Removal of methyl violet dye via adsorption using activated carbon prepared from Randu sawdust (Ceiba pentandra)

Achmad Chafidz¹*, Widi Astuti², Venitaliya Augustia¹, Dinda Tri Novira² and Nur Rofiah²

1 Department of Chemical Engineering, Universitas Islam Indonesia, Yogyakarta 55584, Indonesia
2 Department of Chemical Engineering, Universitas Negeri Semarang, Semarang 50229, Indonesia
*E-mail: achmad.chafidz@uii.ac.id

Abstract. In this study, randu sawdust carbon used as raw material for synthesis of activated carbon via KOH chemical activation assisted to adsorb methyl violet dye in the water. Activation by microwave radiation was conducted to accelerate the activation time. Randu sawdust char/carbon and randu sawdust activated carbon were characterized by FTIR, SEM, and BET. The results showed that the randu sawdust carbon and the activated carbon have a functional group which can adsorb methyl violet. Randu sawdust activated carbon has a larger pore and surface area than the randu sawdust carbon/char. The optimum adsorption occurred at pH 9 and 90 minute of contact time. The maximum adsorption capacity of methyl violet dye by the randu sawdust activated carbon was approximately 531.16 mg g⁻¹.

1. Introduction
Dye production in the world is estimated at 7 x 10⁵ to 10⁶ tons per years, and approximately 15% of the dye wastes have been discharged to the environment [1]. One type of dyes that is most commonly found is methyl violet, which generally comes from industrial inks, paints and textiles [2]. The existence of this dye is dangerous for aquatic life because it is considered as mutagenic and mitotic poison, and thus carcinogenic. Various methods have been developed to overcome the pollution of this dye in the waters, including photocatalytic [3], membrane [4], and adsorption [5]. Adsorption is a promising alternative method that relatively simple, inexpensive, and can be applied at low concentrations. Several types of adsorbents have been used to reduce dye concentration in the waters. Activated carbon-MnOₓ hydrothermally from coconut shell is able to adsorb azo dye at 99.1% [6]. However, this process requires a relatively high energy, and therefore the active carbon is expensive and difficult to be applied in the industry. Therefore, the synthesis of activated carbon which is simple and inexpensive is needed. One of the example is the synthesis of activated carbon assisted by microwave radiation as heating system and with KOH as the activator.

Microwave is an electromagnetic wave that gives a heat effect when the wave is absorbed on the body object. Microwave radiation offers several advantages over conventional heating methods, including rapid temperature rise, a uniform temperature distribution, and reduction of processing time, as well as the energy consumption [7]. In this study, the synthesis of activated carbon using randu sawdust as a raw material has been investigated. Randu is widely available on the Java Island, but it has limited use and it has a low of economic value because it is generally used for casting of concrete for the building, but then go into the waste. Therefore, the potentials of this randu to be used as a raw material for the synthesis of an activated carbon have been investigated. Randu as an adsorbent has an ability to give
the adsorption percentage over 90% [8], [9]. In the current study, synthesis of activated carbon prepared from randu sawdust was investigated. The prepared char/carbon and activated carbon were characterized for surface area and pore size distribution, Fourier Transform Infra-Red (FTIR) spectroscopy, and Scanning Electron Microscopy (SEM). The adsorption capacity of activated carbon was evaluated using methyl violet dye as the adsorbate. The effect of operating parameters, such as pH, contact time, initial methyl violet concentration were investigated.

2. Materials and methods

2.1. Adsorbate
Methyl violet (chemical grade reagent) was used as the adsorbate without further purification. The sample solution is prepared by dissolving methyl violet powder into distilled water at different initial concentrations (50, 100, 150, 200, 250, 300, 350, 400, 450, and 500 mg/L). The chemical structure of methyl violet shown in Figure 1.

![Figure 1. Chemical structure of methyl violet](image)

2.2. Carbonization of Randu wood dust
Randu sawdust used as a raw material in this study was obtained from the local sawmill. To prepare the activated carbon, the randu sawdust was washed and then dried in the oven at 105°C to remove the moisture. The dried randu sawdust was then crushed and sieved using a 150 mesh sieve. Afterward, carbonization of the randu sawdust was achieved by heating it in a furnace at temperature of 700°C for 2 hours.

2.3. Microwave-induced Activation Process
The prepared char/carbon was mixed with potassium hydroxide (KOH) with an impregnation ratio of 1:1 (wt/wt%). The resulted char slurry was then placed in a glass reactor installed in the microwave chamber. The microwave was operated with an input power of 180 W and frequency of 2.45 GHz. The heating time was set at 10 min. Pure nitrogen flow was maintained at a flow rate of 1 cm$^3$ min$^{-1}$ during the activation and cooling processes. The resulted activated carbon was washed with 0.1 M HCl and then rinsed with distilled water until pH of 6-7 was attained and finally dried in an oven at 120°C. The dried activated carbon is ready to use for the adsorption tests.

2.4. Characterization of char and activated carbon
The surface area of the char and activated carbon was determined using the Brunauer-Emmet-Teller (BET) method. Whereas, the average width of the pores and pore size distribution was determined using the Barrett-Joyner-Halenda (BJH). The surface functional groups were characterized by Fourier Transform Infra-Red (FTIR) spectroscopy in the scanning range of 4000-400 cm$^{-1}$. The surface morphology of char and activated carbon was characterized using a Scanning Electron Microscopy (SEM).

2.5. Adsorption experiments
Several batch adsorption experiments were conducted in 250 mL Erlenmeyer flasks containing 0.06 g of activated carbon and 100 mL of methyl violet solution and placed in a shaker at 120 rpm. The effect of pH in the range of 3, 5, 7, and 9 was studied. The pH was adjusted using 0.1 M HCl and 0.1 M
NaOH. The effect of contact times (5, 10, 15, 20, 30, 60, 90, 120, 150, and 180 min) was also carried out to study the equilibrium adsorption time. Methyl violet with different initial concentrations (50, 100, 150, 200, 250, 300, 350, 400, 450, and 500 mg/L) were also studied. The concentrations of methyl violet before and after the adsorption were analyzed via absorbance measurement using a UV-Vis Spectrofotometer at 581 nm. The methyl violet adsorbed at equilibrium \( q_e \) (mg/g), was calculated using Eq. (1):

\[
q_e = \frac{(C_o - C_e) V}{M}
\]

where \( C_o \) (mg/l) and \( C_e \) (mg/l) are the initial and equilibrium concentrations of methyl violet, respectively, \( V \) (L) is the volume of solution and \( M \) (g) is the dry mass of *randu* sawdust activated carbon [10].

3. Results and discussion

3.1. Characterization results of char and activated carbon

The FTIR analysis was conducted to confirm the presence of functional groups in the char and activated carbon of *randu* sawdust are capable to adsorb the methyl violet. The FTIR spectrum are shown in Figure 2.

![Figure 2. FTIR spectrum of char and activated carbon](image)

The results of the *randu* carbon FTIR spectra showed broad absorption peak at 3431.32 cm\(^{-1}\) indicating the presence of O-H group, which were derived from the alcohol compounds. Absorption peaks at 1435.12 cm\(^{-1}\) indicating the presence of aromatic C=C groups. Whereas, the presence of group C-O-H was indicated by absorption peak at 877.15 cm\(^{-1}\). There was also a decrease in absorption peaks at wavenumber of 3431.32 cm\(^{-1}\) and 1435.12 cm\(^{-1}\). The reduced intensity of absorption peaks at wave number of 1435.12 cm\(^{-1}\) that belongs to C=C group was probably caused by a reaction between some Carbon with the KOH. Whereas, the reduced OH group at wave number of 3431.32 cm\(^{-1}\) was likely caused by the partial OH group, which reacted with KOH. While, the widening of the peak at about wave number of 1500 cm\(^{-1}\) was probably caused by the group C-O formation of aldehyde numbers waves almost coincide with the C=C. Additionally, Scanning Electron Microscopy images of the char and activated carbon at 5000 X magnification are shown in Figure 3.
As seen in Figure 3a, the char seemed to have a lot of impurities product of carbonization. While the activated carbon was more pure, which is likely due to the N₂ flowing during the activation process (see Figure 3b). Additionally, the BET analysis shows that the randu sawdust activated carbon has a larger of specific surface area, i.e. 69.486 m²/g. The pore size distribution of the activated was analyzed using the method of Barret Joyner Halenda (BJH), and was found to be approx. 17.230 nm. Whereas, the randu char/carbon has a specific surface area of 5.587 m²/g with a pore size distribution approx. 17.185 nm.

3.2. Adsorption of methyl violet
Effect of pH on the adsorption of methyl violet studied at various pH 3, 5, 7, and 9 is shown in Figure 4. The figure shows that at pH 9 dye adsorbed amount reached the highest rate (99.76%). Randu sawdust activated carbon inclined protonated at low pH so that the active sites to be positively contents. This causes the repulsion between the active sites with methyl violet that was also positively contents, and hence the adsorption process is difficult to occur. It can be concluded that the optimum pH of methyl violet adsorption by randu sawdust activated carbon is at pH = 9.

The effect of contact time on the adsorbed of methyl violet by randu sawdust activated carbon at initial concentration of 100 mg/L is shown in Figure 5. Both the curves showed that the adsorption increased rapidly in the first 10 min, and thereafter gradually slowed down until it reached the equilibrium time. This phenomena was likely due to a large number of vacant surface sites were available for adsorption during the initial stage, and hence the tendency of methyl violet adsorbed by activated carbon was still high. Once the equilibrium was attained, the amount of methyl violet adsorbed did not change with the further increase of time.

Figure 3. SEM micrographs of a) char and b) activated carbon

Figure 4. Effect of pH on the adsorbed of methyl violet (condition: initial concentration = 100 mg L⁻¹, contact time = 120 min, activated carbon dose = 0.6 g L⁻¹)
Figure 5. Effect of contact time on the adsorbed of methyl violet (condition: initial concentration = 100 mg L\textsuperscript{-1}, pH = 9, activated carbon dose = 0.6 g L\textsuperscript{-1})

Figure 6 shows that the amount of methyl violet adsorbed increased with the increase of methyl violet initial concentration and remained constant after reached the equilibrium. This was likely due to the fact that increasing concentration will also increase the driving force, so the rate of mass transfer of adsorbate onto the activated carbon will also be faster [11].

Figure 6. Effect of initial concentration on the adsorbed of methyl violet (condition: pH = 9, contact time = 90 min, activated carbon dose = 0.6 g L\textsuperscript{-1})

4. Conclusion
The current study has demonstrated the suitability of randu sawdust for the preparation of activated carbon by microwave heating-induced KOH activation. The high surface area activated carbon was produced in a short activation time by the microwave heating system. The optimum adsorption of the
methyl violet was occurred at pH 9 and the equilibrium time of 90 minute. The maximum adsorption capacity of methyl violet dye by randu sawdust activated carbon was approximately 531.16 mg g$^{-1}$.

5. References

[1] Gupta V K and Suhas 2009 Aplication of Low-cost Adsorbent for Dye Removal – A Review Journal Enviromental Management 90: 2313-2342.

[2] Christina M, S Mu’nisanatun, Saptaji R, Marjanto D 2007 Studi Pendahuluan Mengenai Degradasi Zat Warna Azo (Metil Orange) dalam Pelarut Air Menggunakan Mesin Berkas Elektron 350 kev/10 ma Journal Forum Nuklir Vol. 1 No. 1.

[3] Zhang Y, Sun X, Yang G, Zhu Y, Si H, Zhang J, and Li Y 2016 Preparation and Characterization of Bifunctional BiOCl$_x$I$_y$ Solid Solutions with Excellent Adsorption and Photocatalytic Abilities for Removal of Organic Dyes Materials Science in Semiconductor Processing 41: 193-199.

[4] Shi J, Wu T, Teng K, Wang W, Shan M, Xu Z, Lv H, and Deng H 2016 Simultaneous Electrospinnning and Spraying Toward Brach-Like Nanofibrous Membrans Functionalised with Carboxylated MWCNTs for Dye Removal Materials Letters 166: 26-29.

[5] Fontana K B, Chaves E S, Sanchez J D S, Watanabe E R L R, Pietrobelli J M T A, and Lenzi G G 2016 Textile Dye Removal from Aqueous Solution by Malt Bagasse: Isotherm, Kinetic and Thermodynamic Studies Ecotoxicology and Environmental Safety 124: 329-336.

[6] Xu L, Li X, Ma J, Wen Y, and Liu W 2014 Nano-MnO$_x$ on Activated Carbon Prepared by Hydrothermal Process from Fast and Highly Efficient Degradation of Azo Dyes Applied Catalysis A: General 485: 91-98.

[7] Yuen F K and Hameed B H 2009 Recent Developments in the Preparation and Regeneration of Activated Carbon by Microwaves Advances Colloid Interface Science 149: 19-27.

[8] Astuti W, Sulistyaningsih T, and Maksiola M 2016 Chemical Modified Kapok Sawdust as Adsorbent of Methyl Violet Dye from Aqueous Solution Jurnal Teknologi 78(9): 35-42.

[9] Maziyyah D F 2015 Modifikasi Adsorben Berbasis Kayu Randu dengan Metode Pemanasan dan Aplikasinya sebagai Penjerap Zat Warna Methyl Violet pada Limbah Industri Batik Tugas Akhir Jurusan Teknik Kimia Universitas Negeri Semarang.

[10] Njoku V O, Foo K Y, Asif M, and Hameed B H 2014 Preparation of Activated Carbon from Rambutan (Nephelium lappaceum) peel by Microwave-induced KOH Activation for Acid Yellow 17 Dye Adsorption Chemical Engineering Journal 250: 198-204.

[11] Zou W, Bai H, Gao S, Li K 2013 Characterization of modified sawdust, kinetic and equilibrium studyabout methylene blue adsorption in batch mode. Korean Journal of Chemical Engineering 30 (1): 111-122.