Synthesis of Rice Straw as Biosorbent for Colour Removal in Batik Industrial Waste which is Represented by Methylene Blue

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Abstract. Use of rice straw as a biosorbent for water treatment in batik industry is not fully developed. Liquid waste for the colour's adsorption using rice straw biosorbent represented by methylene blue solution. Rice straw biosorbent has been activated by HNO₃ 1 M and NaOH 0,75 M. Then characterized using Scanning Electron Microscopy with Energy Dispersive Spectroscopy (SEM EDS) dan Fourier Transform Infrared (FTIR) Spectroscopy. The variation of dosage and drying temperature applied to know the optimum dosage for utilization of biosorbent and optimum drying temperature for biosorbent synthesis. The equilibrium were fitted to Langmuir isotherm and Pseudo Order 2 kinetics. The optimum adsorption obtained in 1,67 gr/L biosorbent with 100°C drying temperature in 4 ppm methylene blue waste simulation solution with 95.27% adsorption capacities and 4 ppm batik industrial waste solution with 30.59% adsorption capacities.

1 Introduction

Batik is one of the world cultural heritage derived from Indonesia. Batik becomes an important part in industrial growth in Indonesia, especially in batik producing area. Productivity of batik does not only affect the increase of regional income, but also impact on other problems, especially environmental problems. One of the environmental problem is caused by batik production process that produced liquid waste which comes from residual of batik colouring process. The liquid waste by some industries directly discharged into the river without treatment [1].

Rivers have the ability to clean themselves (self purification). But if the waste is discharged continuously and exceeds the self purification capability of the river, it will result in the occurrence of river pollution [2]. Colour is the easiest parameter to determine whether the river is clean or not. The clean river has a clear flow of water. If the river flow is not clear, it can be indicated that the river is not suitable for daily needs. Rivers in batik industrial areas have been polluted dyes derived from residual of batik colouring process [3]. Based on these parameters can be indicated that the river is not feasible for the continuity of the river ecosystem and the needs of water to surrounding communities.

There are several alternatives to handle the waste problem. The adsorption method becomes one of the ways to absorb the dye on batik industrial waste. This study also focused on using natural material adsorbent (biosorbent) derived from agricultural waste as an alternative to conventional adsorbents. Agricultural wastes are selected as the basic ingredients for the synthesis of biosorbents because of their abundant availability. In addition, its use can be optimal because it does not compete with anything [4]. There are various

agricultural wastes, such as coconut shells, rice husks, rice stalks, corncobs, palm oil bunches and others. Agricultural waste is a material that has the potential to be processed into biosorbent [5]. Agricultural waste used in this research is rice straw. Rice straw is chosen because its availability is very abundant and rarely reused. After the harvest season, rice straws are directly burned without being processed first [6]. Rice straw contains C, O, H and N content of 87% of its total weight and Si (4.6%), K (2.5%), P (0.5%), Ca (0.3%) And Mg (0.3%) (Wang, 2007, p.315). These elements content are beneficial to adsorption process, so that rice straw is potentially processed into biosorbent [7].

This study made biosorbent from rice straw that activated using HNO₃ 1 M and NaOH 0.75 M. HNO₃ and NaOH were selected become media activation based on Rocha's research, et al [8]. Both were able to make pore of the rice straw have a greater absorbence to adsorbate. Then the biosorbent will be applied to absorb the dissolved dyes in the liquid waste of batik industrial. This research uses methylene blue to represent liquid waste of batik industrial. Methylene blue is a cationic dye commonly used by textile industry [9].

The objective of this work were to convert rice straw to biosorbent with high sorption capacity, and to examine potential application of this new biosorbent in batik's colour wastewater treatment.

Fig. 1. Chemical structure of Methylene Blue.

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2 Materials and Methods

2.1 Materials

Rice straw and batik industrial waste were collected from Pekalongan City, Central Java, Indonesia. Methylene blue (Merck), NaOH (Merck) and HNO₃ (65%, Puduk Scientific). All solution were prepared by using distilled water.

2.2 Preparation of modified biosorbent

Rice straw washed by water, dried in an oven at 60°C for 8 hours. And then crushed to obtain a small size. This material called as SMP. 10 g of SMP was activated by 50 mL of HNO₃ 1 M and agitated for 1 hour at room temperature. Next, the material washed by water to removed the excess acid. After the pH was neutral, 10 g of SMP activated by 100 mL of NaOH 0,75 M and agitated for 1 hour at room temperature. The SMP washed again by water until the pH was neutral and dried in an oven with the variation of drying temperature for 4 hours. Rice straw that has passed through this stage is called BMP. BMP crushed and sieved with the mesh 75 (193.5 µm).

Methylene blue is used as a waste simulation solution. Methylene blue solution was prepared by dissolving 4 mg of methylene blue into 1 L of distilled water. Analysis of dissolved methylene blue concentration using UV-VIS spectrophotometer with maximum wavelength of 668 nm.

2.3 Experimental methods and measurements

2.3.1 Drying temperature

Drying temperature variation is carried out in the second drying process. The temperature variation used are 60°C, 100°C and 140°C. The second drying was done by using the oven for 4 hours.

2.3.2 Biosorbent dosage

Variation of dosage were performed by adding biosorbents of 0.1, 0.5, and 1 g to 300 ml of methylene blue solution. The initial concentration of methylene blue solution used was 4 mg/L. The adsorption studies was performed using a batch system in a 600 mL beaker glass that was stirred using a magnetic stirrer at pH 6 and room temperature.

2.3.3 Equilibrium studies

The equilibrium studies is carried out by contacting the rice straw biosorbent with a methylene blue solution. The length of contact time is 2 hours with sampling every 5 minutes. The adsorption study was performed on a 600 mL beaker glass using a magnetic

stirrer. Initial and equilibrium concentration were measured using a UV-VIS spectrophotometer with a wavelength of 668 nm. The value of the adsorption equilibrium is calculated by the following formula.

$$q_e = \frac{(C_0 - C_e) v}{w} \times 100 \quad (1)$$

Where C₀ and C_e are initial concentration and equilibrium concentration, v is the volume and m is the dose of the biosorbent. Percent removal is calculated using the following formula.

$$\text{Removal percentage} = \frac{C_0 - C_e}{C_0} \times 100 \quad (2)$$

2.3.4 Kinetics studies

The kinetics studies is carried out by contacting 300 mL of methylene blue solution with different biosorbent doses. The studies was performed using a 600 mL beaker glass and magnetic stirrer at room temperature and pH 6.

2.3.5 Characterization of biosorbent

There are two characterization performed in this research. The pore morphology on the surface of rice straw was observed using a Scanning Electron Microscopy with Energy Dispersive Spectroscopy (SEM EDS FEI type Quanta 650, Oxford). Then, functional groups on the surface of rice straw was analysed using a Fourier Transform Infra Red (FTIR Tensor 27, Bruker). FTIR spectra were recorded over the wavenumber range of 600-4000 cm⁻¹.

3 Results and Discussion

3.1 Scanning Electron Microscopy with Energy Dispersive Spectroscopy (SEM EDS)

SEM characterization results were performed to analyze the pores which formed on the surface of the biosorbent shown in Fig. 2. Based on SEM test results, the pores formed on the surface of the biosorbent are not uniform. Pores are various in size, ranging from 14.08 to 20.57 µm. Pores on the surface of the biosorbent cause dye adsorption. The adsorbate particles will be trapped into the pores so that the adsorbate content in the waste simulation solution will decrease [10].

The element content on the biosorbent surface is detected by using EDS and presented in Table 1. The results obtained surface of the biosorbent are dominated by elements C, O, Si with a value of 58.07% atoms, 37.44% atoms and 3.35% atoms, respectively. These elements are involved in the adsorption process [11].

3.2 Fourier Transform Infra Red (FTIR) Spectroscopy

The result of functional group identification of biosorbent is shown in Fig. 3. Based on Fig. 3, peaks appeared at 1058 cm^{-1} and 1350 cm^{-1} , which are represented C-O stretching group and C-C group. The absorbance band at 1650 cm^{-1} was assigned to C=O stretching group. Then, the absorbance band at 2810 cm^{-1} and 3440 cm^{-1} was attributed to C-OH stretching group and O-H group, respectively. The results of the FTIR studies are summarized in Table 2.

3.3 Influence of drying temperature

The ability of rice straw biosorbent in dye absorbing is shown in Fig. 4. Biosorbent with 100°C and 140°C drying temperature has sorption capacities 95.27% and 94.39%. Both types of biosorbents also reached a state of equilibrium at 30 minutes. While the biosorbent with a 60°C drying temperature, has a lower adsorption capacities of 88.47%. The equilibrium state for biosorbent with 60°C drying temperature was reached at 95 minutes. If the drying temperature is higher, then the pores that formed on the surface of the biosorbent are more numerous as the amount of H_2O and other volatile substances that can be evaporated is also more.

This relates to the number of active sites formed on the surface of the biosorbent [12]. The optimum drying temperature is specific for each type of biosorbent. Biosorbent with 100°C drying temperature has a higher %sorption capacities when compared by biosorbent with 140°C drying temperature. This is because at a drying temperature of 140°C some of the biosorbent pores begin to damage, this is proven by the sorption capacities for biosorbent with a drying temperature of 140°C lower than the sorption capacities for biosorbent with a drying temperature of 100°C but not far adrift.

3.3 Influence of Biosorbent Dosage

The correlation between ability of rice straw biosorbent in absorbing methylene blue based on adsorbent dose is shown by figure 5. In this analysis, a 100°C drying temperature biosorbent is used. As the adsorption studies proceeded, the adsorption capacities of rice straw biosorbent to the methylene blue is increased. The graph also explains that the more doses of biosorbent added, the more adsorbate absorbed. This is related to the number of active sites available [13]. Adsorption capacities for biosorbent at doses of 0.33 g/L, 1.67g/L and 3.33g/L were 92.78%, 95.27% and 95.42%, respectively. Based on the value of sorption capacities achieved, difference of sorption capacities value is not significant in the increase of biosorbent dose. This is because the availability of active sites at small doses is sufficient.

Fig. 2. SEM study of rice straw biosorbent in 100°C drying temperature with 500x magnification (above) and 1000x magnification (below).

Tabel 1. EDS study of rice straw biosorbent of 100°C drying temperature on spectrum 1.

Element	Apparent Concentration	Wt%	Atomic %	Standard label
C	12.01	47.53	56.51	C Vit
O	21.64	44.15	39.41	SiO ₂
Si	4.34	7.33	3.73	SiO ₂
Ca	0.56	0.99	0.35	Wollastonite
Total		100	100

Fig. 3. FTIR study of rice straw biosorbent 100°C drying temperature.

Table 2. The result of functional group analysis on rice straw biosorbent in 100°C drying temperature.

IR peak	Frequency (cm ⁻¹)	Functional groups	Type of bond	Intensity
1	785	Si-O		
2	1058	C-O	stretching	Strong
3	1350	C-C		Weak
4	1650	C=O	stretching	Strong
5	2810	C-OH	stretching	Weak
6	3440	OH

Fig. 4. Adsorption capacities of each rice straw biosorbent with a dose of 1.67 g/L to 300 mL methylene blue.

Fig. 5. Adsorption capacities of each rice straw biosorbent dose of 100°C drying temperature to 300 mL of methylene blue.

3.5 Adsorption isotherm studies

There are two isotherms equations used, Langmuir isotherm and Freundlich isotherm. Determination of appropriate isotherms based on the value of R^2 which obtained.

Isotherm Langmuir explains the assumption that optimal adsorption occurs when the solute molecules formed a monomolecular layer on the biosorbent surface, constant adsorption energy, and no mass transfer of adsorbate molecules on the biosorbent

surface. Isotherm Langmuir is expressed by the following equation.

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{1}{q_m} C_e \quad (3)$$

q_m and K_L are Langmuir constants which represent the maximum adsorption capacity for solid phases and energy constants associated with the adsorption heat. While q_e and C_e describe the equilibrium condition.

Freundlich isotherm expresses an empirical relationship that explains the adsorption of solutes to the surface of the adsorbent and takes the assumption that the adsorbate formed a multimolecular layer on the biosorbent surface. Freundlich isotherm illustrates the relationship between the amount of adsorbate adsorbed per unit of adsorbent mass and the concentration of adsorbate at equilibrium.

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (4)$$

K_f and n are Freundlich constants, K_f and n are indicators of adsorption capacity and adsorption intensity. While q_e and C_e describe the equilibrium condition.

The result of the analysis of R^2 value for each biosorbent is shown in Tabel 3. Based on the calculation, biosorbent is more suitable with Langmuir isotherm equation. Langmuir isotherm curve can be seen in figure 6. The results of the Langmuir isotherm analysis show that the active surface of biosorbent has homogeneous properties and adsorbate is absorbed on the biosorbent surface forming a monomolecular layer.

3.6 Adsorption kinetics studies

The colour adsorption kinetics that occur between the adsorbate and the rice straw biosorbent progress quickly. At first the adsorption process that occurs is rapid adsorption. Then the adsorption process slows down over time and then enters a state of equilibrium.

Kinetic studies were analyzed using the kinetic equation of Pseudo Order 1 and the kinetic equation of Pseudo Order 2. Determination of corresponding kinetic based on the value of R^2 which achieved. Kinetic equation of Pseudo Order 1 is shown in the following equation.

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (5)$$

k_1 is a constant on the kinetic equation of Pseudo Order 1. q_t and q_e are the amount of adsorbate at t and at equilibrium.

The kinetic equation of Pseudo Order 2 is shown in the following equation.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (6)$$

k_2 is a constant on the kinetic equation Pseudo order 2. q_t and q_e is the amount of adsorbate at time t and at equilibrium.

Based on the value of R^2 in table 4, the adsorption phenomenon that follows the kinetic equation of Pseudo order 2, which means that adsorption is chemical adsorption. Pseudo order 2 kinetics curve can be seen in figure 7. The results of this study are similar to Kazembeigi's research [14].

Tabel 3. The value of R^2 in the isotherm analysis of each biosorbent.

Biosorbent		R^2	
T (C)	Dose (gr)	Freunlich	Langmuir
60	0.1	0.9308	0.876
	0.5	0.8818	0.9361
	1	0.9041	0.9748
100	0.1	0.8274	0.9123
	0.5	0.8961	0.9912
	1	0.9504	0.9984
140	0.1	0.8402	0.8729
	0.5	0.8895	0.9867
	1	0.9507	0.9971

Fig. 6. Langmuir's isotherm curve for adsorption study with rice straw biosorbent 100°C drying temperature dose 0.5 g in 300 mL methylene blue.

3.7 Aplication of the biosorbent studied for water waste treatment

The adsorption studies for batik industrial waste is carried out under the same conditions as using methylene blue, by using rice straw biosorbent temperature of 100°C and a dose of 0.5 g in 300 mL waste solution. Based on these studies can be seen the ability of biosorben rice straw of batik waste adsorption. The test results showed the dye sorbed increased. Sorption capacities achieved by 30.59%.

Before the adsorption studies, pretreatment is performed for batik liquid waste. Pretreatment performed include sedimentation, filtration and centrifugation. The adsorption capacities of these studies is not as good as when using methylene blue solution.

This is because the substances dissolved in batik liquid waste waste are not only dyes, but many impurities such as azo dye, salts, waxes, and other impurities [15]. Salt contained in the waste solution is useful as a color amplifier, so that the color attached to the fabric does not quickly fade.

Tabel 4. The value of R^2 in the isotherm analysis of each biosorbent.

Biosorbent		R	
T (C)	Dose (gr)	Pseudo order 1	Pseudo Order 2
60	0.1	0.9136	0.9996
	0.5	0.9878	0.9983
	1	0.9601	0.9641
100	0.1	0.992	1
	0.5	0.9807	0.9999
	1	0.9743	0.9959
140	0.1	0.9888	1
	0.5	0.9671	0.9998
	1	0.8502	0.9913

Fig. 7. Pseudo order 2 kinetic curve for adsorption study with rice straw biosorbent of 100°C drying temperature dose 0.5 g in 300 mL methylene blue.

4 Conclusions

This study confirmed that rice straw was excellent biosorbent for colour removal in liquid waste of batik industries which is represented by methylene blue. The optimum adsorption was in a 100°C drying temperature biosorbent at dose of 0.5 g in 300 mL of a 4 ppm methylene blue solution. The achieved of sorption capacities was 95.27% and reach equilibrium state after 30 minutes of adsorption. Sorption capacities that achieved for the adsorption studies using batik liquid waste was 30.59%. The isotherm and kinetic equation of rice straw biosorbent adsorption are following the Langmuir isotherms and the kinetic Pseudo order 2.

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