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Effect of H_3PO_4 and KOH as the Activating Agents on the Synthesis of Low-Cost Activated Carbon from Duckweeds Plants

(Kesan Agen Pengaktif terhadap Sintesis Karbon Teraktif Kos Rendah daripada Tumbuhan Kiambang Itik)

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ABSTRACT

Adsorption is a simple and easily operated treatment process for water and wastewater reclamation. However, the cost of activated carbon (adsorbent) is an obstacle for this process to be widely employed in developing and underdeveloped countries. Hence, a low-cost and easily available Duckweeds plant has been used as the raw material for the synthesis of low-cost activated carbon. In this study, the effect of activating agents; potassium hydroxide (KOH) and phosphoric acid (H_3PO_4) on the properties of the activated carbon produced from Duckweeds plants was investigated. Duckweeds plants that were impregnated with an activating agent with a ratio 1:2 were carbonized in a tube furnace for two and a half hour at 550ºC with continuous nitrogen flow. After that, the synthesized activated carbon was used to remove methylene blue dye from aqueous solution. It was observed that activated carbon impregnated with H_3PO_4 possessed a more extensive exfoliated and multilayer structure, which gave rise to better adsorption performance compared to activated carbon impregnated with KOH. Furthermore, the porosity of the activated carbon impregnated with was much higher (38 ± 6%) compared to the sample impregnated with KOH (22 ± 4%). Indeed, the removal of dye for the former was slightly better (3-5%) and achieved equilibrium adsorption within a shorter duration. The findings show that H_3PO_4 is a better activating agent to induce exfoliated and multilayer structures on the activated carbon, where both of these characteristics are important for a good adsorption process. Overall, Duckweeds plants are a feasible source for the synthesis of low-cost activated carbon. Considering that Duckweeds plants can be used to remove nutrients presence in the wastewater, the activated carbon synthesized from the plants can be incorporated into the existing wastewater treatment plant as an additional purification process.

Keywords: Activated carbon; duckweeds; wastewater treatment; low-cost adsorbent; chemical activation

INTRODUCTION

Water, being one of the essential elements for life on Earth, has been taken for granted by humankind. Water quality across the world has been degraded significantly in just a few decades due to intensive anthropogenic activities. The release of industrial discharge and domestic effluent without proper treatment to the waterway has polluted the water resources. This indicates that the clean water resources have been in dwindling trend and it has become a serious issue worldwide since water scarcity will disrupt the daily life routine and economic development. More worryingly, rapid urbanization, high population growth and increased agricultural and industrial activities have further imposed stress on limited clean water resources (Wu et al. 2018). World Health Organization has predicted that by 2025, half of the world's population will be living in water-stressed areas, with the majority living in developing and underdeveloped countries (World Health Organization 2018). Not only the shortage of clean water will interrupt with the societal and economic development, but it will affect the public health too. Without proper access to clean water, the community will be exposed to diseases such as cholera, diarrhea, typhoid and polio, which are associated with contaminated water and poor sanitation.

In order to cope with the problem of dwindling clean water resources, several technologies such as coagulation, ion exchange and membrane filtration have been developed to remove the contaminants present in the polluted water (Mahmoudi et al. 2015). Though the aforementioned processes can remove the contaminants such as heavy metals, dyes, natural organic matter and pesticides, the adoption of such processes has its own challenges and secondary problems. The high dosage consumption of metallic coagulants and production of huge amount of sludge in coagulation process has been a concern for many due to the difficulty in dealing with the secondary sludge waste (Comninellis et al. 2008). Even though membrane filtration process is highly capable in removing contaminants, its high capital and operating costs have been a major financial obstacle for many developing and underdeveloped countries to adopt it in their water and wastewater treatment plants (Ng et al. 2013). Hence, a simple, low-cost and easily operated process that could remove the contaminants and at the same time feasible for developing and underdeveloped countries has to be explored.

Adsorption is one of the most popular physicochemical treatment for the removal of contaminants from water and wastewater. It has been known as one of the most competent environmental control technologies (Baccar et al. 2013). The adsorption process is commonly used for the removal of various pollutants from water such as dyes and heavy metals (Burakov et al. 2018; Gisi et al. 2016). For instance, Hameed et al. (2007) reported that adsorbent can effectively remove water pollutants such as Methylene Blue, which is a common pollutants present in textile, plastic and dye industrial effluents. Its wide acceptance in water and wastewater treatment could be attributed to its ease of operation, convenience and simplicity of design (Bhatnagar et al. 2015). One of the most commonly adopted adsorbents is activated carbon. Activated carbon is a porous adsorbent material that provides a surface for the ions or molecules (pollutants) to adhere onto. It is available in two different forms (powdered activated carbon and granular activated carbon) and its adsorptive properties mainly depend on pore size and internal surface area of the pores (Randtke & Horsley, 2012). During the synthesis of activated carbon, chemical activation, which involves the impregnation of the carbon structure with an activating agent (either an acid or base), is normally used to obtain the desired adsorbent properties (Rocha et al. 2015). Though activated carbon adsorption has been recognized as one of competent material for water treatment process, its application is sometimes restricted due to its higher adsorbent cost (Gautam et al. 2014).

In order to cope with the financial constraint, a large variety of low-cost adsorbents have been proposed and examined for their ability to remove various types of pollutants from water and wastewater (Bhatnagar et al. 2015). For instance, literature has shown that activated carbon could be successfully synthesized from fruit peels, agricultural wastes and industrial wastes (Bhatnagar et al. 2015; Rocha et al. 2015; Namasivayam & Kavitha 2002). In general, an adsorbent can be considered as low cost if it does not require complicated processing for production and it can be easily obtained or abundantly available in nature. Hence, the aforementioned sources can be considered as low-cost adsorbents since it can be easily obtained with little cost. One interesting low-cost adsorbent candidate that has not been explored is duckweeds. Duckweeds are the aquatic plants that have been extensively studied for wastewater treatment due to their rapid growth and high nutrient uptake (Toyama et al. 2018). At the same time, duckweeds are also an ideal feedstock for production of biofuels. This results in dual benefits for the wastewater treatment plants that have adopted duckweeds as part of the treatment processes. Considering that duckweeds can be produced abundantly in a short period of time, it could be a low-cost source for the production of activated carbon. The activated carbon produced from duckweeds can be applied as an adsorbent to purify the wastewater further.

This study aimed to synthesize low-cost activated carbon from easily available duckweeds. Chemical activation with different agents: potassium hydroxide (KOH) and phosphoric acid (H_3PO_4) were used in the synthesis process to observe the impact of the activation agent on the adsorptive property of duckweeds-activated carbon. The adsorption performance was examined on the removal of methylene blue (dyes pollutants) from the aqueous solution. Findings from this study will provide an opportunity for wastewater treatment plant that has adopted duckweeds as part of the treatment process to have an additional purification (adsorption) process for the wastewater.

METHODOLOGY

MATERIALS

All the chemicals used in this study were of analytical grade. KOH and H_3PO_4 were supplied by Merck, Malaysia while hydrochloric acid (HCl) was obtained from Accot Lab Supplies, Malaysia. The dye used as pollutant in this study, methylene blue was purchased from Sigma-Aldrich, Malaysia. The duckweed plant was taken from the Plants House at National University of Malaysia.

PREPARATION OF ACTIVATED CARBON FROM DUCKWEEDS

The duckweeds roots were removed and the leaves were washed with clean water to remove any impurities attached on it. The cleaned duckweeds leaves were then dried in an oven with temperature of 70ºC for 8 hours. The synthesis process of activated carbon was adopted from the method employed by Hidayah (2015). The dried duckweeds leaves were impregnated overnight with 1 M of H_3PO_4 with a ratio of 1:2 for leaves to H_3PO_4. The mixture was then filtered to obtain the impregnated sample (carbon precursor), which was then dehydrated overnight in oven at 70ºC. The dried impregnated sample was carbonized and activated in a tube furnace (Carbolite Furnace MTF 12/38/250, UK) for duration of two and a half hours at 550ºC. The heating rate and nitrogen gas flow were set at 18ºC/min and 100 mL/min, respectively. After that, the sample was washed with 1 M of HCl followed by distilled water to get rid of the chemical residue. The sample was then dried in oven overnight at 100ºC to obtain the activated carbon. The synthesis process was repeated with KOH replacing H_3PO_4. The morphological structure of the activated carbon was observed using Field Emission Scanning Electron Microscopy (FESEM) (Gemini Model SUPRA 55VP-ZEISS, Germany). The overall porosity of the adsorbents (ε) was determined using gravimetric method (Fridland et al. 2003), as defined in Equation (1):

$$\varepsilon = \frac{\omega_1 - \omega_2}{V \times d_w} \quad (1)$$

where ω_1 is the weight of the adsorbents when saturated with water, ω_2 is the weight of the oven-dried adsorbent, V is the overall volume of the adsorbent (m^3), d_w is the water density (998 kg/m^3).

ADSORPTION TESTING

The aqueous solution containing methylene blue at concentration of 10 mg/L was prepared by adding 0.01 g of the dye into 1 L of distilled water. For the adsorption process, 100 ml of aqueous solution was poured into a conical flask. Then, the as prepared activated carbon (0.5 g) was dosed into the conical flask and agitated by an isothermal shaker with a speed of 200 rpm for 5 hours. Supernatant was extracted for analysis from time to time. After the extraction, the supernatant was filtered with 45 µm membrane to remove the adsorbent that might interfere with the analysis. The above procedure was repeated with different amount of activated carbon (0.7 g and 1.0 g). All the tests and analyses were repeated three times to minimize errors. The equilibrium amount of dye adsorbed per unit mass of adsorbent (q_e) (mg/g) was calculated using Equation (2), where C_o and C_e denote the initial and equilibrium dye concentrations in the solution (mg/L), respectively; V is the volume of solution in the flask (mL); and M is the dry weight of the adsorbent (g).

$$q_e = \frac{(C_o - C_e)V}{M} \qquad (2)$$

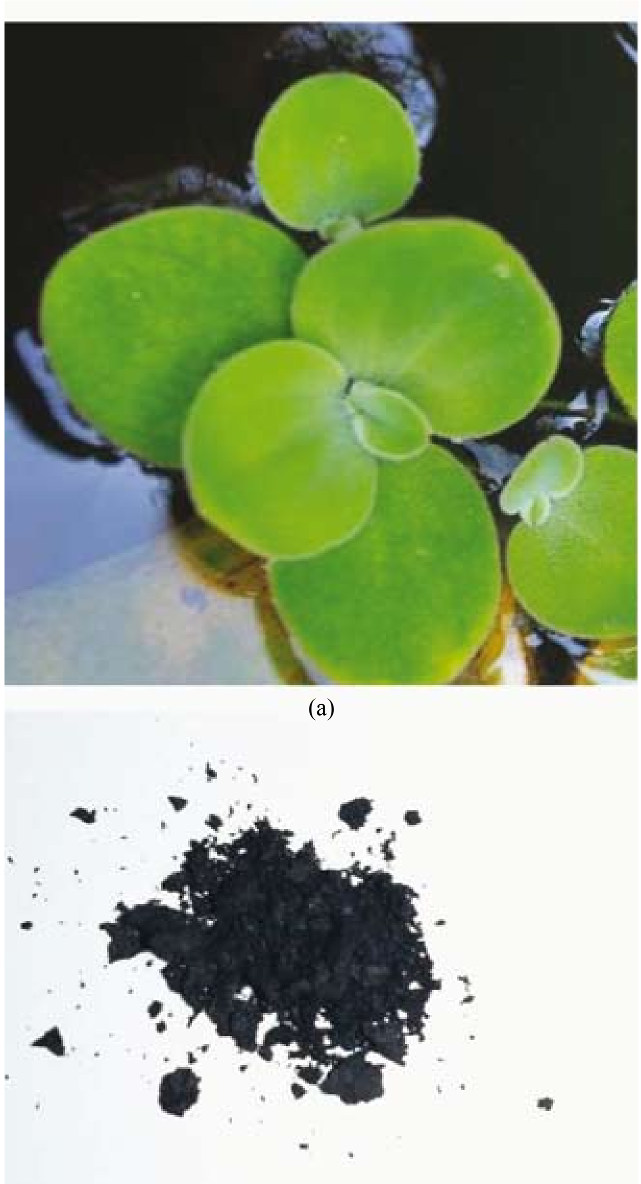
The removal rate of methylene blue (R) was calculated using Equation (3). The concentration of the methylene blue was determined using UV-vis Spectrophotometer (Perkin Elmer Lambda-35, UK) at 663 nm wavelength.

$$R = \frac{(C_o - C_e)}{C_o} \times 100\% \qquad (3)$$

RESULTS AND DISCUSSION

MORPHOLOGICAL STRUCTURES OF THE ACTIVATED CARBON

Figure 1 shows the leaves before and after the carbonization process. The color change indicates that the carbonization process was successful. After activation in the tube furnace with the KOH and H_3PO_4, the sample was observed using FESEM and the results were displayed in Figure 2. As can be seen from Figure 2(a) (sample impregnated with KOH), the general feature of activated carbon are present (Ou et al. 2012). The surface of the sample was rough and full of pores, which could provide the adsorption sites for pollutants. Zhang et al. (2010) reported that high surface area and high porosity contributed to good adsorption performance where the pollutants can attach onto the porous surface. Interestingly, activated carbon impregnated with H_3PO_4 (Figure 2(b)) presented a distinctive structure. From the FESEM image, it is completely obvious that this sample has a more exfoliated structure, almost similar to multilayer graphene structure as reported by other researchers (Ou et al. 2012).

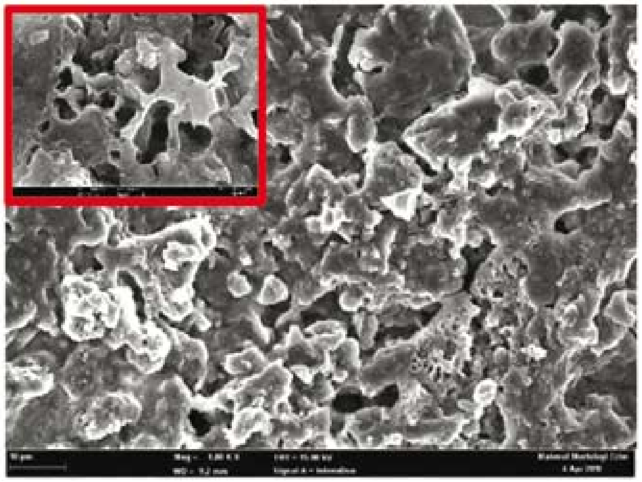


(a)

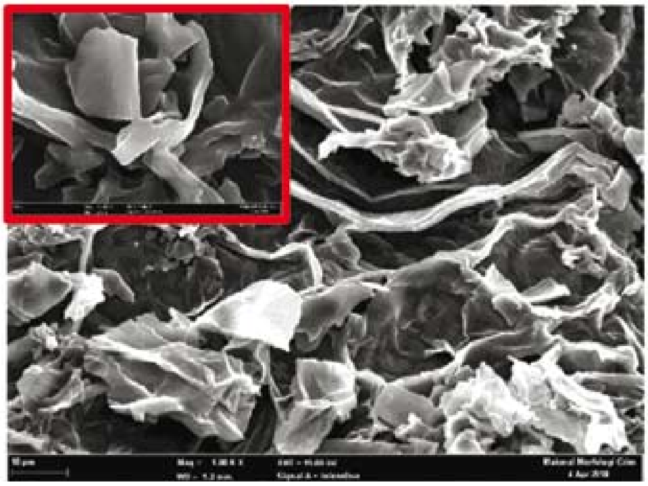
(b)

FIGURE 1. Appearance of (a) Fresh Duckweeds plants (b) Carbonized and activated sample

This postulation was supported by the porosity value of the adsorbent. The porosity of the sample impregnated with KOH was 22 ± 4% while it was observed that the prosity of the sample impregnated with H_3PO_4 recorded much higher value at 38 ± 6%. This finding could be directly related to the surface area of the adsorbent as the adsorbent with higher porosity tends to have higher surface area due to the exfoliated and porous structures (Yalçın et al. 2000). From these observations, it was discovered that the impregnation of the sample with different activating agents has dramatic effect on the structures of the activated carbon. This will give rise to different adsorption performance.



(a) Activated carbon impregnated with KOH



(b) Activated carbon impregnated with H_3PO_4

FIGURE 2. Morphological structure of activated carbon impregnated with different activating agents (magnification scale of 1000 for larger images and 10000 for inset images)

Adsorption Testing

(a)

(b)

FIGURE 3. Methylene blue solution before (a) and after (b) the adsorption process (sample on the leftmost side is control for comparison purpose)

Figure 3 shows the physical observation of the dye solution before and after the adsorption process. it can be seen that after adsorption process, the color of the solution faded, indicating that the dye molecules were removed by activated carbon. The equilibrium amount of dye adsorbed per unit mass of activated carbon and percentage of dye removal for activated carbon impregnated by KOH and H_3PO_4 were shown in Figure 4 to Figure 7. Overall, both sets (activated carbon impregnated with KOH and H_3PO_4) possess the same increasing trend for equilibrium adsorption capacity and removal percentage. However, the results show that under lower dosage of activated carbon (0.5 g/200 ml), the equilibrium amount of dye adsorbed per unit mass of adsorbent was higher compared to the cases with higher dosage. It was postulated that the lowest dosage in this study already exceeded the optimum amount of activated carbon for the removal of pollutants (dye). Higher dosage of activated carbon would not help to increase the equilibrium capacity, as there are not many available pollutants that could be captured by the activated carbon that present in excess. Hence, higher dosage of activated carbon (0.7 g/200 ml and 1.0 g/200 ml) would only lead to lower equilibrium capacity and the adsorbent which present in excess would be untapped since there are no more pollutants to be adsorbed.

The duration of time to achieve equilibrium adsorption for activated carbon impregnated with H_3PO_4 was shorter (30-50 minutes) in comparison to the activated carbon impregnated with KOH (50-150 minutes). This can be explained by the difference in physical structure of the activated carbon. As shown in Figure 2, activated carbon impregnated with H_3PO_4 has more exfoliated structure, which enabled it to adsorb the pollutants faster due to its higher surface area. Similar observation has been reported by Lorenc-Grabowska & Gryglewicz (2007).

In both cases, the equilibrium adsorption was achieved in shorter time for higher dosage of activated carbon. This could be attributed to the present of more activated carbon, which provided more actives site for the adsorption of pollutants. Hence, more pollutants can be removed in a shorter time at higher dosage.

The synthesized activated carbon impregnated with both activating agents could achieve 95% or higher of dye removal. In addition, optimal removal of dye was achieved in a shorter time with a higher dosage of activated carbon. This is due

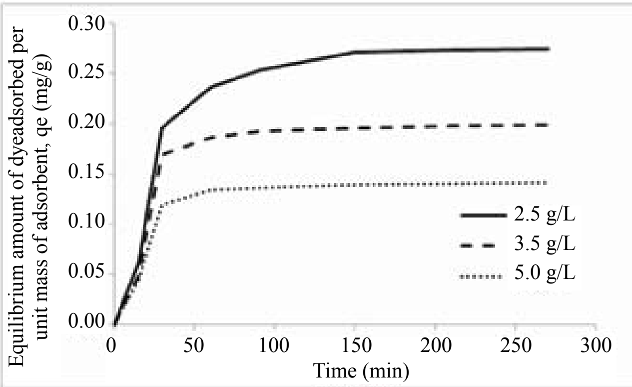


FIGURE 4. Equilibrium amount of dye adsorbed per unit mass of adsorbent vs time for activated carbon (impregnated with KOH) at different dosage

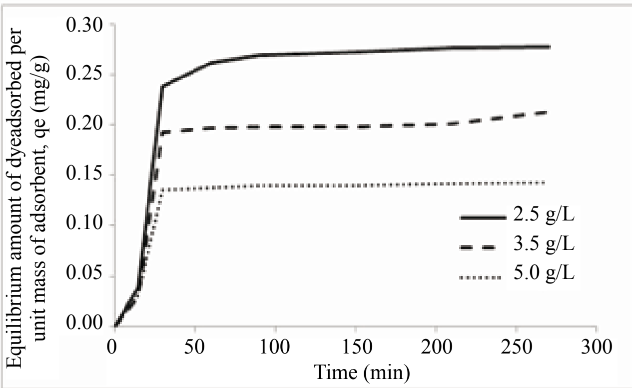


FIGURE 5. Equilibrium amount of dye adsorbed per unit mass of adsorbent vs time for activated carbon (impregnated with H_3PO_4) at different dosage

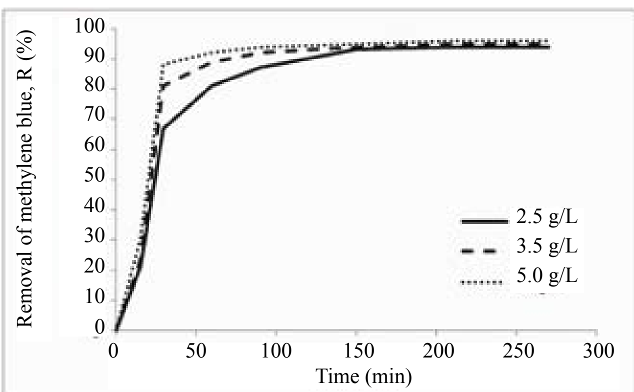


FIGURE 6. Removal efficiency of methylene blue of activated carbon impregnated with KOH

to the fact that the presence of more activated carbon could adsorb more pollutants and thus contributed to rapid removal of dye. However, for the activated carbon impregnated with H_3PO_4, it was observed that the final removal percentage was 3-5% higher compared to the activated carbon impregnated with KOH. This high and rapid adsorption performance could be attributed to the fact that phosphoric acid has higher etching properties in comparison to KOH (Sabatini et

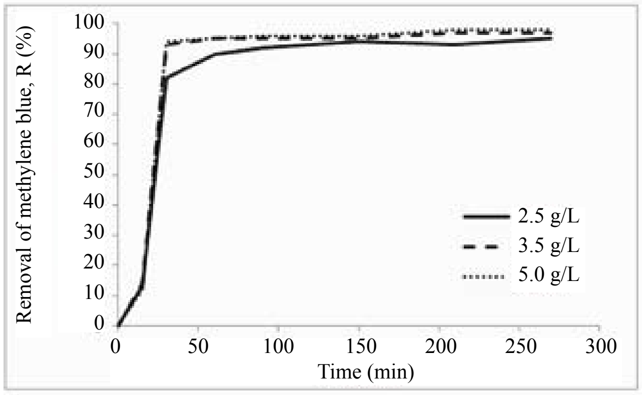


FIGURE 7. Removal efficiency of methylene blue of activated carbon impregnated with H_3PO_4

al. 2013). This property leads to the formation of a highly poriferous and exfoliated structure for the activated carbon impregnated with H_3PO_4. Poriferous and exfoliated structures of the activated carbon (as supported by FESEM images and porosity value) lead to a better and higher adsorption capacity (Yalçın et al. 2000).

The findings from this study show that the duckweeds is a great green material for the synthesis of activated carbon which could remove pollutants like dye. It was also discovered that the activating agent, H_3PO_4, could exfoliate the activated carbon and gave rise to better adsorption performance compared to KOH. The exfoliated activated carbon possesses higher surface layer and thus could adsorb more pollutants in a shorter period of time. Overall, activated carbon generated from duckweeds can be a low-cost adsorption materials that could help to further purify the industrial wastewater without incurring too much of financial burden on the existing treatment process.

CONCLUSION

Activated carbon synthesized from Duckweeds plants is capable to remove dye from the aqueous solution. Activating agent has a significant impact on the morphological structure of the activated carbon synthesized. Activated carbon impregnated with H_3PO_4 possessed more exfoliated and multilayer structures, as evidenced by the morphological FESEM images and porosity value (38 ± 6%). These properties were good for adsorption since it provided larger surface area for dye to be adsorbed onto it, as supported by the 3-5% higher dye removal rate compared to activated carbon impregnated with KOH. Based on the comparison study of activated carbon impregnated with two different activating agents, it can be seen that H_3PO_4 is a stronger etching agent that could create more exfoliated and poriferous structures of activated carbon. Considering Duckweeds plants can grow rapidly and absorb the nutrients presence in the wastewater, the idea of converting Duckweeds plants into activated carbon is quite attractive since it can be used as a low-cost source for mass production of activated carbon in adsorption process to further purify the wastewater.

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