#### The 1<sup>st</sup> International Seminar on Chemical Education 2015 September, 30<sup>th</sup> 2015

## **Removal of Methyl Orange in Aqueous Solution using Rice Husk**

Tri Esti Purbaningtias<sup>1\*</sup>, Bayu Wiyantoko<sup>1</sup>, Puji Kurniawati<sup>1</sup>, Yorfan Ruwindya

<sup>1\*</sup>Chemical Analyst Program, Faculty of Mathematics and Natural Sciences, Islamic University of Indonesia, Jl. Kaliurang Km 14.5 Yogyakarta 55584 Corresponding author: <u>tri.esti.p@uii.ac.id</u>

#### Abstract

The ability of rice husk adsorbent was invertigated for adsortive removal of methyl orange from aqueous solution. Various parameters were optimized in batch technique, such as pH, equilibrium contact time and initial dye concentration. Adsorption of methyl orange was optimum at medium pH 3 and it had optimum contact time in 180 min. The kinetic studies were identified using first order, second order, pseudo first order and pseudo second order. Adsorption of methyl orange using rice husk fitted to Langmuir and Freundlich isoterm.

**Keywords:** adsorption, methyl orange, rice husk

### Introduction

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). Part of utilization dye, azo compound is the greatest concentration. One of them is a methyl orange. Methyl orange is an anionic azo dyes are most widely used in the printing industry, textiles, photography and color indicator. Azo dyes such as methyl orange is known to be carcinogenic. Therefore, before discharged into the environment, pollutant needs to be done prior treatment (Kodom et al, 2012). One treatment to eliminate waste substances such as methyl orange color is adsorption.

Adsorption is an efficient technique to face the problem of contamination of domestic and industrial wastewater, because it can eliminate odors as well as lower levels of dye from solution perfectly without turning it into a more dangerous compounds. In addition the use of adsorbent has several advantages such as having pores large, hydrophobic, stable in high temperatures, do not have catalytic activity and easily regenerated (Wahab et al., 2005). 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). Chen and Chang (1991) reported that rice husk ash contains 80-90% silica (SiO<sub>2</sub>). Based on these statements, then this research will study the adsorption of methyl orange dye that use natural materials

#### The 1<sup>st</sup> International Seminar on Chemical Education 2015 September, 30<sup>th</sup> 2015

rice husk as an adsorbent. Natural materials rice husk been in previous studies, the adsorbent has been used successfully as a natural adsorbent to reduce the acid number of patchouli oil (Purbaningtias et al, 2014). 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

Methyl orange solution with the same initial concentration was made by varying the pH of a solution of 2, 3, 4, 5, 6, 7, 8 and 9 by adding a solution of 0.01 M HNO<sub>3</sub> and NaOH 0.01 M. A 10 mL phenol at various pH is contacted with 20 mg of adsorbent. Mixture shaked for 24 hours at room temperature. The mixture is then filtered through 42 Whatman filter paper and a Buchner funnel in order to separate between the filtrate and residue. Concentration of methyl orange which in the filtrate was analyzed by UV-Vis spectrophotometer.

### The effect of variation of contact time

The 20 mg of the adsorbent material is contacted with 10 mL of methyl orange 100 ppm on optimum pH. Mixture shaked with time variations of 15, 30, 60, 90, 120, 150 and 180 minutes. The mixture is then filtered through 42 Whatman filter paper and a Buchner funnel in order to separate between the filtrate and residue. Concentration of methyl orange which in the filtrate was analyzed by UV-Vis spectrophotometer.

## The Effect of Initial Concentration

A total of 10 mg of the adsorbent material is contacted with a solution of methyl orange with a concentration of 15, 30, 45, 60, 80 and 120 ppm were made at optimum pH. Mixture shaked for optimum time and then filtered using 42 Whatman filter paper and a Buchner funnel so

#### The 1<sup>st</sup> International Seminar on Chemical Education 2015 September, 30<sup>th</sup> 2015

that it can be separated between the filtrate and residue. Concentration of methyl orange which in the filtrate was analyzed by UV-Vis spectrophotometer.

## **Results and Discussion** The effect of pH

The results shows that adsorption concentration of methyl orange with natural materials in the rice husk ash increases in pH range 2-3. Surface area of rice husk ash contains divalent metal cations, such as  $Si^{2+}$  and trivalent metal cations such as  $AI^{3+}$ . Under acidic conditions, methyl orange dye tends to negatively charged due to the addition of  $H^+$  and it will bond with rice husk ash surface positively charged. The process of methyl orange dye adsorption on the surface of the rice husk ash material can be used to see changes in the amount of methyl orange dye that is absorbed in accordance with changes in pH.

The figure 1 shows that pH 4 to 7 adsorption decreases, this is because the amount of methyl orange dye adsorbed on the surface of the rice husk ash material decreases too. 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<sup>-</sup> ions in solution have competition between the dye methyl orange with OH<sup>-</sup> ions to occupy the rice husk ash. Physical characteristics of the adsorbent (surface and porosity) determine the area available for adsorption.

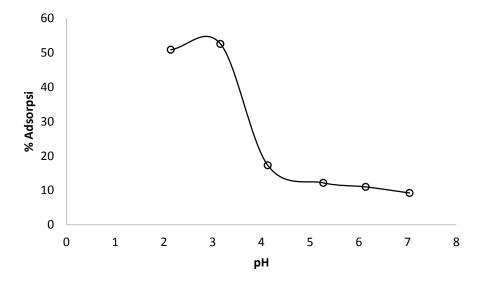


Figure 1 Effect of pH on removal methyl orang using rice husk ash

#### The 1<sup>st</sup> International Seminar on Chemical Education 2015 September, 30<sup>th</sup> 2015

### The effect of contact time

Based on the results of this experiment, the longer the contact time will be obtain the greater the adsorption capacity. The capacity adsorption of methyl orange in various contact time using rice husk ash will be expression in unit of mg/g. Figure 2 shows that the adsorption of methyl orange with rice husk ash on contact time of 1 to 3 hours there was an increase adsorption capacity significantly and reached equilibrium at the contact time of 7 hours. Based on these data, a model of adsorption kinetics can be searched by using the model of the first order, second order, pseudo first order and pseudo second order. Results of linear equations to plot a graph calculation kinetics model can be seen in Table 1.

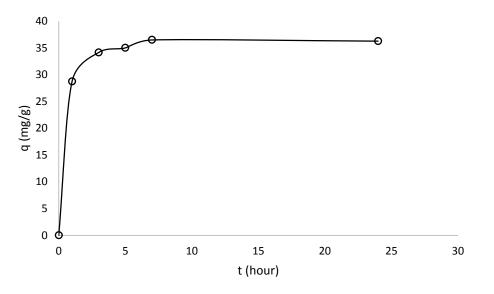


Figure 2 Effect of contact time on removal of methyl orange using rice husk ash

Kinetic Model	•	k	$\mathbf{R}^2$
1 <sup>st</sup> Order	min <sup>-1</sup>	$8.657 \cdot 10^{-1}$	0.866
2 <sup>nd</sup> Order	$\mathrm{m}\mathrm{M}^{-1}\mathrm{min}^{-1}$	2.268 10-1	0.876
Pseudo 1 <sup>st</sup> order	min <sup>-1</sup>	$4.125 \cdot 10^{-1}$	0.937
Pseudo 2 <sup>nd</sup> order	$\mathbf{m}\mathbf{M}^{-1}\mathbf{min}^{-1}$	$2.465 \cdot 10^{-2}$	0.999

Table 1 Kinetic models of methyl orange removal using rice husk ash

Table 1 shows that the adsorption of methyl orange using rice husk ash followed the pseudo second-order kinetic model showed with the highest coefficient of determination on the plot graphs of linear equations. A pseudo second order equation based on solid phase sorption.

#### The 1<sup>st</sup> International Seminar on Chemical Education 2015 September, 30<sup>th</sup> 2015

This model based on assumption that the rate limiting step may be exchange of electron between sorbent and sorbate.

### The effect of initial concentration

The result of initial concentration adsorbate on adsorption mecanism using rice husk ash will be seen in Figure 3.

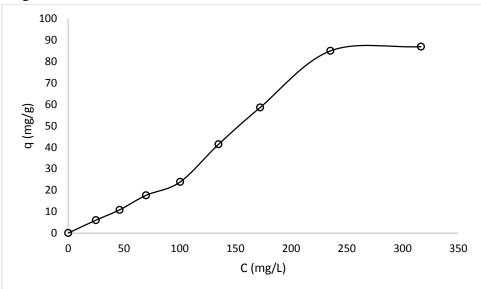


Figure 3 The effect of initial concentration on removal of methyl orange using rice husk ash

Figure 3 shows that capacity adsorption will be increases and linear with increases of initial concentration. The equilibrium of initial concentration of methyl orange reach in 230 mg/L. The data will be reported using Langmuir and Freundlich isoterm model.

Table 2 Isoterm Models Equation					
Isoterm	Nonlinear equation	Linear equation	Plot graph		
Langmuir	$q_{e} = \frac{q_{maks}K_{L}C_{e}}{1 + (K_{L}C_{e})}$	$\frac{C_{e}}{q_{e}} = \frac{1}{K_{L}q_{maks}} + \frac{C_{e}}{q_{maks}}$	$\frac{C_e}{q_e}$ vs $C_e$		
Freundlich	$q_e = K_F(C_e)^{1/n}$	$\log q_e = \log K_F + \frac{1}{n} \log C_e$	$\log q_e \ vs \ log \ C_e$		

Plot of linearized form of Langmuir and Freundlich isoterm model showed that removal of methyl orange in aqueous solution using rice hush ash fitted to Langmuir model than Freundlich model with maximum of capacity adsorption is 243.902 mg/g.

#### The 1<sup>st</sup> International Seminar on Chemical Education 2015 September, 30<sup>th</sup> 2015

### Conclutions

Removal of methyl orange on aqueous solution using rice husk ash effective occurred at pH 2 and optimum contact time of 7 hours. Adsorption of methyl orange in accordance with pseudo second order kinetic model and fitted on the Langmuir isotherm with the maximum adsorption capacity of 243.902 mg/g.

### Acknowledgements

The authors are thanksful for the funding by DPPM Universitas Islam Indonesia (UII) Yogyakarta.

## References

- Kodom, T.,Etsri A., Gbandi, dan Limam M.B., 2012, Photocatalytic Discoloration of Methyl Orange and Indigo Carmine on TiO2 (P25) Deposited on Conducting Substrates:Effect of H<sub>2</sub>O<sub>2</sub> and S<sub>2</sub>O<sub>8</sub><sup>2-</sup>, *J. Chemical Technology*, 4(2), 45-56.
- Kusumaningsih, T., Desi S.H., dan 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.
- Purbaningtias, T. E., Wiyantoko, B., Kurniawati, P., Wardhani, M. K., 2014, Pengaruh Jenis Adsorben dan Waktu Kontak Terhadap Penurunan Bilangan Asam Minyak Nilam, *Eksakta*, 14, 1, 67-76.
- Siriluk, C. dan 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.
- Wahab, O. A., Nemr, A. E., Sikaily, A.E., dan Khalded, A, 2005, Use of Rice Husk for Adsorption of Direct Dyes from Aqueous Solution: A case Study of Direct F. Scarlet, *Egyptian Journal of Aquatic Research*, 31, 2005.