Effect of Carbonization Time of Mesoporous Carbon in the Dyes Adsorption: Rhodamine B, Methylene Blue and Carmine

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Abstract

Study of dyes adsorption (rhodamine B, methylene blue and carmine) carried out by using mesoporous carbon synthesized at various carbonization time. The purpose of this research was to understand influence of carbonization time to performance of the mesoporous carbon in dyes adsorption. In addition, adsorption performance of the mesoporous carbon and commercial carbon were compared. The adsorption test were conducted at conditions: 0.1 g of adsorbent, 25 mL of dyes solutions 100 ppm and shaking rate 125 rpm for 4 hour. Filtrate was used to determine remain concentration of the dyes with UV-visible spectrophotometry. Result of the research showed that the carbonization time from 1 to 3 hours improved the adsorption, whereas from 3 to 5 hours decreased it. The best character of the mesoporous carbon obtained at carbonization time of 3 hours with adsorption values of 96.43 ± 0.37 % for rhodamine-B, 38.80 ± 1.44 % for methylene blue and 48.51 ± 1.55 % for carmine. The adsorption values of the mesoporous carbon were 0.97 times for rhodamine B, 0.48 times for carmine, and 0.39 times for methylene blue compared with the commercial activated carbon.

Keywords: Carbonization Time, Rhodamine B, Methylene Blue, Carmine

INTRODUCTION

Mesoporous carbon is one of the potential adsorbents used to adsorb some dyes because it has a size match. The results prove that mesoporous carbon has advantages over mesoporous silica, which is more resistant to heat, acids and bases, and mechanical stress [1]. Types of dyes that can be adsorbed include rhodamine B, methylene blue and carmine which have sizes close to the mesoporous diameter, so it possible to use mesoporous carbon adsorbents more effectively.
One source of mesoporous carbon that has prospects as a raw material is textile industry sludge waste [2]. The carbon obtained has the pore character as mesoporous carbon, so it is possible to be used to adsorb various types of dyes, especially large molecular dyes. In addition, the study found that there was a change in mesoporous carbon character including pore volume and specific surface area due to carbonization time, which could affect the adsorption performance. This is supported by Li et al. [3] that the pore volume and surface area affect the carbon adsorption capacity. So that, the adsorption study of three types of dyes was carried out consisting of rhodamine B, methylene blue and carmine to determine the mesoporous carbon adsorption performance.

Rhodamine B, methylene blue and carmine dyes have different sizes, structures and functional groups. Also in terms of the charge, rhodamine B and methylene blue are cation dyes while carmine is an anion dyes [4, 5,6]. Methylene blue is a dye that often used to determine the adsorption capacity of an adsorbate against the adsorbate of organic compounds [7]. Rhodamine B and carmine are examples of dyes commonly used in industry [8,9]. Differences properties of dyes are expected to be a model of study on mesoporous carbon performance in adsorption of other dyes that have similar characteristics. Therefore, the synthetic mesoporous carbon can be an alternative treatment of dyestuff waste in the waters. According to the Environmental Impact Management Agency, dyes found in water waste are classified as hazardous and toxic waste if the concentration exceeds the waste quality standard, for example methylene blue with a concentration of 5-10 mg/L [10]. According to Mathur et al., 2016, as much as 10-250 mg/L dyes from the textile industry are wasted into the water, so that high dyestuff content in water needs serious treatment to maintain environmental safety and security [11]. In this study, a comparative test of adsorption performance between mesoporous carbon and commercial activated carbon was carried out.

**MATERIALS AND METHODS**

The materials used in this study are mesoporous carbon with carbonization time variations of 1, 2, 3, 4 and 5 hours, commercial activated carbon, hydrochloric acid 37%, distilled water, dyes including rhodamine B, methylene blue and carmine. The equipment used in this research is analytical balance, pH meter (Inolab WTW), a set of glassware, oven, shaker, centrifuge and spectrophotometer (Thermo Scientific Genesys 20 UV-Visible).

**Sample Preparation**

Mesoporous carbon with a size of 250 - 300 mesh is homogenized, and then heated in oven at 110 °C for 1 hour. The mixture cooled in a desiccator for 30 minutes and weighed until a constant weight. The same method applied for commercial activated carbon.

**Spectrophotometric analysis**

Spectrophotometric analysis of dyes carried out by maximum wavelength determination by measuring the dye solution at variations of wavelength using spectrophotometry instrument. From the analysis, results obtained the maximum wavelength value with the highest absorbance value. Furthermore, the initial calibration curve is made from a series of concentrations of dye solution: 0; 40; 45; 50; 55; 60 and 65 ppm for rhodamine B, 0; 2; 2.5; 3; 4; 4.5 and 5 ppm for methylene blue and 0; 3; 3.5; 4; 4.5; 5; 5.5 and 6 ppm for carmine. Determination of the maximum wavelength is obtained by measuring the 70 ppm rhodamine B solution at a wavelength variation of 510-570 nm, 5 ppm methylene blue at a wavelength variation of 580-650 nm and 10 ppm carmine at a wavelength variation of 490-560 nm. From the measurement, results obtained the maximum wavelength value that gives the highest absorbance value. And then the absorbance was measured at a wavelength of 554 nm for rhodamine B, 630 nm for methylene blue and 530 nm for carmine. Absorbance versus concentration curve was made to obtain the linear regression equation y = ax.

**Dyes Adsorption Test**

A 0.1 g of mesoporous carbon added to 100 ppm of dye solution and stirred at 125 rpm for 4 hours at room temperature. The mixture separated by centrifuge at a speed of 4200 rpm. The filtrate obtained was used to determine the concentration of dye in the sample solution. Furthermore, the % adsorption of dyes calculate by using equation:

\[
\% \text{ Dyes adsorption} = \frac{C_0 - C_s}{C_0} \times 100\%
\]

\(C_0 = \) dye concentration before adsorption
\(C_s = \) dye concentration after adsorption

The same procedure used for the activated carbon.

**RESULT AND DISCUSSION**

Adsorption tests carried out on several dyes, namely rhodamine B and methylene blue as cation dyes, and carmine as anion dyes using mesoporous carbon adsorbents synthesized at various carbonization times (1-5 hours). To optimize the adsorbents ability, research starts from the sifting mesoporous carbon samples, which aims to uniform the mesoporous carbon
particle. Furthermore, heating at a temperature of 110 °C, which aims to remove H2O, contained on the surface of carbon, to obtain dry mesoporous carbon. In this research, the study of dyes adsorption by mesoporous carbon focused on the effect of carbonization time on the mesoporous carbon performance to adsorb dyes, and compared with commercial activated carbon.

**Effect of Carbonization Time on Dyes Adsorption using Mesoporous Carbon**

Percent adsorption of dyes using mesoporous carbon synthesized at carbonization time variations is shown in Table 1.

Table 1 shows that carbonization time has a significant influence on the ability of mesoporous carbon adsorption. This performance is known by studying the physical characteristics of mesoporous carbon with the percent adsorption of dyes. It accordance with research reported by Li et al. [3] that the volume and surface area of pore affect the carbon adsorption capacity.

Percent adsorption of three dyes increased from carbonization time of 1 hour to 3 hours, and decreased from carbonization time of 3 hours to 5 hours. Increase in pore volume from carbonization time of 1 to 3 hours is indicated by an increase in the height of curve peak, which means an increase in the number of pore cavities formed.

Table 2 shows that the greater mesoporous volume increases the number of pore cavities. The greater of mesoporous carbon surface area, increasing the surface as a place where dyes are absorbed in the adsorbent. It accordance with research reported by Zheng et al. 2017 which uses activated carbon from coconut shells for adsorption of anion dyes [12].

Adsorption of dyes is carried out at acidic pH where the functional groups on the mesoporous carbon surface and dyes have changed charge. Adsorption of rodamine B that works at pH 5.06, the carboxyl group bound to carbon polymers is more dominant as a carboxylic ion as shown in Figure 1. The pKa value for benzoic acid is 4.18 [13] with the extension of the aromatic group, it is assumed that it can increase the pKa value. While at solution pH of 5.06 which is greater than the pKa value, the carboxyl group will be dominant in the form of carboxylic ion.

In addition, for hydroxyl groups in mesoporous carbon polymers will remain as hydroxyl groups. The pH of the solution is lower than the pKa value as explained in the case of the rodamin B dye above. The molecular structure of carmine shown in figure 2.

Table 2 Characteristics of mesoporous carbon in various carbonization periods using the POD method

| Mesoporous Carbon Character | Unit | Carbonization time (Hours) |
|-----------------------------|------|---------------------------|
|                             |      | 1       | 2       | 3       | 4       | 5       |
| $V_{p\text{ meso}}$ | cm$^3$/g | 0.0154  | 0.0212  | 0.0503  | 0.0183  | 0.0136  |
| $S_{p\text{ meso}}$ | m$^2$/g | 17.7003 | 21.2752 | 42.7702 | 22.6121 | 16.6236 |
| $r_{p\text{ meso}}$ | Å     | 17.3982 | 19.8846 | 23.5210 | 16.1954 | 16.3668 |
| $d_{p\text{ meso}}$ | Å     | 34.7965 | 39.7692 | 47.0367 | 32.3908 | 32.7336 |

Table 1. Percent adsorption of dyes using mesoporous carbon

| Time Carbonization (hours) | % Adsorption |
|---------------------------|--------------|
|                           | Rhodamine B  | Methylene blue | Carmine    |
| 1                         | 92.64 ±0.39  | 24.07±0.00    | 28.77±1.70 |
| 2                         | 94.22 ±0.67  | 30.28±1.50    | 39.35±0.00 |
| 3                         | 96.43 ±0.37  | 38.80±1.44    | 48.51±1.55 |
| 4                         | 94.89 ±0.00  | 25.86±1.55    | 42.14±0.00 |
| 5                         | 93.32 ±1.04  | 14.78±1.65    | 30.74±0.00 |

Table 2 Characteristics of mesoporous carbon in various carbonization periods using the POD method

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whereas hydroxyl groups on mesoporous carbon remain as hydroxyl groups, as explained in the case of rhodamine B [18].

For rhodamine B and methylene blue dyes, the positive charge on the quaternary ammonium dyes will interact with the carboxylic ion (-COO-) of mesoporous carbon through electrostatic attraction due to differences in ion charge; ion exchange occurs between the positive charge in the quaternary ammonium dye and the proton from the phenol carbon group. The interaction occurs with the release of proton H⁺ which causes changes in the pH of the solution to become more acidic as report by Marrakchi et al. 2017 [19], changes in the pH of the solution are also derived from the release of proton H⁺ by the group on the mesoporous carbon surface. For carmine and rhodamine B dyes, interactions also occur through hydrogen bonds between hydroxyl groups (-OH) in the dyes and OH groups in mesoporous carbon.

**Comparison of Dyes Adsorption by Commercial Activated Carbon and Mesoporous Carbon**

Mesoporous carbon performance in adsorption of dyes is known by comparing with commercial activated carbon. Percent adsorption of dyes using commercial activated carbon and mesoporous carbon at the optimum carbonization time is shown in the Table 3.

| Dyes        | % Adsorption Mesoporous carbon | % Adsorption Commercial activated carbon | Ratio of % adsorption |
|-------------|--------------------------------|-----------------------------------------|-----------------------|
| Rhodamine B | 96.43 ±0.37                    | 99.38 ±0.61                             | 1 : 1.03              |
| Carmine     | 48.51 ±1.55                    | 99.73 ±0.00                             | 1 : 2.05              |
| Methylene blue | 38.80 ±1.44                        | 99.90 ±0.02                             | 1 : 2.57              |

The tertiary amine function group and the quaternary ammonium contained in the fixed methylene blue as tertiary amine and quaternary ammonium as shown in figure 3.

The adsorption mechanism that occurs in the three dyes is the aromatic structure of dye ion interacts with carbon polymers on the mesoporous carbon surface, which also has an aromatic structure; this interaction involves van der Waals interaction.

Table 3 shows that the percent adsorption of commercial activated carbon is greater than the mesoporous carbon. Table 4 shows that the average pore diameter of commercial activated carbon is smaller than mesoporous carbon, thereby increasing the match between the diameter of the dyes with the pore diameter of the commercial activated carbon which can increase the attractiveness of the dyes ions because it is closer to the surface of the adsorbent [20].
In addition, the pore volume and large specific surface area allows dyes adsorption up to two times for methylene blue and carmine. This can be explained by the structure size of methylene blue and carmine which are almost the same and smaller so easily adsorbed. It contrary to the structure of Rhodamine B which is larger and bulky, it inhibits the absorption of the dye into the adsorbent.

CONCLUSION

Dyes adsorption of mesoporous carbon has increased in carbonization time of 1 to 3 hours and decreased in carbonization time of 3 to 5 hours, this is in line with the increase and decrease in mesoporous carbon character, especially volume and surface area. The optimum carbonization time was obtained at 3 hours, with dye adsorption percentages of 96.43 ± 0.37% for rhodamine-B, 38.80 ± 1.44% for methylene blue and 48.51 ± 1.55% for carmine. The adsorption value of commercial activated carbon is greater than the mesoporous carbon.

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REFERENCES

[1] Z.-P. Hu, J.-T. Ren, D. Yang, Z. Wang, and Z.-Y. Yuan, “Mesoporous carbons as metal-free catalysts for propane dehydrogenation: Effect of the pore structure and surface property,” Chinese Journal of Catalysis, vol. 40, no. 9, pp. 1385–1394, 2019.

[2] S. Wong, N. A. N. Yac’cob, N. Ngadi, O. Hassan, and I. M. Inuwa, “From pollutant to solution of wastewater pollution: Synthesis of activated carbon from textile sludge for dye adsorption,” Chinese Journal of Chemical Engineering, vol. 26, no. 4, pp. 870–878, 2018.

[3] S. Li, Z. Jia, Z. Li, Y. Li, and R. Zhu, “Synthesis and characterization of mesoporous carbon nanofibers and its adsorption for dye in wastewater,” Advanced Powder Technology, vol. 27, no. 2, pp. 591–598, 2016.

[4] X. Yue, C. Li, and Z. Yang, “A novel colorimetric and fluorescent probe for trivalent cations based on rhodamine B derivative,” Journal of Photochemistry and Photobiology A: Chemistry, vol. 351, pp. 1–7, 2018.

[5] Z. Ezzeddine, I. Batonneau-Gener, Y. Pouilloux, and H. Hamad, “Removal of methylene blue by mesoporous CMK-3: Kinetics, isotherms and thermodynamics,” Journal of Molecular Liquids, vol. 223, pp. 763–770, 2016.

[6] S. A. Maruyama, S. R. Tavares, A. A. Leitão, and F. Wypych, “Intercalation of indigo carmine anions into zinc hydroxide salt: A novel alternative blue pigment,” Dyes and Pigments, vol. 128, pp. 158–164, 2016.

[7] N. Hegyesi, R. T. Vad, and B. Pukánszky, “Determination of the specific surface area of layered silicates by methylene blue adsorption: The role of structure, pH and layer charge,” Applied Clay Science, vol. 146, pp. 50–55, 2017.

[8] C. M. Magdalane et al., “Evaluation on the heterostructured CeO2/Y2O3 binary metal oxide nanocomposites for UV/Vis light induced photocatalytic degradation of Rhodamine - B dye for textile engineering application,” Journal of Alloys and Compounds, vol. 727, pp. 1324–1337, 2017.

[9] F. V. de Andrade, G. M. de Lima, R. Augusti, M. G. Coelho, J. D. Ardisson, and O. B. Romero, “A versatile approach to treat aqueous residues of textile industry: The photocatalytic degradation of Indigo Carmine dye employing the autoclaved cellular concrete/Fe2O3 system,” Chemical Engineering Journal, vol. 180, pp. 25–31, 2012.

[10] Menteri Lingkungan Hidup, “Keputusan Menteri Negara Lingkungan Hidup Nomor 51 tahun 1995, Tentang Baku Mutu Limbah Cair,” Jakarta, 1995.

[11] N. Mathur and Shwani Kumar, “Environmental Pollution by Textile Industries: Case Studies and Analysis,” in Anthropogenic pollution Causes and Concern, 1st ed., Daya Publishing New Delhi, 2016.

[12] Y. Zheng et al., “Highly efficient simultaneous adsorption and biodegradation of a highly-concentrated anionic dye by a high-surface-area carbon-based biocomposite,” Chemosphere, vol. 179, pp. 139–147, 2017.

[13] Z. Wang, H. Deng, X. Li, P. Ji, and J.-P. Cheng, “Standard and Absolute pKa Scales of Substituted Benzoic Acids in Room Temperature Ionic Liquids,” J. Org. Chem., vol. 78, no. 24, pp. 12487–12493, 2013.

[14] D. B. Troy and P. Beringer, Remington: The Science and Practice of Pharmacy. Lippincott Williams & Wilkins, 2006.

[15] National Center for Biotechnology Information. PubChem Database. Rhodamine B,
https://pubchem.ncbi.nlm.nih.gov/compound/Rhodamine-B (accessed on Jan. 15, 2020).

[16] National Center for Biotechnology Information. PubChem Database. Indigo carmine., https://pubchem.ncbi.nlm.nih.gov/compound/Indigo-carmine (accessed on Jan. 15, 2020)

[17] National Center for Biotechnology Information. PubChem Database. Methylene blue, https://pubchem.ncbi.nlm.nih.gov/compound/Methylene-blue (accessed on Jan. 15, 2020)

[18] D. L. Postai, C. A. Demarchi, F. Zanatta, D. C. C. Melo, and C. A. Rodrigues, “Adsorption of rhodamine B and methylene blue dyes using waste of seeds of Aleurites Moluccana, a low cost adsorbent,” *Alexandria Engineering Journal*, vol. 55, no. 2, pp. 1713–1723, 2016.

[19] F. Marrakchi, M. J. Ahmed, W. A. Khanday, M. Asif, and B. H. Hameed, “Mesoporous-activated carbon prepared from chitosan flakes via single-step sodium hydroxide activation for the adsorption of methylene blue,” *International Journal of Biological Macromolecules*, vol. 98, pp. 233–239, 2017.

[20] M. Kılıç and A. S. K. Janabi, “Investigation of Dyes Adsorption with Activated Carbon Obtained from Cordia myxa,” vol. 1, no.2, pp. 87-104, 2017.