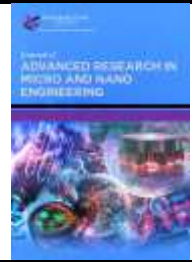




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Performance of Activated Carbon from Corn Cob for Methylene Blue Removal

Eizlan Johari¹, Raudah Mohd Adnan^{1,*}, Muhammad Tariq Baig Saiful Anuar Baig¹, Dilaeleyana Abu Bakar Sidik¹, Hafsa Mohammad Noor², Nur Shahirah Mohd Aripin¹

¹ Department of Science and Mathematics, Center for Diploma Studies, Universiti Tun Hussein Onn Malaysia, 84600 Pagoh, Johor, Malaysia

² Department of Mechanical Engineering, Center for Diploma Studies, Universiti Tun Hussein Onn Malaysia, 84600 Pagoh, Johor, Malaysia

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ABSTRACT

Methylene blue (MB) is a commonly used cationic dye in Malaysia textile and allied sectors, poses serious environmental problems due to its persistence, toxicity, carcinogenicity, and mutagenicity. Significantly, amounts of it are also released into groundwater and surface waterways through wastewater. This study purposely to create and characterise activated carbon made from corn cobs that used to filter wastewater containing the MB dye. Physical and chemical activation techniques are used to create activated carbon. The wide surface area and well-established porous structure of corn cob activated carbon (CCAC) increase its potential for adsorption. Scanning Electron Microscope (SEM) imaging and Fourier-Transform Infrared Spectroscopy (FTIR) analyses both support the existence of functional groups that aid in adsorption and the porous nature of CCAC. The adsorption tests show that CCAC can successfully remove MB at various starting concentrations. The findings indicate that when MB concentration rises (200-600 mg/L), clearance percentages increase (87-95%). The best conditions for CCAC adsorption are determined to be at a concentration of 600 mg/L, which results in high removal rates for colour, chemical oxygen demand (COD), and turbidity. In conclusion, CCAC provides a cost-effective and effective method for removing MB dye from wastewater, and more study is advised to better understand its kinetics, regeneration, and potential applications to other contaminants as well as to determine how economically viable it is.

1. Introduction

Methylene blue (MB) dye is one of the widely used in Malaysia as cationic dyes that is persistent in the environment, poisonous, carcinogenic, and mutagenic. It is frequently used as a synthetic dye to colour fabrics in the apparel and textile industries, as well as to colour papers and leathers. A significant amount of wastewater containing the dye MB is released into groundwater and surface waters because of the industrial scale of consumption [1].

* Corresponding author.

E-mail address: raudah@uthm.edu.my

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Urbanisation, industrial operations, and human activity all contribute to water contamination, which is a major problem. Hazardous chemicals and sewage can pollute water bodies, putting aquatic and ecological life at peril. MB widely used in various sectors, are environmental toxins, and their unregulated discharge into aquatic reservoirs as industrial effluent due to their excessive use is an undesired and damaging phenomenon [2]. Particularly the textile sector generates enormous amounts of pathogen-, chemical-, and organic compound-containing effluent [3]. The intensification of water colour caused by dye effluents injected into bodies of water can harm aquatic life [4]. A popular textile dye called MB is recognised to be bad for both people and marine life [5]. Extended exposure to MB can cause health problems such as eye and skin irritation, nausea, accelerated heartbeat, and respiratory issues, making it a serious concern for both environmental and occupational safety [6]. This problem has been addressed using traditional wastewater treatment procedures [7].

Activated carbon, an amorphous carbon material with graphitic layers, sp^2 hybridization and a large surface area [8]. Corn cob-derived activated carbon, with its wide surface area and microporous structure, is particularly effective at removing synthetic dyes from wastewater, making it a popular adsorbent for the treatment of methylene blue (MB) [4]. Activated carbon made from agricultural waste, however, has been the subject of investigation because of its high price [9]. In Malaysia, corn cobs are a plentiful byproduct of the corn industry and may be pyrolysed and chemically activated to create activated carbon [10]. The abundance and reasonable cost of activated carbon are caused by the accessibility of the corn cobs used in its manufacturing, where activated carbon can be derived via pyrolysis and chemical activation [11].

Due to their low cost and wide availability, corn cobs present a possible option to produce activated carbon for MB treatment [12]. In addition, the large surface area and porous structure of the activated carbon are a result of the well-developed pores causing the adsorption of MB increase. Waste activated carbon derived from corn cobs may be utilised as an adsorbent, providing a chance for waste management and a reasonably priced way to purify water [3]. The aim of this study is to elucidate the performance of methylene blue adsorption on synthesized corn cob activated carbon (CCAC).

2. Methodology

2.1 Materials

The corn cob was obtained from a supplier. All the chemical solutions for preparation of the CCAC such as methylene blue, potassium hydroxide (KOH), distilled water, and hydrochloric acid (HCl) were purchased from BT Science, Malaysia.

2.2 Preparation of Corn Cob Activated Carbon

To remove contaminants, the corn cob (CC) was rinsed with distilled water as Figure 1. The CC was dried in an oven for 15 hours at 140°C before being crushed using a grinder into powder form. The CC was then carbonised in the furnace for two hours at 700°C for carbonisation process. Following that, the carbonised samples were cooled to room temperature. The carbonised samples were then chemically activated with KOH using the impregnation procedure. The carbonised sample was immersed in a water bath for 2 hours at 90°C in a 1:1 (w/v%) KOH solution. The CCAC is dried in an oven at 100°C for 8 hours before washing with 0.1M hydrochloric acid and distilled water.

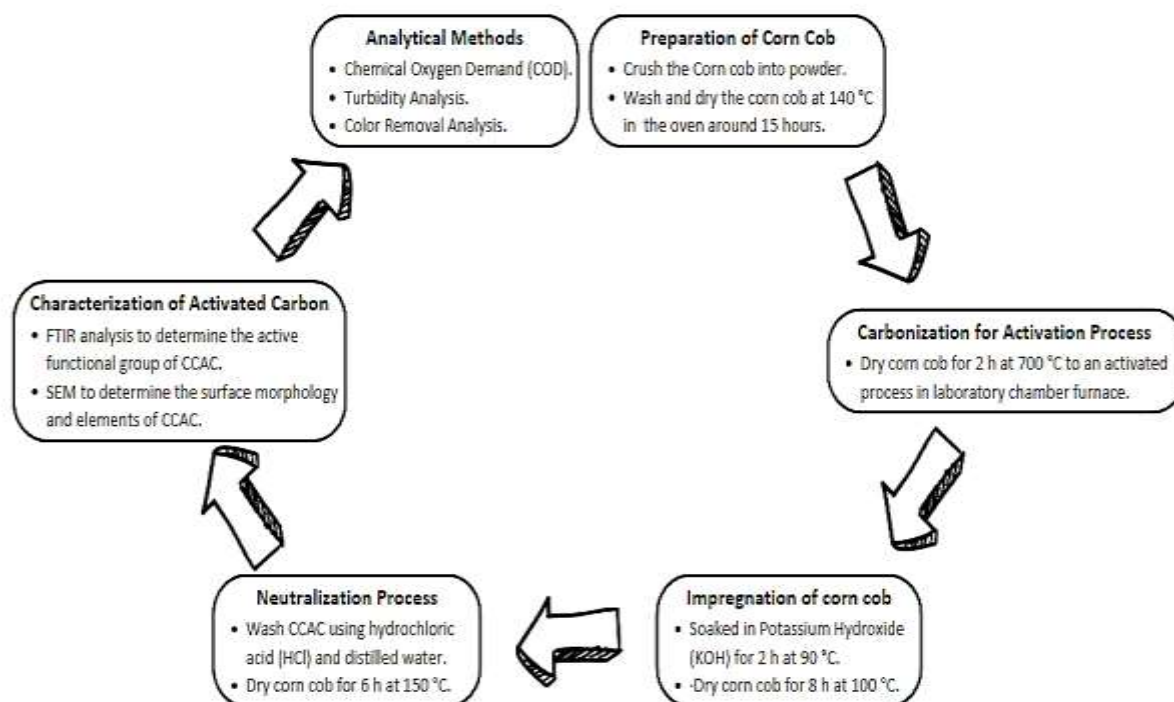


Fig. 1. Flowchart preparation of CCAC

2.2.1 Impregnation of corn cob activated carbon

In order to activate the carbon via a chemical method, 100g of corn cob activated carbon (CCAC) was impregnated in 100 ml of 0.1M potassium hydroxide (KOH) at a 1:1 ratio for 12 hours. To ensure that the impregnation ratio is 1:1, the volume of KOH and the weight of CCAC were calculated using Eq. (1) [13].

$$\text{Impregnation} = \frac{\text{Volume of KOH solution (mL)}}{\text{Weight of Corn Cob (g)}} \quad (1)$$

2.3 Characterisation of Corn Cob Activated Carbon

The previously synthesised corn cob activated carbon was characterise using Fourier-Transform Infrared Spectroscopy (FTIR) brand Cary 630 FTIR Spectrometer with ATR sampling module to determine the structural and compositional information regarding the active functional group of CCAC. The surface morphology and elements contained in CCAC were examined using a scanning electron microscope brand COXEM EM-30^N Benchtop SEM [14].

2.4 Adsorption of Methylene Blue

The stock solution was prepared using volumetric flask to produce 600 mg/L MB stock solution. The stock solution was then diluted into 4 different concentrations ranging from 200, 300, 400 and 600 mg/L.

2.5 Adsorption Experiment

The adsorption process was done by pouring the 15 g activated carbon and the 100 mL of methylene blue solution with the concentration of 200, 300, 400 and 600 mg/L into 4 separate 250 mL beaker and was placed on the hot plate with the magnetic stirrer with an agitation speed of 120 rpm at 30°C for 2 hours [15]. Then the MB solutions were filtered by using a conical flask and filter paper to treat the MB solutions with the use of CCAC as the absorbent [16].

2.6 Analytical Method

The performance of CCAC on the adsorption of methylene blue for colour removal analysis was done for the colour, COD and turbidity test. The colour test was determined with Hach Digital Reactor Block (DR6000) according to the standard Hach program 120 Color, at 455 nm wavelength as per platinum-cobalt (Pt/Co). The COD high range was measured using a COD reactor and a Hach Digital Reactor Block (DR6000). The turbidity data was collected using a turbidity metre. The following calculation may be used to calculate the % removal of colour (CR%), COD, and turbidity from the MB sample [17].

$$CR\% = \frac{C_0 - C_t}{C_0} \times 100 \quad (2)$$

where C_0 refers to the initial concentration of pure MB and C_t refers to the final concentration of treated MB. All tests were done in three runs, and the final result was the average of the three runs.

3. Results

3.1 Characterisation of Corn Cob Activated Carbon

Investigations have been done on FTIR brand Cary 630 FTIR Spectrometer with ATR sampling module and SEM brand COXEM EM-30N Benchtop SEM. analysis of CCAC. Then, the research about the removal of colour, COD, and turbidity in relation to methylene blue concentrations that range from 200 to 600 mg/L by using CCAC as the treating medium was done.

3.1.1 Fourier-Transform Infrared Spectroscopy (FTIR) analysis of CCAC

The CCAC sample that was characterised in the FTIR in Figure 2 was analysed based on the characteristic peaks and functional groups by comparing the spectrum to reference spectra. The CCAC sample observed peaks at 3727, 2564, 1690, 1498 and 1150 cm^{-1} represent the hydroxyl O-H bond, C-H bond, C=O carbonyl group, C-H bond for aromatic compound and C-O bond, respectively [18].

The peak at 3727 cm^{-1} indicates the presence of hydroxyl (-OH) groups. The large peak in this area is usually connected with stretching vibrations of O-H bonds in cellulose and other lignocellulosic components of corn cob. The explanations for the peak at 2564 cm^{-1} include stretching vibrations of carbon-hydrogen (C-H) bonds. It indicates the presence of hydrocarbons or organic substances. The peak at 1690 cm^{-1} is attributable to the C=O (carbonyl) stretching vibrations, which may result from carboxyl groups, ketones, or aldehydes in the activated carbon. The peak at 1498 cm^{-1} is frequently connected to aromatic compound C-H bending vibrations. The peak at the fingerprint region 1150 cm^{-1} corresponds to C-O stretching vibrations, which can arise from various functional groups such as

esters, ethers, or carboxylic acids. Thus, it shows that the functional groups present in the CCAC that was analysed, proved to be the most effective method to treat MB.

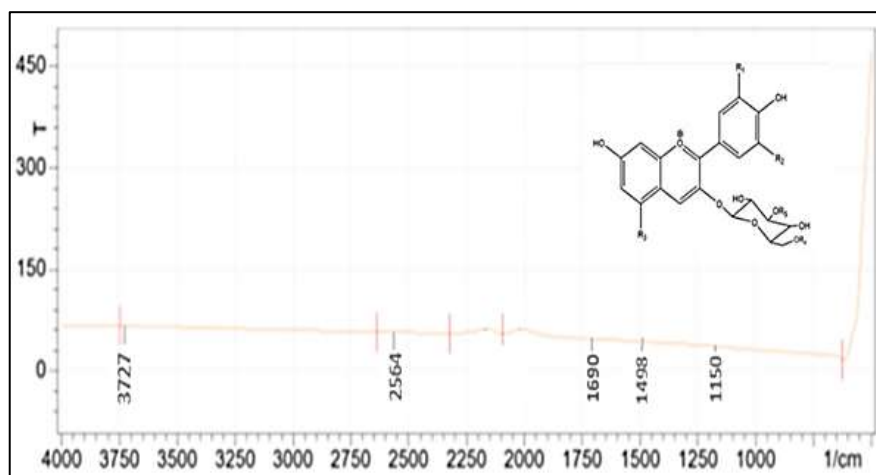


Fig. 2. FTIR spectrum for CCAC

3.1.2 Scanning Electron Microscopy (SEM) analysis of corn cob activated carbon

The results of the SEM used to examine the morphology of the CCAC samples are depicted in Figure 3. Figure 3 microscopy images depict a sheet structure for CCAC. The structure of CCAC has a honeycomb-like pattern with tiny channels that are easily visible. The large surface area and porous structure of the activated carbon result from the well-developed pores, which are consistent with SEM findings. Porous carbon made from corn cobs has a larger specific surface area and pore size than porous carbon from other sources.

For instance, corn cob activated carbon has a specific surface area of $1067 \text{ m}^2\text{g}^{-1}$ coconut activated carbon has a specific surface area of $797 \text{ m}^2\text{g}^{-1}$ [19]. Moreover, there were also tiny pores in the honeycomb structure that allowed the MB to flow smoothly during the adsorption process. In addition, MB can be easily treated at one time because more OH^- can be attached at the CCAC [20]. In this case, it shows that KOH and HCl, in neutralising CCAC, were quite successful in developing pores on the CCAC surface. Therefore, based on the specific surface area values, it can be concluded that corn cob activated carbon has a higher potential for adsorption and other surface-based applications compared to coconut activated carbon.

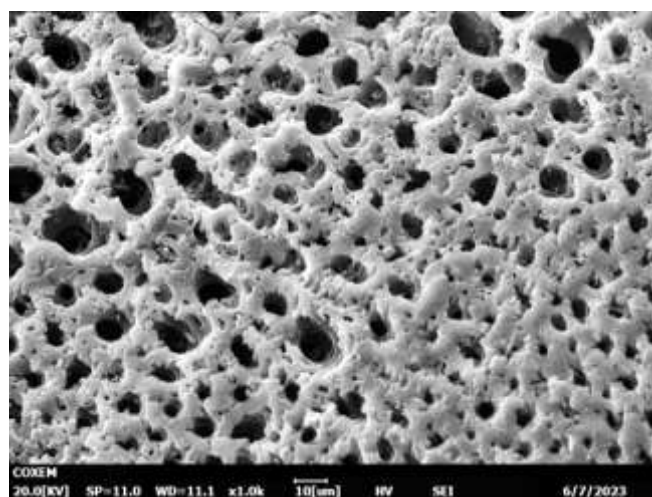


Fig. 3. SEM images of CCAC

3.2 Adsorption of Methylene Blue with Corn Cob Activated Carbon with a Different Initial Concentration

The characteristics of colour, COD, and turbidity at different MB concentrations of 200, 300, 400, and 600 mg/L before and after treatment are compared in Table 1. The outcome demonstrates the ongoing decline at a 200 mg/L concentration, the colour concentration was originally high at 2693 PtCo units. However, the colour concentration considerably dropped to 341 PtCo units following the therapy. The fact that the colour concentration dropped following treatment at concentrations of 300, 400, and 600 mg/L further shows how successful the method is at lowering colour.

Additionally, the initial chemical oxygen demand (COD) concentration was 221 mg/L at a concentration of 200 mg/L. Following the treatment, the COD level dropped to 198 mg/L, showing a decrease in the number of organic contaminants present. Following treatment, COD concentrations of 300, 400, and 600 mg/L all showed the same downward trend. Moreover, the initial measurement for turbidity at a 200 mg/L concentration was 6.42 NTU. The treatment increased the clarity as the turbidity dropped to 4.31 NTU. At 400 and 600 mg/L, however, the turbidity significantly rose following the treatment, reaching 9.22 NTU and 7.23 NTU, respectively. It is important to note that the turbidity at a concentration of 600 mg/L following treatment appears to be lower than the starting value 10.26 NTU, indicating a potential improvement despite the rise from the immediate post-treatment value.

Table 1

Characteristic of MB with CCAC before and after the treatment at different adsorption concentration

Parameter	Concentration (mg/L)							
	200		300		400		600	
	Before	After	Before	After	Before	After	Before	After
Colour (PtCo)	2693	341	4286	353	5140	374	8133	394
Chemical oxygen demand (COD) (mg/L)	221	198	348	301	462	388	712	511
Turbidity (NTU)	6.42	4.31	8.10	5.63	9.22	7.23	10.26	9.10

The amount of colour, COD, and turbidity removal at various MB concentrations is depicted in Figure 4. There was an 87.45% removal rate of colour at a concentration of 200 mg/L of MB. The removal percentages improved to 91.76%, 92.7%, and 95.13%, respectively, when the concentration rose to 300, 400, and 600 mg/L. According to these rising removal percentages, the colour is being removed by the treatment procedure more successfully as MB concentration rises. At a MB concentration of 200 mg/L, the elimination percentage for COD was 10.41%. The removal rates rose to 13.51%, 16.02%, and 28.23%, respectively, with concentrations reaching 300, 400, and 600 mg/L. These greater removal percentages show that the COD levels in the sample may be reduced more successfully at higher MB concentrations.

After that, the percentage of turbidity removed was 32.87% at a MB concentration of 200 mg/L. The removal percentages reduced slightly for the concentrations of 300, 400, and 600 mg/L, which was 30.49%, 21.58%, and 11.31%. These reduced removal percentages imply that as the concentration of MB rises, the treatment process ability to reduce turbidity declines. As a result, it can be determined that a concentration of 200 mg/L MB is the best condition for corn cob activated carbon adsorption because it was the lowest concentration with high removal of colour, COD and turbidity.

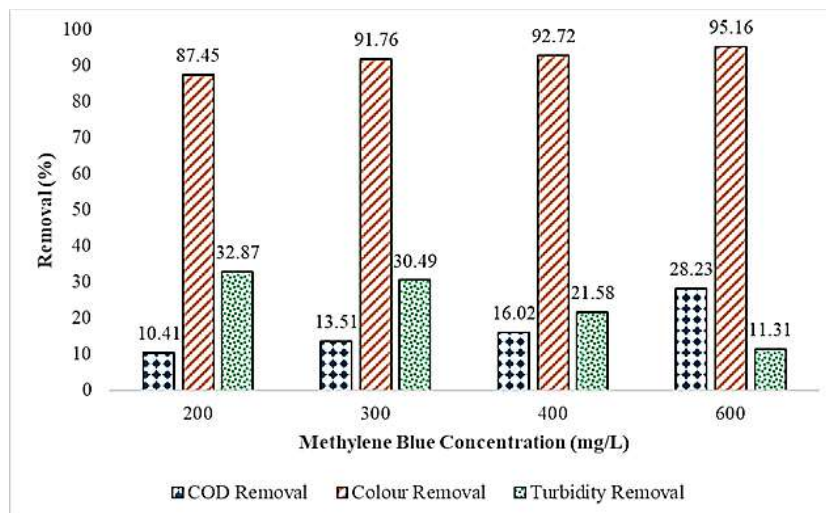


Fig. 4 Adsorption characteristic removal for different concentration

4. Conclusions

In conclusion, this study reveals that MB dye was effectively and affordably removed from wastewater using CCAC, which is produced using physical and chemical activation techniques. The CCAC possesses significant adsorption capacity due to its advantageous properties, which include a large surface area and a well-developed porous structure. The presence of functional groups that facilitate adsorption is confirmed by FTIR analysis, and the porous character of CCAC is confirmed by SEM imaging. According to the results of the adsorption trials, CCAC effectively removes MB at concentration 200, 300, 400 and 600 mg/L, and its producing higher removal percentages. After all the most effective concentration is 600 mg/L to remove MB because of the high removal percentages in colour, COD and turbidity. It is advised that research be carried out in the areas of adsorption kinetics and equilibrium isotherms, regeneration and reusability, application to other pollutants, techno-economic evaluations, and fostering cooperation with industry and stakeholders in order to advance the field of study. Continued study in this area will help treat wastewater sustainably and provide areas with dye pollution problems with an affordable water purification alternative.

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