Preparation of Carbon Monolith Derived from Resorcinol - Formaldehyde Resin and Its Application for Antibiotic Adsorption

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Abstract. The presence of antibiotics in wastewater discharged to the waterbody has negative effects. The antibiotics can induce bacteria to be persistent. Hence, efforts to limit the concentration of antibiotics in wastewater are required. In this work, the removal of antibiotics was performed by adsorption using nanoporous carbon in the form of a monolith. The carbon monolith was prepared by pyrolysis of templated resorcinol formaldehyde polymer at 600°C and 800°C. The material was characterized systematically by scanning electron microscopy and an N₂-sorption analyzer. As a comparison, commercial carbon of coconut shell-derived was also employed in the study. The characterization showed that porous carbon monolith has a high specific surface area up to 594 m²/g. In the adsorption test, the results indicated that carbon monolith was better at adsorbing antibiotics compared to the commercial one.

1. Introduction
The hospital is a health service institution that has the potential to pollute the environment due to waste generated from its activities. Hospital wastewater that comes from domestic or medical waste generally has high pollutant compounds, pathogenic microorganisms, toxic chemicals and radioactivity that require further processing. One of the ingredients that can be contained in hospital wastewater is antibiotic drugs such as ibuprofen and metronidazole if not treated properly. Metronidazole (2-methyl-5-nitroimidazole-1-ethanol or MNZ) is an antibiotic for infections caused by bacteria. MNZ is widely used for the treatment of infectious diseases caused by various kinds of anaerobic bacteria and various protozoa [1].

Due to the high solubility of MNZ in water, it is difficult for MNZ to be separated from conventional wastewater treatment. Hospital wastewater treatment plant (IPAL) which is ineffective in causing wastewater to still contain MNZ, causing the development of antibiotic-resistant bacteria, fish reproduction changed due to estrogen compounds, and photosynthesis inhibition in algal plants due to β-blockers [2]. Many methods have been carried out in research to remove contaminants such as using adsorption, coagulation and flocculation methods, nanofiltration, ultrafiltration, reverse osmosis, etc. Adsorption is the most promising processing method. Adsorption using carbon has many advantages such as easy to operate, efficient, and adsorbent can be regenerated and reused. Adsorption is an effective and low-cost method to remove pharmaceutical compounds from aqueous solutions and activated carbon is frequently used due to its chemical and textural properties[3,4].
Adsorption is a phenomenon in which molecules of adsorbed material are attracted to the surface of a solid field that acts as an adsorbent. MNZ will be absorbed using the adsorption method. Ahmed and Theydan (2013) [5] investigated the adsorption of MNZ on activated carbon from agricultural waste and showed that the adsorption rate followed a pseudo-second-order kinetic model and estimation of the heat of adsorption revealed that the adsorption of MNZ was endothermic. According to research conducted by Carrales Alvarado (2014) [6], metronidazole adsorption with different kinds of carbons will produce different adsorption results depends on the material of the carbon.

In this work, the study of adsorption of MNZ using carbon monolith derived from phenolic resin. The resorcinol-formaldehyde (RF) resin has more advantages because it can dry at room temperature. Carbon monolith has advantages over conventional granular activated carbon e.g. more similar size, binderless, and low-pressure drop when used in a continuous process. The properties of carbon were characterized using the standard method and the performance of adsorption of MNZ was discussed and compared with commercial activated carbon.

2. Materials and Method
2.1. Materials
The materials used in this study include mesoporous porous type carbon polymers made from formaldehyde analytical grade (37%) and resorcinol analytical grade used for the synthesis of RF resins and carbon monolith were purchased from Merck, Germany.

2.2. Preparation of Resorcinol-Formaldehyde Resin
Resorcinol-formaldehyde (RF) resins were prepared as precursor of carbon monolith. Around 4.5 g of resorcinol was dissolved in 13.2 mL of formaldehyde (26 wt%) containing 0.9 g of iron nitrate as catalyst. The solution was stirred until homogeneous. The homogeneous solution was put into a cylindrical mold measuring 25 mm in diameter and 50 mm high. In one mold there are 100 cylindrical holes.

2.3. Carbonization
Before carbonization, the RF resins product was dried at room temperature. Drying was completed until a constant weight is obtained. The dried RF resins product was then used for carbonization and called as a porous carbon precursor. Carbonization process began with heating using furnace from room temperature to 150°C under N2 gas flow. Nitrogen gas was used to expel the presence of oxygen in the furnace and as a carrier gas substance that came out of carbonized material. Carbonization was performed by raising the temperature slowly with a certain ramp rate of 2°C/min. The holding time at each carbonization temperature was 2 hours while the temperature used in the carbonization process was 600°C and 800°C. The nomenclature of material is CM-600 and CM-800 for carbon monolith prepared by carbonization at 600°C and 800°C, respectively.

2.4. Material Characterization
In this study, to determine the pore volume, average pore diameter, pore size distribution and surface area of porous carbon, N2-Sorption analysis was employed (NOVA 2000, Quantachrome Instrument). Scanning electron microscope (SEM, JSM-6360LA (JEOL) was used to observe the morphology of carbon monolith.

2.5. Antibiotic Adsorption
A 50 mL of MNZ solution (variations of concentration of 20, 40, 60, 80, 100, 140, 200 ppm) was prepared in a beaker glass. Then the carbon was added to the beaker glass and stirred using a shaker at room temperature (30°C) and atmospheric pressure for 48 hours. The shaker speed was set at 300 rpm. The filtrate was analyzed using HPLC LC-2010 CHT by Shimadzu, Japan using a calibration standard method to determine the concentration after adsorption. In comparison, the performance of carbon polymer adsorption will be compared with commercial carbon made from coconut shell materials.
3. Result and Discussion

3.1. Morphology of Carbon Monolith

The resulting carbon monolith (CM) was characterized using the scanning electron microscope for surface morphology analysis (Figure 1). SEM results showed that CM prepared with 600°C pyrolysis temperature had many voids/channels. On the contrary, CM prepared with pyrolysis temperature of 800°C displayed different characters. CM-800 forms microfiber on its surface which is likely related to carbonization temperature and a presence of iron during polymerization (Thanh, 2017).

![Figure 1. Morphology of (a) CM-600 and (b) CM-800.](image)

3.2. Pore Structure of Carbon Monolith

3.2.1. Nitrogen Adsorption-Desorption Isotherm. The pore structure characteristics of a carbon material are strongly influenced by the origin of the raw material so that each material certainly has different pore structure characteristics. This will also affect the ability of the carbon to absorb and desorption a compound, such as nitrogen gas [8]. One way to find out the characteristics of porous carbon pores is by observing the equilibrium of the adsorption-desorption isotherms in absorbing nitrogen gas. The N$_2$ adsorption-desorption isotherms curve for carbon with pyrolysis temperatures of 600°C and 800°C are presented in Figure 2.

From the N$_2$ adsorption-desorption graph of carbon at 600°C, it can be concluded that this carbon follows Type I isotherm. This type shows that CM-600°C has many micropore structures with a little small part of meso-porous. This curve depicts monolayer adsorption and is usually formed on adsorption on porous carbon.
By contrast, CM-800°C has a type of N₂ adsorption-desorption isotherm curve following type IV. This is indicated by the transition from monolayer to multilayer. This type of equilibrium model generally shows that the material has micro and mesopores sized pores. Figure 2 also shows that there is a vertical curve in carbon when the partial pressure (P / Po) approaches 1. This phenomenon is referred to as loop hysteresis and occurs only in a certain range (P / Po> 0.4). This phenomenon indicates that the portion of the meso-sized pore tends to be more dominant compared to other pore types [9]. From Figure 2 it can be concluded that the pore size of carbon monolith from the polymer is dependent on carbonization temperature.

3.2.2. Pore Size Distribution. The pore size distribution CM-600 and CM-800 is presented in Figure 3. Based on these images, it can be seen that the distribution of CM-800 tends to be more dominant in size above 2 nm. Pore distribution tends to be uniformly characterized by narrow distribution areas at 5 nm in size, this indicates that carbon 800 tends to have a mesoporous pore type. Whereas on CM-600 there are two peaks, namely peaks which are under 2 nm and above 2 nm. This proves that CM-600 has two-pore structure characters, namely mesoporous type and tends to be more micropore type. This is characterized by a narrower peak distribution area at sizes below 2 nm. This proves CM-600 and CM-800 are micro and mesoporous types.

Figure 2. N₂ adsorption and desorption (a) CM-600°C and (b) CM-800°C.
3.2.3. Pore Textural Parameter. The structural characteristics of carbon monolith which include specific surface area, mean pore diameter, and pore volume obtained from the calculation results of Brunauer-Emmett-Teller (BET) analysis are presented in Table 1. The table shows that the carbon monoliths have micropore and mesopore structural characteristics following the IUPAC classification with a mean diameter of 0.9 nm (CM-600) and 3.6 nm (CM-800).

Table 1. Characteristics of carbon monolith with various pyrolysis temperatures.

| Characteristic                  | Material | CM-600 | CM-800 |
|--------------------------------|----------|--------|--------|
| Specific surface area ($S_{BET}$), (m$^2$ g$^{-1}$) | 595      | 354    |
| Micropore area ($S_{Mic}$), (%)     | 94%      | 57.8%  |
| Total pore volume ($V_T$), (cm$^3$ g$^{-1}$) | 0.26     | 0.32   |
| Micropore volume ($V_{Mic}$), (%)    | 65.9%    | 39.2%  |
| Mean pore diameter ($d_V$), (nm)    | 0.9      | 3.6    |

3.3. Adsorption of Antibiotics Using Carbon Monolith

Based on the Figure 4, CM-800 adsorbed higher antibiotics concentration than that of CM-600. This is likely since CM-800 has the mesoporous character that causes MNZ easier to diffuse into the internal pores of the carbon. Hence all pores can be occupied by MNZ.

Figure 3. CM-800 and CM-600 pore size distribution.
As a comparison, commercial carbon of coconut shell-derived carbon was also tested in this study. The results displayed that commercial carbon adsorbs more MNZ than CM-600. This is because the surface area of commercial carbon \( (S_{\text{BET}} \, 974 \text{ m}^2/\text{g}) \) is greater than CM-600, so it can adsorb more MNZ molecules than CM-600. However, commercial carbon adsorbs less MNZ compared to CM-800 although the specific surface area is lower than commercial carbon. This can be related to the pore structure of CM-800 which is dominated by the mesoporous parts. Based on the prior research by Santana (2017), MNZ has a molecule size around 1.8 nm so it is easier for MNZ to be adsorbed by CM-800 than CM-600 because the size of the pore of CM-800 is bigger although the surface area is smaller than CM-600.

Accordingly, the adsorption capacity of the materials followed the order: CM-800 > commercial carbon > CM-600. The best performance was offered by CM-800 material \( (S_{\text{BET}}=354 \text{ m}^2/\text{g}) \), with outstanding maximum adsorption capacity values for MNZ drugs. Apart from the extremely high specific surface area of this material, its high pore volume together with a mean pore size that allowed the entrance of the target pollutants into the pore structure must be noted to explain its outstanding performance. These changes in the porous structure of the materials can also be associated with the increased crystallinity developed in the carbon monolith by increasing the synthesis temperature, evolving from amorphous carbon to graphitic structure which needs to be investigated further [11].

4. Conclusions
The adsorption of metronidazole antibiotic by carbon monolith is greater when compared with commercial carbon. The increase of the synthesis temperature of the carbon monolith will affect the changes of the pore size. This will affect in the performance of the adsorption by the carbon monolith. The adsorption capacity of the materials followed the order: CM-800 > commercial carbon > CM-600.

Acknowledgments
This work was funded by the program of 2019 Final Project Recognition, Universitas Gadjah Mada (RTA Grant No. 3348/UN1/DITLIT/DIT-LIT/LT/2019).

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