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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

Abstrak (Indonesian)

Telah dilakukan uji adsorpsi beberapa zat warna yaitu rodamin B, metilen biru dan karmin dengan adsorben karbon mesopori hasil sintesis pada berbagai waktu karbonisasi. Hal ini bertujuan untuk mengetahui bagaimana pengaruh waktu karbonisasi terhadap kemampuan karbon mesopori dalam mengadsorpsi zat warna. Selain itu juga dilakukan uji kemampuan adsorpsi antara karbon mesopori dan karbon aktif perdagangan. Uji adsorpsi dilakukan dengan kondisi: 0,1 g adsoben, 25 mL larutan zat warna 100 ppm dan kecepatan pengadukan 125 rpm selama 4 jam. Filtrat digunakan untuk penentuan konsentrasi sisa zat warna dengan menggunakan spektrofotometer UV-Visible. Hasil penelitian menunjukkan bahwa lama karbonisasi dari 1 hingga 3 jam meningkatkan kemampuan adsorpsi, sedangkan dari 3 hingga 5 jam menurunkan kemampuan adsorpsi. Karakter karbon mesopori terbaik diperoleh pada waktu karbonisasi 3 jam dengan nilai adsorpsi 96,43 ± 0,37 % untuk rodamin-B, 38,80 ± 1,44 % untuk metilen biru dan 48,51 ± 1,55 % untuk karmin. Nilai adsorpsi karbon mesopori adalah sebesar 0,97 kali untuk rodamin B, 0,48 kali untuk karmin dan 0,39 kali untuk metilen biru dibandingkan karbon aktif perdagangan.

Keywords: waktu karbonisasi, karbon mesopori, rodamin B, metilen biru, karmin

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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 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 adsorbent 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 rodamine 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:

$$\%\ Dyes\ adsorption = \frac{C_0 - C_s}{C_0} \times 100\%$$

C_o = 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 H_2O, 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.

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

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 pKa value on phenol is 9.89 [14]. With the aromatic group extension, it is assumed that it can reduce the value of pKa. While at solution pH 5.06 that is lower than the pKa value, causing the hydroxyl group on the mesoporous carbon to remain as the hydroxyl group.

Carmine adsorption, which works at pH 3.48. Carboxyl and hydroxyl groups bound to carbon polymers are more dominant in the form of carboxyl and hydroxyl groups, because 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.

Adsorption of methylene blue works at pH 5.26. Carboxyl groups bound to mesoporous carbon polymers are more dominant as carboxylic ions,

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
$V_{p\ meso}$	cm^3/g	0.0154	0.0212	0.0503	0.0183	0.0136
$S_{p\ meso}$	m^2/g	17.7003	21.2752	42.7702	22.6121	16.6236
$r_{p\ meso}$	Å	17.3982	19.8846	23.5210	16.1954	16.3668
$d_{p\ meso}$	Å	34.7965	39.7692	47.0367	32.3908	32.7336

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

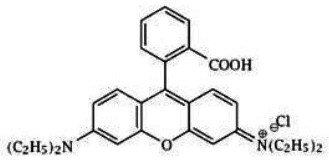

Figure 1. Rhodamine B Structure [15]

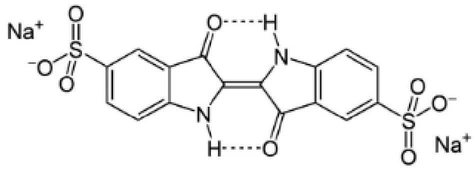

Figure 2. Carmine Structure [16]

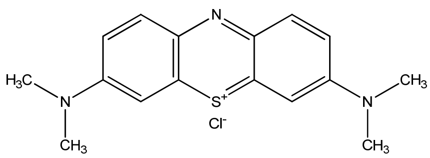

Figure 3. Methylene Blue Structure [17]

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.

Tabel 3. Percentage of adsorption of dyes by commercial activated carbon and mesoporous carbon at optimum synthesis conditions

Dyes	% Adsorption		Ratio of % adsorption
	Mesoporous carbon	Commercial activated carbon	
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].

Table 4. Characteristics of commercial activated carbon and mesoporous carbon at optimum condition of carbonization time

Character	Unit	C-mesoporous	C-commercial activated
V_p	cm^3/g	0.0503	0.1929
S_p	m^2/g	42.7702	230.737
r_p	Å	23.5210	16.7284
d_p	Å	47.0421	33.4568

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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