Synthesis of silica of rice husk modification (3-aminopropyl) trietoxysilane for adsorption methylene blue

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Abstract. In this study, modified silica (3-Amynopropyl) triethoxysilane (APTES) synthesis and adsorption test of MB dye were performed. Silica is synthesized by sol-gel method and modified with APTES. APTES modified silica is characterized using several instruments, scanning electron microscopy (SEM), fourier transform infrared (FTIR), surface area analyzer (SAA) and UV-Vis spectrophotometer. The composite has a large surface area and has a mesoporous shape. At alkaline pH, MB dye can adsorb well. In addition, MB absorption is also maximized with the longer time of adsorption. The APTES modified silica adsorption process follows the Langmuir isotherm pattern. Thus, APTES modified silica can be used as an alternative to environmentally friendly and low-cost adsorbents.

1 Introduction

Environmental pollution is one of the problems facing the society lately. This pollution occurs in various types. Among them is, disposal of industrial waste into the aquatic environment [1]. In industrial waste contains compounds or elements that can endanger the biota and the environment around the water. Organic dyes are one of the compounds contained in industrial waste[2]. The nature of this organic dye is difficult to decompose by microorganisms because of its complex structure and difficult to separate from water [3]. One of the organic dyes is Methylene Blue. MB is a thiazine dye that can have harmful effects, such as can cause heart rate be quick, shock, nausea, vomiting and others [4-8]

Various studies have been conducted to reduce the pollution of substances organic colors in waters by chemical or physical methods. Among them are, coagulation / flocculation [9], membrane separation [10] and adsorption [11]. The method of adsorption is one method that can be done in reducing pollution in the aquatic environment. The adsorbent used should have pore size, pore distribution and surface area [12,13]. One of the adsorbents that can be used for adsorption of organic dyes is silica. Silica itself can be found in nature, such as in husks rice. Where rice husk contains silica as much as 87-97% dry weight [14]. The silica was synthesized using a sol-gel method then modified with an organic functional group aimed at enhancing the adsorption ability [15].

2 Methods

Rice husk that has become charcoal is burned to ashes. Rice husk ash is added with 6M HCl then refluxed. After reflux, the mixture is washed with DM aqua until it is lost of acidic properties. Then the mixture was added 1M NaOH and refluxed again. The result of reflux is filtered and washed with hot DM aqua, then filtrate of the filtered product with 1M HCl to form gel at neutral pH. The formed gel is washed with aqua DM to Cl-free. Gel that is free from Cl- is then dried. The formed silica was then suspended in toluene and added a silane (3-aminopropyl) triethoxysilane (APTES) and refluxed coupling agent [16].

Methylene Blue solution with a concentration of 10 ppm was prepared under pH conditions 3, 5, 7, 8 and 10. Then add modified silica APTES and shaken at 180 rpm for 30 minutes. Methylene Blue solution with 10 ppm concentration of APTES modified silica was then shaken at 180 rpm for 10, 20, 30, 40, 50, 60 min.

Methylene Blue solution was made with various concentrations of 30, 60, 90, 120 and 150 ppm at pH conditions and optimum contact time. Then APTES modified silica was then shaken at 180 rpm.

3 Results and discussion

Silica and silica-APTES that have been formed are then characterized using several instruments. In Fig. 1 is a morphological form of silica of synthesis and silica that has been modified using SEM (Scanning Electron Microscopy) instrument. From the figure it can be seen that at magnification 500 particle size of modified silica APTES 20 µm. Whereas silica has particle size 50 µm.

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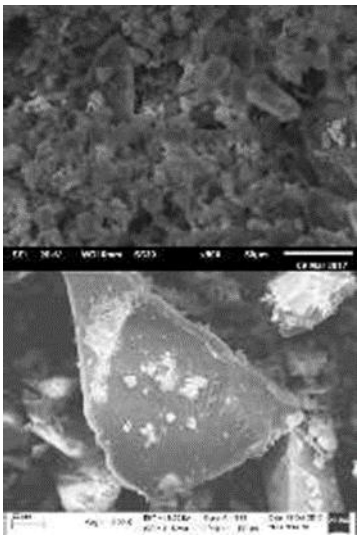

Fig. 1. SEM image silica and silica-APTES.

Based on fig.1, the APTES modified silica particle size is smaller than that of silica. In addition to its changing size, the silica-particles and silica-APTES are different. In silica the form of the particles is uniform while on the silica-APTES the particle shape is bulk and not uniform

In addition to morphology, the constituents in silica and silica-APTES also differ. This can be known through EDX instruments (Electron Dispersive X-Ray). In silica there are only Si and O elements, whereas in silica-APTES it is seen that new elements are increasing, ie N and C. The addition of these elements is assumed to be derived from APTES used.

Table 1. Silica and Silica-APTES Composition.

Element	Silica	Silica-APTES
	Mass (%)	
Silicon (Si)	44,85	27,44
Oxygen (O)	55,15	43,69
Nitrogen (N)	-	3,45
Carbon (C)	-	25,21

In addition to SEM-EDX, silica and silica-APTES instruments are also characterized using FTIR. The spectral form of silica and silica-APTES can be seen in Figure 2. The absorption bands at wavelengths 790.81 cm^{-1} and 968.27 cm^{-1} are vibrations of Si-O symmetric Si-O-Si and vibration of Si-O Si-O from Si -OH. While the strong absorption bands occur at a wavelength of 1091.71 cm^{-1} which is a symmetrical vibration of Si-O from Si-O-Si. The absorption bands at wavelengths of 1639.49 cm^{-1} and 3340.71 cm^{-1} are vibrations of Si-OH buckling and symmetrical vibration of OH-Si-OH.

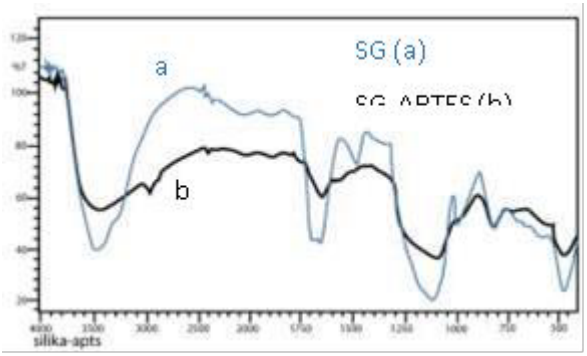

Fig. 2. FTIR Spectrum of silica and silica APTES.

The absorption bands at wavelengths 968.27 cm^{-1} as seen on silica, now on silica APTES already lost. This shows that silica-APTES does not contain Si-O from Si-OH. In addition, in silica-APTES a decrease of absorbing band 3423.65 cm^{-1} indicates secondary N-H bending vibration and the emergence of new bands at 2926.01 cm^{-1} indicates the presence of aliphatic chains due to vibration -CH2-so that APTES modified silica has been successfully established. Based on Fig. 3, the silica-silica-APTES adsorption-desorption and silica pattern follow type IV indicating that the pore shape is mesoporous. This mesoporous form is seen on the P / Po curve above 0.5.

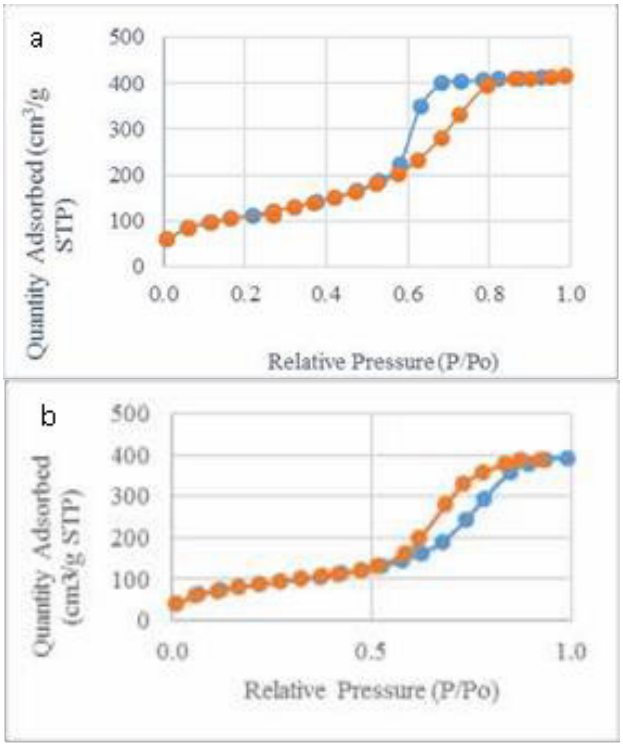

Fig. 3. BET Result of silica and silica APTES.

3.1 Adjustable silica adsorption test of APTES effect of pH

The pH value can affect the adsorption process. Where will the charge distribution occur on the adsorbent due to the reaction of protonation and deprotonation on the active adsorbent site. In figure 4 it can be seen that with

increasing pH, the absorption of MB dye will be greater. In the highest absorption silica occurs at pH 8 with an adsorption capacity of 5.688 mg / g as well as silica-APTES most absorption occurs at pH 8 also with an adsorption capacity of 5.815 mg / g. This is because the alkaline pH causes the hydroxyl group to increase and will attract the cluster N + on the MB compound.

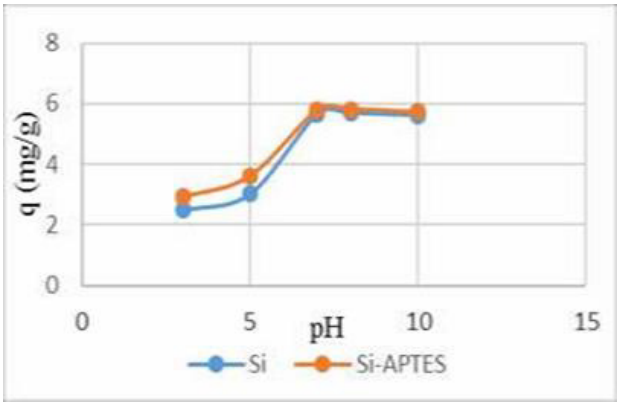

Fig. 4. Effect of initial pH value on the adsorption capacity.

3.2 Influence of contact time

The contact time may also affect the adsorption process. Where the longer the adsorption time the adsorption molecule absorption will last better until it reaches a stable state. Because the longer the adsorption molecule adsorption molecules will be maximally absorbed in the adsorbent so that the empty space in the adsorbent is fully charged.

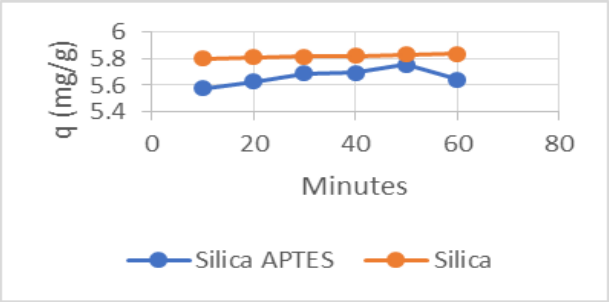

Fig. 5. Effect of contact time on MB removal.

In figure 5, it can be seen that silica and silica-APTES capabilities have a time difference in absorbing MB dye. In silica, 50 minutes is the maximum absorption with an adsorption capacity of 5.755 mg / g and at 60 minutes the capacity assumes that the adsorbent has a heterogeneous surface and each molecule has different absorption potentials. The formula in determining Freundlich isotherm is: adsorption down. mIt this because silica adsorbent is in saturation state or can no longer absorb MB dye while in silica-APTES the longer its adsorption capacity is 5,831 mg / g. This is because the increase of functional groups on silica-APTES causes silica-APTES to take longer to absorb MB dye until it reaches equilibrium.

3.3 Isotherm model

Isotherm Langmuir introduces the concept of monomolecular adsorption on a homogeneous surface. The adsorbent which is a Langmuir isotherm has a fixed place, absorbing one molecule and forming a monolayer. The formula used in determining the Langmuir isotherm is as follows:

$$\text{Log } qe = \text{Log KF} + n \text{ Log Ce} \quad (1)$$

Where qe is the amount of adsorbat adsorbed (mg / g), qm is the adsorbent capacity in adsorption, KF is Freundlich and Ce constant is the concentration of adsorbate (mg / L). Where qe is the amount of adsorbed adsorbated (mg / g), qm is the adsorbent capacity in adsorption, KL is Langmuir and Ce constant is the concentration of adsorbate (mg / L).

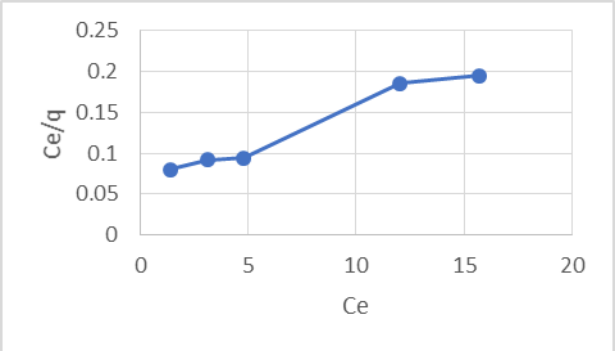

Fig. 6. Langmuir isotherm model.

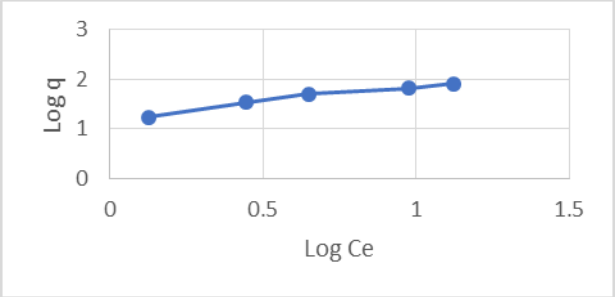

Fig. 7. Freundlich isotherm model.

Figure 6 is a graph of the Langmuir isotherm of silica-APTES. When Ce graphic is made to Ce / q it will give the equation of line y = 0.0078x +0.0614 with slope 0.0078 and intercept 0.0614 with correlation coefficient (R^2) equal to 0.9691.

Freundlich of silica-APTES. When created graph Log Ce to Log q it will give the equation line y = 0.6539x +1.2098 with slope 0.6539 and intercept 1.2098 with correlation coefficient (R^2) of 0.9595. Of the two isotherms models, the Langmuir isotherm has a correlation coefficient (R^2) which is close to 1 compared to the Freundlich isotherm. So it can be said that silica-APTES more follows the Langmuir isotherm pattern.

4 Conclusions

Based on the research done by APTES modified silica adsorption it is concluded that the APTES modified silica adsorbent has a large adsorption capacity when pH 8 and the longer the adsorption time. In addition, APTES-modified silica follows a langmuir isotherm pattern in which adsorption occurs chemically by forming a monolayer layer on the surface of the adsorbent.

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