Silica-Based Material from Rice Husk and Their use on Methylene Blue Adsorption

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Abstract

Silica-based material prepared from rice husk were dissolved with HCl and calcined at 650°C for 4 hours. Composition analysis by x-ray fluorescence techniques showed that the silica content in the material as much as 78%. The amount of methylene blue before and after adsorption was analyzed by UV-Vis spectrophotometer. Adsorption conducted by batch method that varied in pH and time. The optimum pH for the methylene blue adsorption was found to 6.14 with the percentage adsorption of 64.3 %. While the optimum contact time was 5 hours with the percentage adsorption of 92.6 % and the adsorption capacity of 38.8 mg/g.

Keywords: Silica-based material, rice husk, methylene blue, adsorption, adsorption capacity

Introduction

The development of the industrial sector is currently causing an increase in the use of dyes that can pollute the environment (Chung et al., 2009). In the textile dyeing process generated approximately 24% and 6% dye salt used in the dyeing is then entered into the environment as waste waters (Kusumaningsih et al, 2012). One of the dyes used in this industry is methylene blue. Methylene blue compound has a structure that is difficult outlined benzene is toxic, carcinogenic and mutagenic (Ljubas, 2010). In addition, the number of dye molecules in water will interfere with the process of photosynthesis (Batista et al., 2010).

Wastewater treatment dye commonly performed include biological treatment, catalytic oxidation, filtration, absorption and processing combinations (Ong et al, 2011). Processing methods other dye is photocatalytic degradation of dye. Some research on the photocatalytic degradation of methyl orange has been carried out, among others, using ZnO nanoparticles coated polystyrene (Hong et al, 2009), parylena / TiO2 (Zhiyong et al, 2008), meso-tetrafenil metaloporphyrin (Fe, Co, Mn, and Cu) which adsorbed on TiO_2 (Zhou et al, 2012). Shrivastava (2012) also investigated the photocatalytic degradation of methylene blue and metallic chromium in wastewater using TiO_2 nanocrystalline semiconductors. Process wastewater treatment dye photocatalytic has a weakness in the form can produce byproducts which also has the same dangers with dye waste itself, such as hydrogen peroxide (H_2O_2) in

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the process of photocatalytic degradation of methyl orange using parylena / TiO_2 of 0.5 mg / L (Zhiyong et al, 2008). On the other hand, the waste treatment process uses dye absorption process does not produce harmful side products. There was also a dye waste treatment techniques are simple and are not sensitive or stable / not damaged to toxins (Tong et al, 2010). Therefore, the processing of the dye that is taken in this study is the adsorption process.

One of the adsorbent efficient, economical, and practical is rice husk which is a waste of agricultural produce. Rice husk ash can be used as an adsorbent because besides being a porous material also has an active group that is Si-O-Si and Si-OH (Siriluk & Yuttapong, 2005). According to Chen and Chang (1991) contains silica (SiO_2) in rice husk ash reaches 80-90%. Based on these statements, then this research will study the adsorption of the dye is methylene blue using natural materials rice husk as an adsorbent. Therefore, it is expected dye processing can be done also by using rice husk ash adsorbent.

Experimental Methods

Preparation of Rice Husk Ash

Natural materials are used as adsorbent in this study is rice husk ash. Preparation of rice husk ash is done by rice husk cleaned and washed with distilled water. Rice husk is clean as much as 100 grams and added 500 mL of HCl solution 3 M and the mixture is refluxed at temperature of 80°C for 3 hours. After the reflux, the solids are washed with double destillation water until neutral (acid free) and dried at a temperature of 120°C overnight. Rice husks that have been dried and then calcined at temperature of 650°C for 4 hours.

The Effect of pH

A 10 mL methylene blue at various pH 2, 3, 4, 5, 6, and 7 are contacted with 20 mg of adsorbent. The tube is covered with plastic, shaken with a shaker for 24 hours. The adsorbent is separated from the solution by filtering using filter paper whatmann 42 . The filtrate obtained is inserted into 50 mL volumetric flask. Then added aquabides to mark boundaries. Determined the concentration of methylene blue before and after adsorption with UV - Vis spectrophotometer. Adsorption capacity values are calculated based on the amount of methylene blue adsorbed on the adsorbent.

The effect of contact time

Adsorbent rice husk ash as much as 20 mg put in 10 mL of methylene blue solution with optimum pH has been obtained. Tube covered with plastic, shaken with a shaker with time variation 1 ; 3 ; 5 ; 7 hours. The adsorbent is separated from the solution by filtering using filter paper whatmann 42. The filtrate obtained is inserted into 50 mL volumetric flask. Aquabides then added to your limit. Determined the concentration of methylene blue before and after adsorption with UV - Vis spectrophotometer. Adsorption capacity values are calculated based on the amount of methylene blue adsorbed on the adsorbent.

Results and Discussion

X - Ray Fluorescence (XRF)

XRF characterization is a semi- quantitative characterization of an initial characterization of the composition of the metal in the adsorbent . XRF analysis results from natural zeolite adsorbent, bagasse and rice husks are shown in Table 1. Table 1 that the compounds highest of rice husk ash is silica that is by 78 %.

Table 1 XRF analysis results

No.	Komposisi	% wt
1	SiO_2	78,0
2	K_2O	11,3
3	P_2O_5	2,2
4	CaO	4,19
5	Fe_2O_3	0,72
6	MnO	1,2
7	ZnO	0,074
8	NiO	1,38
9	TiO_2	0,19

The effect of pH

The determination of the optimum pH is performed to determine the ability of the adsorption material rice husk ash to the compound methylene blue, so that the function of rice husk ash material can be used with either the environment. Methylene blue solution that has been arranged various pH 2, 3, 4, 5, 6, and 7 with a volume of 10 ml in contact with the material rice husk ash as much as 20 mg for 24 hours by a batch method. Methylene blue solution before and after adsorption was analyzed using a UV-Vis spectrophotometer at a wavelength of 664 nm maximum. The measurement results are presented in Table 2 below.

Data from the absorbance values before and after adsorption obtained, then used to determine the concentration before adsorption (Co), the concentration after adsorption (Ce), by interpolating the results of methylene blue absorbance of the solution at various pH into the equation generated from graphs the calibration curve. Table 2 shows the results of methylene blue adsorption with adsorbent rice husk ash at various pH. While the relationship between the pH of the adsorption percentage can be seen in Figure 1.

Table 2. Results of methylene blue adsorption with various pH

pH	Co (mg/L)	Ce (mg/L)	Cads (mg/L)	% Adsorpsi
2.08	108.0207	81.65671	26.364	24.40643
3.1	113.0785	76.59896	36.47949	32.26034
4	107.0649	65.08961	41.97531	39.20548
5.05	99.37873	53.46077	45.91796	46.20502
6.15	105.1135	37.53086	67.58264	64.29492
7.25	95.71485	39.60175	56.1131	56.1131

Co = concentration before adsorption
Ce = concentration after adsorption
Cads = Co – Ce
$\% \, \boldsymbol{Adsorption} = \frac{C\,ads}{Co} \times \mathbf{100}\%$

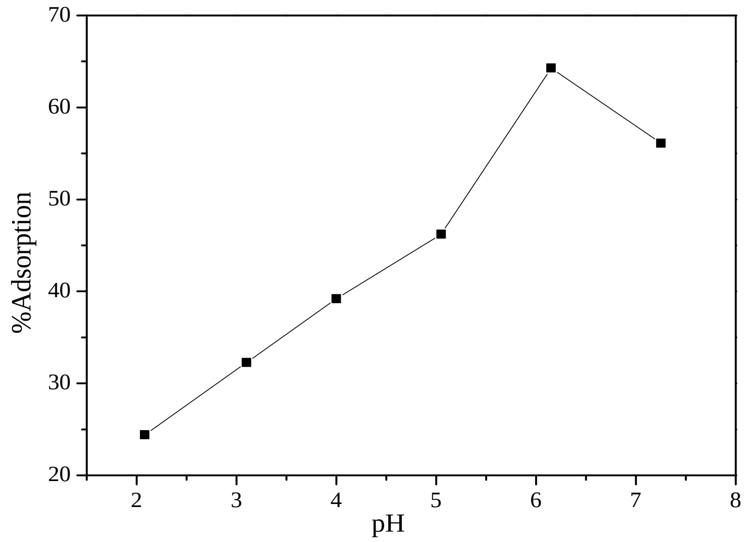


Figure 1 Effect of pH on removal methyline blue using rice husk ash

Based on Table 2 and Figure 1 it can be seen that a pH of 6 is the optimum conditions for adsorption of methylene blue using rice husk ash as adsorbent with the percentage of adsorption at 64.29492%, where the equilibrium between the dye with the hydroxyl ions in the solution, so that the dye is able to capture hydroxyl ions are added. This shows that the dye methylene blue has undergone dissociation, thus negatively charged. This causes the interaction with rice husk ash material. Along with the increase in the pH of the dye methylene blue becomes negatively charged which will lead to interaction, so that the adsorption decreases. At a pH of 6 to 7 decreased adsorption presentation, this is because the amount of methylene blue dye adsorbed on the surface of the rice husk ash material decreases. This is expected because material nature rice husk ash positively charged diminishing. If the pH of the solution is higher, then the amount of free OH^- ions in solution have competition between the dye methylene blue with OH^- ions to occupy the rice husk ash. At alkaline OH- ions present in the solution causes the competition , so that the adsorption process is more optimal in acidic conditions. The adsorption amount was less in acidic media but remained almost constant in basic conditions as shown in Fig.2. The observed low adsorption rate of MB on the gypsum at pH < 7.5 may be because the surface charge becomes positively charged, thus making (H^+) ions compete effectively with dye cations causing a decrease in the amount of dye adsorbed (Rauf et al, 2009).

The effect of contact time

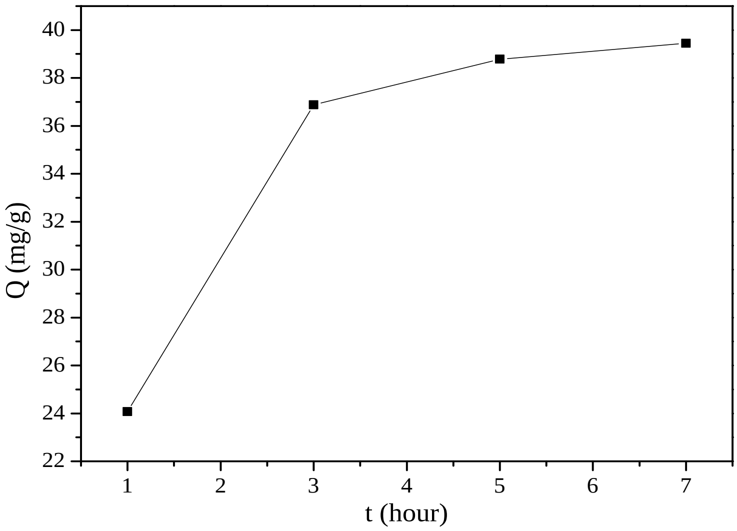
The time variation of the adsorption was conducted to determine the capacity of rice husk ash adsorbent in the adsorption process methylene blue . Methylene blue solution with a volume of 10 mL , in contact with the material rice husk ash as much as 20 mg . Then the ocean in a shaker with a different time is 1 ; 3 ; 5 ; 7 hours before it is set in the state of optimum pH solution is 6. After the solution was analyzed using a UV - Vis spectrophotometer at a wavelength of 664 nm to determine the concentration of methylene blue in the solution . Results of the adsorption of methylene blue with time variation can be seen in Table 3. Relations with the time variation of the adsorption capacity can be seen in Figure 2.

Table 3 Result of Adsorption Methylene Blue with Time Variation

Time (hours)	**Co (mg/L)**	**Ce (mg/L)**	**Cads (mg/L)**	**% Adsorption**	**Q (mg/g)**
1	84.12585	35.9777	48.14815	57.23348	24.07407
3	83.76742	10.01195	73.75548	88.04792	36.87774
5	83.76742	6.188769	77.57865	92.61196	38.78933
7	106.0693	27.17642	78.89287	74.37861	39.44644

Co = concentration before adsorption Ce = concentration after adsorption

Cads = Co – Ce $\qquad Q = \frac{V\,x\,(Co - Ce)}{m}$, V = 10 mL; m = 20 mg



$$\%\,Adsorpsi = \frac{C\,ads}{Co} \times 100\%$$

Figure 2. The effect of time on the adsorption capacity of Methlylene Blue

The adsorption capacity (in terms of Q) of Methylene Blue by rice husk ash was found to increase, reach a maximum value with increase in contact time (Figure 2). In same cases it almost become constant with increase in contact time, after 5 hours. Based on these results, 5 hours was taken as the equilibrium time in adsorption experiments. The removal of Methylene Blue from aqueous solutions by adsorption on rice husk ash increases with time, till the equilibrium is attained (Sarioglu & Atay, 2006). In batch type adsorption process monolayer of adsorbate is generally formed on the surface of adsorbent (Al-Qodah, 2000) and removal rate of adsorbate species from aqueous solution is controlled especially by the rate of transport of the adsorbate species form the outer sites to interior sites of the adsorbent particulars (Kannan & Sundaram, 2001).

Conclusions

The highest compound on the adsorbent rice husk ash is silica that is by 78 % . Removal of methylene blue on aqueous solution using rice husk ash which effectively occurred at pH 6 and optimum contact time of 5 hours.

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References

Al-Qodah Z. (2000) Adsorption of dyes using shale oil ash, *Water Research*, 34(17), 4295-4303.

Batista, A.P. L., Carvalho, H. W., Luz, G. H. P., Martins, P. F. Q., Goncalves, M., and Oliveira, L. C. A. O, (2010), Preparation of CuO/SiO_2 and Photocatalytic Activity by Degradation of Methylene Blue, *Environmental Chemistry Letter*, 8, 63-67.

Chen, J. M. and Chang F. W., (1991), The Chlorination Kinetics of Rice Husk, *Ind. Eng. Chem. Res*.,30, 2241-2247

Chung, Y.C., Chen, Y.C., (2009), Degradation of Azo Dye Reactive Violet 5 by TiO_2 Photocatalysis, *Environmental Chemistry Letter*, 7, 347-352.

Hong, R.Y., Li, J.H., Chen, L.L., Liu, D.Q., Li, H.Z., Zheng, Y., Ding, J., (2009), Synthesis, surface modification and photocatalytic property of ZnO nanoparticles, *Powder Technology*, 189, 426–432

Kannan N. and Sundaram M.M. (2001) Kinetics and mechanism of removal of methylene blue by adsorption on various carbons- a comparative study, *Dyes and Pigments*, 51, 25-40.

Kusumaningsih, T., Desi S.H., and Yuni L., (2012), Pembuatan Mikrokapsul Kitosan GelTersambung Silang Etilen Glikol Diglisidil Eter (Psf-Egde-Cts) sebagai Adsorben ZatWarna Procion Red Mx 8b. *ALCHEMY J. Penelitian Kimia*, 8(1), 47-56.

Ljubas, D., Curcovic, L., and Dobrovic, S., (2010), Photocatalytic degradation of an Azo Dye by UV Irradiation at 254 and 365 nm, *Transactions of Famena, 34*, ISSN 1333-1124

Ong, S., Keng, P., Lee, W., Ha, S., Hung, Y., (2011), Review: Dye Waste Treatment, *Water*, 3, 157-176

Rauf, M. A. Shehadeh, I., Ahmed, A. and Al-Zamly, A., (2009), Removal of Methylene Blue from Aqueous Solution by Using Gypsum as a Low Cost Adsorbent, *World Academy of Science, Engineering and Technology*, 55, 608-613

Sarioglu, M. And Atay, U. A., (2006), Removal of Methylene Blue by Using Biosolid, *Global NEST Journal*, 8(2), 113-120 .

Shrivastava V. S., (2012), Photocatalytic degradation of Methylene blue dye and Chromium metal from wastewater using nanocrystalline TiO_2 Semiconductor, *Archives of Applied Science Research*, 4, 1244-1254

Siriluk, C. and Yuttapong, S. (2005). *Structure of Mesoporous MCM-41 Prepared from Rice Husk Ash*. The 8th Asian Symposium On Visualization, Chiangmai, Thailand, 23-27 May 2005, Paper Number n 1-7.

Tong, D. S, Zhou, C. H., Lu, Y., Yu, H., Zhang, G. F., Yu, W. H., (2010), Adsorption of acid red G dye on octadecyl trimethylammonium montmorillonite, *Appl Clay Sci*, 50, 427–431

Zhiyong, Y., Keppner, H., Laub, D., Mielczarski, E., Mielczarski, J., Kiwi-Minsker, L., Renken, A., Kiwi, J., (2008), Photocatalytic discoloration of Methyl Orange on innovative parylene–TiO_2 flexible thin films under simulated sunlight, *Applied Catalysis B: Environmental*, 79, 63–71

Zhou, X., Ji, H., Huang, X., (2012), Photocatalytic Degradation of Methyl Orange over Metalloporphyrins Supported on TiO_2 Degussa P25, *Molecules*, 17, 1149-1158