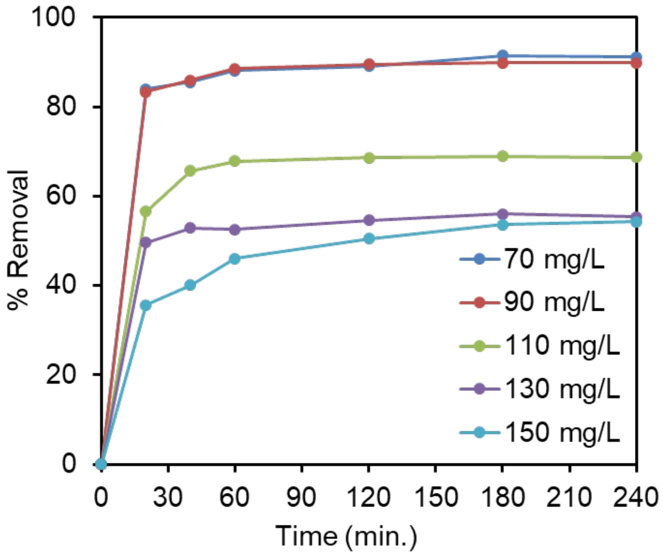

Figure 4: Influence of contact time on MB removal of the activated BC. Conditions: Zn-BC-700 (0,05 g), 100 mL MB with various concentration (70-150 mg/L).

3.4 *E*ffect of pH on MB adsorption ability of activated biochar

pH environment has strongly affected (Sharma et al. 2016) the adsorption process of the carbon-based materials, which was studied in the range from 4-11. In the acidity environment, the MB removal was lower, whereas the higher MB removal was observed in the base environment. A 84.1 % MB removal achieved in the pH of 8.6, suggesting that the synthesized biochar was positive surface charge.

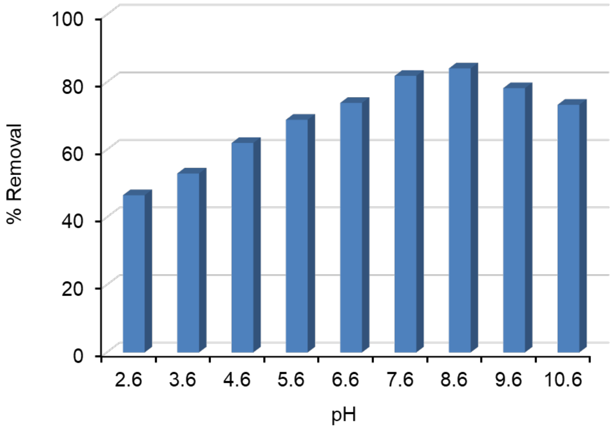

Figure 5: Influence of pH on MB removal of the activated BC. Conditions: Zn-BC-700 (0.05 g), 100 mL MB with various concentration (110 mg/L), time 120 min.

4. Conclusions

The effect of different activating agents including acid (HNO_3), base (KOH), metal salts ($Zn(NO_3)_2$, $FeCl_3$, and $NiCl_2$) on methylene adsorption of the activated biochar was investigated. It was found that the adsorption capacity was in the following order: $Zn(NO_3)_2$ < KOH < $FeCl_3$ < $NiCl_2$ < HNO_3. The $Zn(NO_3)_2$-activated biochar exhibited the best MB adsorption was observed for the first time, with adsorption capacity of 56.9 %. In addition, the effect of pyrolysis temperatures on the MB adsorption was studied. The MB capacity was 12.4, 47.2, 56.9, and 59.7 % for Zn-BC-500, Zn-BC-600, Zn-BC-700, Zn-BC-800. The effect of contact time and pH value was further investigated.

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