

Effect of Acidic and Alkaline Treatments to Methylene Blue Adsorption from Aqueous Solution by Coconut Shell Activated Carbon

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ABSTRACT. In recent years, pollution from dye wastewater becomes a serious environmental problem due to the high demand and the increment of dye application in textile industry. The purpose of this study was to investigate the potential application of coconut shell activated carbon as methylene blue (MB) removal from aqueous solution. The carbonization process was conducted in temperature range from 300 to 500 °C. For the activation process, two different activating agents namely phosphoric acid, H₃PO₄ (acid activating agent) and sodium hydroxide, NaOH (basic activating agent) were used. Physical characterization of coconut shell activated carbon (CSAC) was realized by using X-ray diffraction (XRD) for phase identification. After that, the percentage of dye removal was investigated in order to determine the adsorption capacity of the prepared activated carbon. It can be concluded that when the dosage of CSAC increased, the amount of dye removal would also be increased. The results indicated that the coconut shell activated carbon could be employed as a low cost alternative in controlling wide range of sorption processes.

Keywords: Activated carbon, Coconut shell, Acidic, Alkaline, Methylene blue;

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1. INTRODUCTION

In recent years, contamination of the industrial waters with the organic based creates a serious environmental problem. Synthetic dye is a group of organic pollutants that are extensively used in several industries that can cause hazardous effect once introduced to aqueous solution [1]. Reactive dyes pose the

greatest problem in terms of colour, which is released by the textile industry [2]. Due to their chemical structures, dyes are resistant to light, water and many chemicals. Therefore, dyes are difficult to treat once they are released to the aquatic environment [3]. There are several approaches to remove the organic pollutants from wastewaters such as chemical oxidation, physicochemical and biological processes. Among these, adsorption is considered one of the most promising alternatives for the removal of organic pollutants from wastewater because of its simplicity, ease of operation, high removal efficiency and regeneration capacity [4]. Activated carbon is a well-known adsorbent that has been used effectively for the removal of organic pollutants, because it is a highly porous material and possesses an extensive surface area [5, 6].

Activated carbon could be produced from different raw carbon resources like lignite, peat, coal, as well as biomass resources namely wood, sawdust, bagasse, and coconut shells [7-9]. By reusing and recycling the agriculture waste like coconut shell into activated carbon, it provides another eco-friendly alternative to dispose the waste and reduce the impact of waste to the environment [10-12]. Activation process of native carbon into activated carbon could be realized by two different processes namely physical activation and chemical activation [13,14]. Chemical activation by using acid and alkali treatments could functionalize the surface of native carbon into activated carbon where the surface modification happens at the molecular level [15,16].

In this paper, activated carbon was produced from coconut shell with different activating agents namely H_3PO_4 and NaOH. Physical characterization was realized by XRD. Subsequently, the adsorption study of methylene blue removal from aqueous solution onto activated carbon was conducted using batch and dialysis tube adsorption methods to determine the adsorption capacity of the prepared activated carbon. It is expected that the active surface of CSAC would be able to remove the methylene blue from aqueous solution via adsorption process.

2. MATERIALS AND METHODS

2.1 Preparation of raw material. The coconut shell (CS) was washed repeatedly with tap water and crushed into smaller pieces. Then, the CS was dried in oven for 3 hours at 105 °C to remove the moisture content. Next, the CS was grinded and sieved by using 300 µm sieve.

2.2 Adsorbent preparation using phosphoric acid (H_3PO_4). 85% of orthophosphoric acid was diluted into 40% of phosphoric acid. Then, the CS was soaked in heated solution of 40% phosphoric acid for 1 hour. Then, the CS was placed in furnace at 300 °C for 1 hour for further activation process. Next, the CS was washed and filtered with hot and cold deionized water copiously until the pH reached to neutral. Finally, the CS was dried in oven at 120 °C for 2 hours and stored in the airtight lid container prior to further analysis.

2.3 Adsorbent preparation using sodium hydroxide (NaOH). NaOH pellet was mixed with distilled water and stirred until it was fully dissolved. The CS was soaked in 4% of NaOH for 1 hour (CS:NaOH;1:20). Next, the CS was kept overnight before dried in oven at 105 °C for 3 hours followed by the carbonization process in furnace at 200 °C for 60 min for further activation process. After that, the CS was washed by 0.5 M HCl solution and hot deionized water to neutralize the pH. Later, the CS was rewashed with cold deionized water and dried in oven at 105 °C for 2 hours and subsequently stored in airtight lid container.

2.4 X-ray diffraction (XRD) measurement. Phase identification of activated CSAC (XRD) was recorded on a Bruker D2 Phaser X-ray diffractometer with monochromatized Cu K α radiation ($\lambda=1.5418 \text{ \AA}$).

2.5 Adsorption studies. 0.15 g of methylene blue (MB) powder was weighed and diluted with 20 ml of distilled water in 250 ml beaker. Then, the solution was stirred and added to the 100 ml volumetric flask followed by adding distilled water. Next, the dye solution was filtered by using 0.45 µm Whatman filter paper. Lastly, the prepared dye was stored in the polypropylene bottle. For batch adsorption study, 1 to 5 g of CSAC were weighed and distributed into 5 beakers containing 50 ml of MB with concentration of 50 mg/ml, respectively. Then, the mixture were stirred for 2 hours at 150 rpm and was left in room temperature for 24

hours. After that, the mixture was filtered with 0.45 μm Whatman filter paper. Subsequently, 1.5 ml was taken from MB solution and put into cuvette followed by measurement with UV-VIS spectrophotometer at wavelength of 668 nm.

For adsorption study by dialysis tube, 1 to 5 g of CSAC were filled into 10 cm dialysis tube and tightly tied up. Then, the 1 to 5 g of CSAC were immersed in 5 beakers containing 50 mg/ml of MB each and were left in room temperature for 24 hours. After 24 hours, 1.5 ml was taken from each beaker and put into the cuvette followed by measurement with UV-VIS spectrophotometer at wavelength of 668 nm.

For kinetic study, 5 g of CSAC was weighed and was filled into 10 cm dialysis tube and tightly tied up. The dialysis tube with CSAC inside was immersed in 50 ml and 100 ml of MB with concentration of 100 mg/ml both with continuous stirring. Decolorization of MB was measured by taking 1.5 ml of MB solution in cuvette and observed by using UV-VIS spectrophotometer for each hour in 6 hours. Percentage of dye removal was calculated by using Eq. (1).

$$\text{Percentage of dye removal (\%)} = \frac{C_0 - C_i}{C_0} \times 100 \quad (1)$$

where C_0 is the initial concentration of dye while C_i is the concentration of dye at i -th hour.

3. RESULTS AND DISCUSSION

3.1 Characterization of the activated carbon. XRD analysis of coconut shell activated carbon as depicted in Fig. 1. Fig. 1(a) showed there were three sharp peaks obtained at the angle of 25°, 45° and 55° respectively which revealed the crystalline carbonaceous structure. The percentage of crystallinity for untreated carbon was 32.6% with percentages of amorphous of 67.4% [17]. For CSAC with NaOH activation, the crystalline peak can be seen at 65° followed by three sharp peaks at the angle of 25°, 45° and 55° for amorphous peaks as depicted in Fig. 1(b). The percentage of crystallinity was 29.4% with percentages of amorphous was 70.6%. While for CSAC with H_3PO_4 activation revealed the highest crystalline peaks started at 20°, 30° and 50° followed by three sharp peaks at the angle of 17°, 22° and 18° for amorphous peak as shown in Fig. 1(b). The percentage of crystallinity was 35.2% with amorphous peak was 64.8%. Previous study revealed that the synthesized activated carbons in the form of high amorphous state with low crystallinity [14].

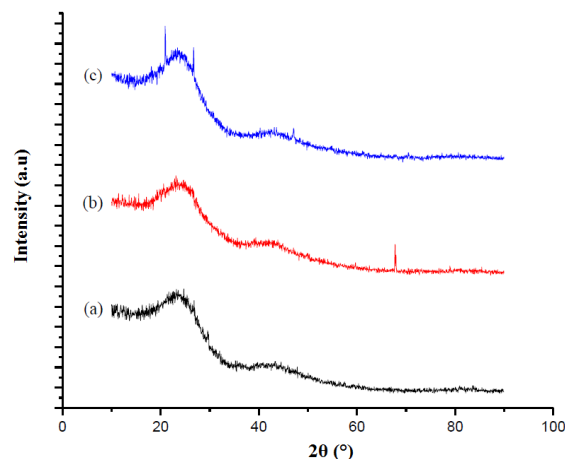


Fig. 1 XRD profile of coconut shell (a) native carbon, (b) activated carbon with NaOH as activating agent and (c) activated carbon with H_3PO_4 as activating agent

3.2 Batch adsorption study. Generally, activated carbon could adsorb the organic material due to the attractive forces between the CSAC surface (non-polar) and the contaminant or adsorbate (MB) which is also non-polar. The attractive force between CSAC surface and the contaminant are found to be stronger than the attractive force of the contaminant with polar solvent (water) [18]. The adsorption rate increased with the increment of adsorbent dosage for 1 to 5 g of CSAC as illustrated in Fig. 2. When the active sites on the adsorbent were fully occupied with adsorbate (MB) molecules, it would be impossible for other adsorbate molecules to bind into the active site [19]. The adsorptive forces can only occur when the organic molecules are closed to the carbon surface.

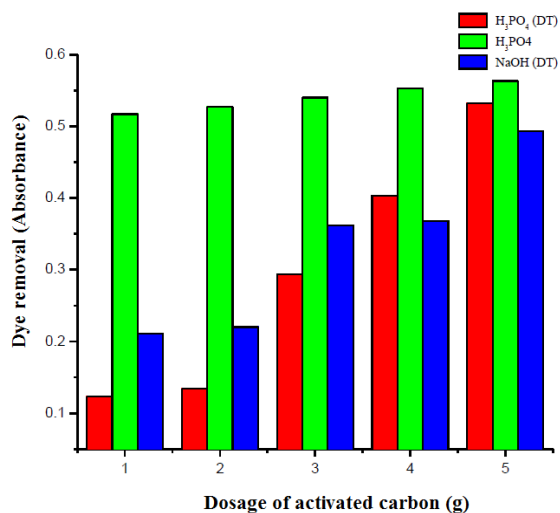


Fig. 2 Adsorption rate of methylene blue is directly proportional to coconut shell activated carbon (CSAC) dosage. (blue: CSAC basic activation with dialysis tube adsorption method, green: CSAC acid activation with batch adsorption method, red: CSAC acid activation with dialysis tube adsorption method)

Investigation of dye removal percentage for 5 g/L of CSAC in 100 ml of 100 mg/L of MB and 50 of 100 mg/L of MB as illustrated in Fig. 3. The dosage of 5 g of CSAC was chosen in this kinetic study because the optimum dye removal could be achieved with this amount of activated carbon.

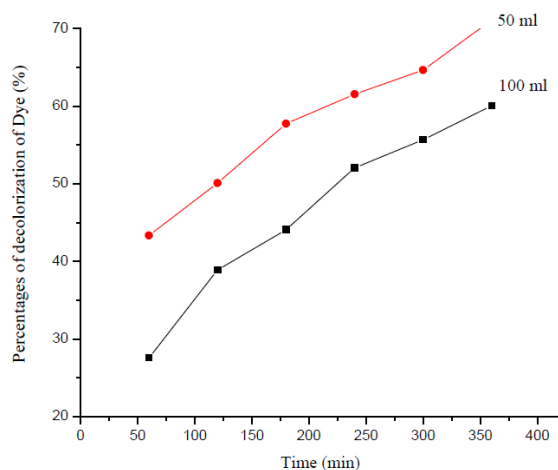


Fig. 3 Comparison of decolorization percentage of methylene blue (%)

It can be seen that the percentages of decolorization of MB increased with the increment of measurement time. The percentages of decolorization of 5 g CSAC in 100 ml of 100 mg/L of MB rose from 27.6 to 60.1% while the percentages of decolorization of 5 g CSAC in 50 ml of 100 mg/L of MB showed an increment from 43.3 to 71.1%. These results proved that the adsorption rate of 5 g CSAC in 50 ml of 100 mg/L of MB was better compared to 100 ml of 100 mg/L MB.

4. SUMMARY

The present study proved that the activated carbon prepared from coconut shell by acid and basic activation agents could be an excellent adsorbent for dye removal from aqueous solution. Characterizations of the prepared activated carbon by XRD revealed the presence of significantly different peaks of CSAC before and after activation process. The adsorption study of methylene blue removal from aqueous solution onto activated carbon was conducted using batch and dialysis tube adsorption methods. It can be concluded that when the dosage of CSAC increased, the amount of dye removal would also be increased. The adsorption rate will reach at the saturation point where the dye molecules will completely bind into CSAC pore and there were no longer molecules could be adsorbed on the CSAC surface. The results indicated that the coconut shell activated carbon could be employed as a low cost alternative in controlling wide range of sorption processes.

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