Synthesis

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Synthesis of chitosan/alumina composite by sol gel method for adsorption of procion blue MX-R dye from wastewater songket industry

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Abstract. Research about the synthesis of chitosan/alumina composite using the sol-gel method and its application to removal procion blue MX-R dye had been conducted. The synthesized chitosan/alumina composite was characterized using FTIR to determine functional group, SEM-EDS to find out the surface morphology and elements composition of chitosan/alumina composite. The pH $_{PZC}$ is used to determine the appropriate pH condition on the adsorption process of chitosan and chitosan/alumina composite on procion blue dye solution. The FTIR spectra of chitosan represent the functional groups O-H, N-H, C-H and C-O while the chitosan/alumina composite is the addition of functional group of Al-O. The morphology of chitosan/alumina composite analysis by SEM showed that is heterogenous and porous. The EDX analysis showed that the present Al element of 5.49 % in the composite which indicates that synthesis of composite has been successful. Chitosan and composite have different pH pzc where chitosan at pH 6.02 and composite at pH 7.26. The optimum condition adsorption of procion blue MX-R using chitosan obtained at an initial concentration of 180 mg/L and contact time of 60 minutes, while the chitosan/alumina composite obtained at an initial concentration of 160 mg/L and 50 minutes contact time. The isotherm model that is suitable for describing the adsorption process is Freundlich isotherm for both adsorbents. The composite has the effectiveness of adsorption on procion blue MX-R from wastewater songket industry greater than chitosan ie 85.696 and 60.829 %, respectively.

1. Introduction

Songket industry is one of the textile industries that is characteristic of the Palembang city. The variety of songket motifs is the main attraction for people so the songket industry more developed. In the process of coloring the thread, synthetic dyes are used. One of the dyes used is procion blue MX-R. The increasing number of songket industries, the more wastewater produced containing dye. The procion blue has a molecular formula $C_{23}H_{14}Cl_2N_6O_8S_2$ and molecular weight is 637.4287 g/mol [1]. The procion blue MX-R are classified as reactive dyes. The presence of benzene groups in dyes causes these dyes to be difficult to degrade. The relative of toxicity procion blue MX-R dyes indicates that this dye is classified as acute toxicity (LC_{50}) to fish (1500 mg/L) a 24 h period [2].

The most of dyes are hazardous, can cause mutagenesis and carcinogenic [3]. In also, the presence of dyes in the waters inhibits photosynthesis and reduces the penetration of light and oxygen in water [4]. One method used to reduce dyes in water is adsorption process. This method is a relatively inexpensive and efficient technique better than other wastewater treatment techniques [3]. The adsorbent used in the adsorption process should be cheap, high sorption capacity and biodegradable. Chitosan is an adsorbent that is often used to removal pollutants such as metal ions and dyes. Biopolymers as adsorbents have the advantage of being biodegradable, biocompatible and nontoxic [5]. Chitosan is the product of chitin deacetylation that is a polymer of acetylamino-D-glucose. Chitosan can be used as an adsorbent because it has an amino (-NH_2) and a hydroxy (-OH) group which has the potential to attract dyes, metal ions [6-8]. Some authors have used chitosan to removal dyes in aqueous such as procion blue MR-X [1], reactive black 5 [7] and reactive yellow [6].

On aqueous media, chitosan is tended to agglomerate and forms a gel so that the ability of active groups to interact with dyes or metal ions is reduced [8]. Modification of chitosan can improve adsorption capacity [6](uzun) and reduce the tendency of agglomeration. Chitosan can be modified with other materials such as tannic acid [9], magnetic [10], cotton fiber [11] and aluminium hydroxide [12]. In this study, chitosan was modified with alumina by sol gel method. The chitosan/alumina composite used to removal procion blue MX-R from wastewater songket industry. The addition of alumina to the chitosan increase the active site of the adsorbent and mechanical properties [8]. Alumina has two active groups play a role in the adsorption process, including the Lewis acid sites (OH_2^+) and Bronsted Lowry site (OH^-) [13].

2. Material and methods

2.1. Material
The material used includes wastewater songket industry from Palembang city, South Sumatra. Chitosan from CV Bio Chitosan Indonesia (de-acetylation of 95.2 %), Al_2O_3, $NaNO_3$, NaOH, HCl from Merck, Procion blue MX-R (CAS Number 13324-20-4) from Sigma Aldrich and distilled water.

2.2. Synthesis of chitosan/alumina composites
About 5 g of chitosan added 100 mL of oxalic acid 10 % (w/v). The mixture is heated using a hot plate at a temperature of 55 ^oC, until it form a gel. Then, 25 g of chitosan gel was added 250 mL of 60 mL aqua distilled, and heated at a temperature of 40-50 ^oC for 15 minutes. After that, added 25 g of alumina and stirred at 250 rpm until homogenous (± 4 hours) and left for 2 hours. The precipitated was decanted, filtered, washed using distilled water and dried in an oven at 55 ^oC for 5 hours. The chitosan/alumina composites were identified by FTIR Shimadzu 5000 and SEM-EDX 6510-LA.

2.3. Determination of pH pzc
Each of the 11 erlenmeyer was added 50 mL of 0.01 M. $NaNO_3$ solution. Then, added of 0.1 M HCl or 0.1 M NaOH solution into each erlenmeyer to the pH range of each erlenmeyer 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, and 12. The composite (0.1 g) was added in the erlenmeyer and stirred for 2 hours using a shaker at 150 rpm. The mixture is left to stand for 2 days and the final pH is measured using a pH meter. The pH pzc is based on the point of intersection between the initial pH and the final pH curve.

2.4. Adsorption study

2.4.1. Effect of contact time. Procion blue MX-R dye solution (25 mL) with concentration of 50 mg/L added 0.1 g of chitosan/alumina composite. The mixture is stirred at 150 rpm with variations contact time for 1, 5, 20, 30, 40, 50, 60, and 120 minutes at pH 5. The solution was filtered and then the filtrate was measured using UV-Vis spectrophotometer (Genesis 20) at the maximum wavelength obtained was 670 nm.

2.4.2. Effect of initial concentration. A total of 25 mL procion blue MX-R with variations in concentrations of 80, 90, 100, 120, 140, 150, 160 and 180 mg/L added 0.1 g composite. The mixture was then stirred at 150 rpm during the optimum contact time. The solution was filtered and then the filtrate was measured by using a UV-Vis spectrophotometer.

2.5. Adsorption of procion blue MX-R in wastewater songket industry

The wastewater songket industry filtered from impurities. Then, 50 mL of wastewater was measured by the concentration of procion blue MX-R dyes by using spectrophotometer UV-Vis at 670 nm. Based on the optimum conditions obtained, chitosan/alumina composite was added in 50 mL of wastewater. The solution was analyzed using spectrophotometer UV-Vis. The efficiency of removal was determined.

3. Result and Discussion

3.1. Characteristic of chitosan/alumina composite

The formation of composite between chitosan and alumina using oxalic acid. The dicarboxylic group in oxalic acid as a bridge between chitosan and alumina [13]. One carboxylic group forms chelate with alumina while the other carboxylic group forms ionic bonds with the amine group on chitosan [14]. Oxalic acid can also hydrogen bonds with OH or NH_2 groups in chitosan.

Identification using FTIR spectroscopy to determine the presence of functional groups. Figure 1 is the FTIR spectra of chitosan and chitosan/alumina composite. The difference in absorption between chitosan and composites at wave number 740.6 cm^{-1} which is not present in chitosan. The wavelength is Al-O uptake. This proves that synthesis chitosan/alumina composite has successfully.

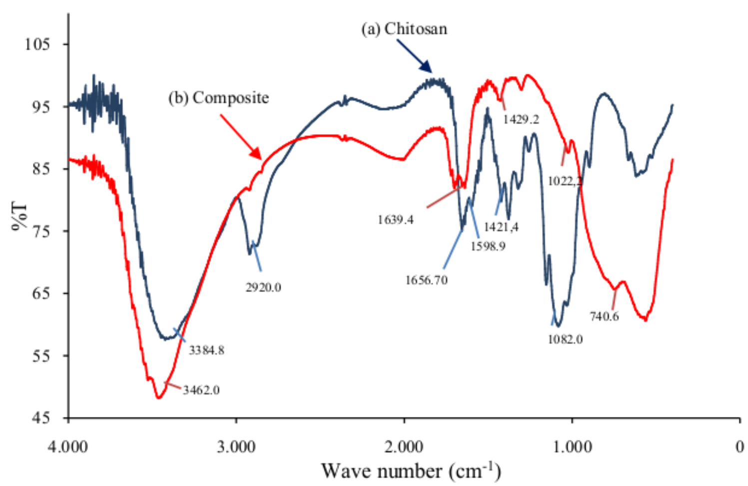

Figure 1. Spectra FITR of (a) chitosan and (b) chitosan/alumina composite

At wave number 3462.0 cm^{-1}, there is an O-H strain group on chitosan/alumina composites, while chitosan appears at wave number 3384.8 cm^{-1}. The C-H strain on chitosan/alumina composites was identified at wave number 2923.9 cm^{-1}, in chitosan appeared at wave number 2920.0 cm^{-1}. The wave number at 1656.7 cm^{-1} show C = O strain on chitosan. The strain function group of C=N appears on chitosan and chitosan/alumina composite at 1639.4 cm^{-1} and 1598.9 cm^{-1}, respectively. The functional groups of β (1-4) glucosamine in chitosan/alumina composite identified at 1022.2 cm^{-1} while in chitosan at 1082.0 cm^{-1}.

Figure 2 shows the morphological of chitosan and chitosan/alumina composite with a magnification of 30,000. It can be seen that chitosan has a fairly large and homogeneous whereas the composite has a porous surface which marks the attachment of alumina to the surface of chitosan. In table 2 present the element chitosan and chitosan/alumina composite. From the table shows the presence of Al in chitosan/alumina composite, increasing percentage O while the percentage C in chitosan decreases. This shows that a composite has been formed.

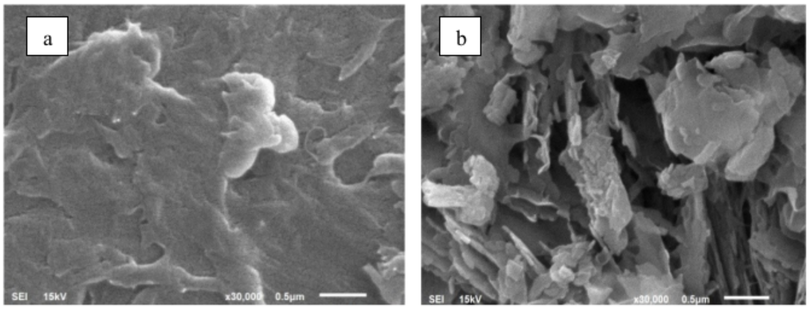

Figure 2. Morphology of (a) chitosan and (b) chitosan/alumina composite

Table 1. The element of chitosan and chitosan/alumina composite

Element	Percentage of mass (%)	
	Chitosan	Chitosan/alumina composite
O	32.8	54.12
Al	-	5.49
Si	-	10.10
K	-	2.53
N	21.14	16.16
C	41.60	10.20

3.2. Adsorption

The pH pzc (Point Zero Charge) is one of the important parameters in the adsorption process. pH affects the positive or negative adsorbent and adsorbate charge in the adsorption process. pH solution has affected the electrostatic charge of dye and surface change of adsorbent [15]. Figure 3 shows the pH pzc of chitosan and chitosan/alumina composite. Chitosan has a pH pzc of 6.02 while the composite is 7.26. At pH solution $<$ pH pzc, the adsorbent is positively charged while pH solution $>$ pH pzc is negatively charged. The procion blue MX-R is an anionic dye (negatively charged) so the adsorption process is effective at pH solution $<$ pH pzc. At acidic pH there is protonation of the amine group in chitosan so that it is positively charged (gnadhi et al, 2010). Procion blue MX-R are anion dyes (negatively charged) so that the adsorption process is more effective at pH $<$ pH pzc. Similar to other studies that optimum pH solution for removal procion blue MX-R by chitosan at pH 4 [1].

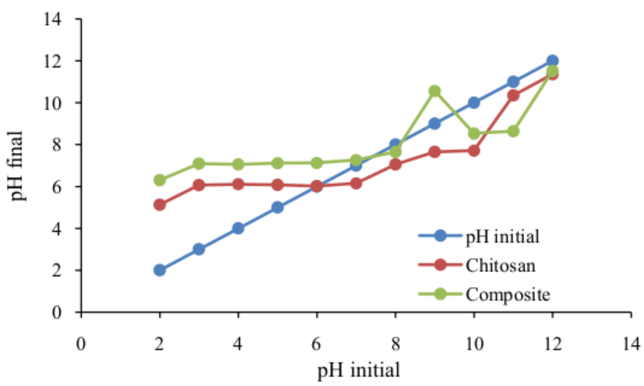

Figure 3. pH pzc of chitosan and chitosan/alumina composite

Determination of the contact time was carried out at a concentration of procion blue 100 mg/L with volume 100 mL, weight of adsorbent 0.1 g, stirring speed 150 rpm, and pH 5.89 (pH of procion blue MX-R in solution), and contact time variation (0, 5, 20, 30, 40, 50, 60, and 120 minutes). Figure 4 shows the effect of contact time on the amount of dye adsorbed by chitosan and composite. At the contact time of 50 minutes, the adsorption equilibrium between the composite and the dye was reached so that the addition of contact time did not affect the absorption. The optimum contact time for adsorption of procion blue dye onto chitosan was obtained at 60 minutes.

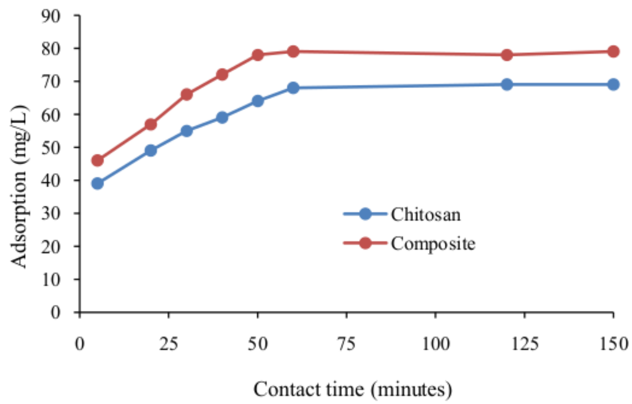

Figure 4. Effect of contact time on sorption of composite and chitosan to procion blue dye

Figure 5 shows the effect of dye concentration on the absorption of chitosan/alumina composite and chitosan. The adsorption process was carried out at contact time 50 minutes for composites and 60 minutes for chitosan with a weight of each adsorbent 0.1 g. We can see in the figure that the greater the concentration of the dye, the more dyes absorbed by the adsorbent. The amount of procion blue MX-R absorbed by composite is greater than chitosan. Addition of alumina causes the addition of active groups which can interact with the dye. Similar to another study [16] that increasing the concentration of dye (congo red) increases adsorption capacity by using bentonite and bentonite inserted organometallic. On the initial concentration of dye 180 mg/L and 200 mg/L amount of dye absorbed relative constant, the number of dyes is increasing while the number of adsorbents remains. The adsorption capacity of the composite in this condition is 30.228 mg/g greater than chitosan which is 28.307 mg/g.

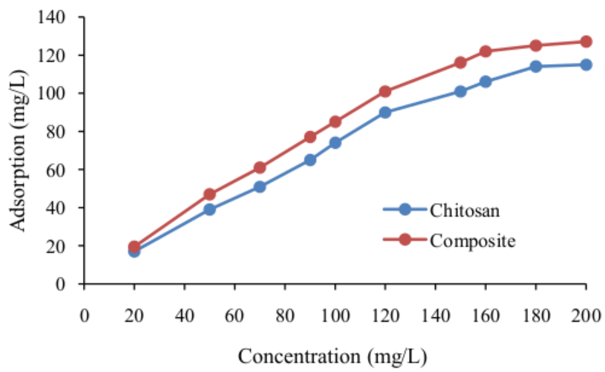

Figure 5. Effect of concentration procion blue dye on sorption of composite and chitosan

3.3. Isotherm Adsorption

The adsorption isotherm illustrates the surface characteristics of the adsorbent. The adsorption isotherm also illustrates how the molecular adsorbate is distributed in a liquid and solid phase state. In this study, Langmuir and Freundlich isotherm was used to determine the isotherm model that was suitable for adsorption of procion blue onto chitosan and chitosan/alumina composites. Langmuir isotherm, expressed in the following equation:

$$\frac{C_e}{q_e} = \frac{1}{q_{max}\, k_L} + \frac{1}{q_{max}} C_e \quad (1)$$

Where q_{max} is adsorption capacity (mg/g), k_L is Langmuir constants related to adsorption energy (L/g). If the plot between $\frac{C_e}{q_e}$ and C_e which is linear indicates suitability with Langmuir. The Freundlich isotherm equation is

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \quad (2)$$

Where q_e the amount of dye absorbed per unit weight of adsorbent (mg/g), k_f is Freundlich contantns and $\frac{1}{n}$ is the adsorption intensity. The adsorption isotherm corresponds to freundlich if it is linearly plotted between $\log q_e$ and $\log C_e$. Table 2 shows the isotherm values of adsorption of procion blue on chitosan and chitosan/alumina composites.

Table 2. The parameters of Langmuir, Freundlich isotherm

Isotherm	Parameters	Chitosan	Chitosan/alumina composite
Langmuir	q_{max} (mg/g)	28.35	32.50
	k_L (L/g)	0.0029	75.3
	R^2	0.928	0.955
Freundlich	$\frac{1}{n}$	0.843	0.482
	k_f (mg/g)	1.129	4.401
	R^2	0.959	0.971

Based on the value of R^2 which shows the relationship of linearity, the Freundlich adsorption isotherm is more suitable to describe the procion blue MX-R adsorption model on chitosan and chitosan/alumina composites. The R value of the Freundlich isotherm is greater than that of Langmuir. The value of $\frac{1}{n} < 1$ indicates the adsorption process is favourable. The adsorption capacity of chitosan which is 28.35 mg/g less than the composite chitosan/alumina is 32.50 mg/g.

3.4. Effectiveness of Adsorption

Chitosan and chitosan/alumina composites are used to removal of procion blue MX-R from wastewater songket industry. Table 3 shows the concentration of dyes before and after adsorption using chitosan and chitosan/alumina composites. The adsorption process is carried out at the optimum conditions that have been obtained. The effectiveness of adsorption using chitosan/alumina composites is greater than chitosan namely 85.696 and 60.829 %, respectively. This result is in accordance with the adsorption capacity where adsorption capacity of chitosan/alumina composite is greater than chitosan.

Table 3. Effectiveness of adsorption

Adsorbent	Concentration (mg/L)		The effectiveness of adsorption (%)
	Before	After	
Chitosan	68.0	26.636	60.829
Chitosan/alumina composite	68.0	9.727	85.696

4. Conclusion
Chitosan alumina composites have been successfully synthesized by sol gel method and applied to removal procion blue MX-R. The composite chitosan/alumina composite has the ability to removal procion blue MX-R is greater compared to chitosan. The appropriate adsorption model is Freundlich isotherm that the surface of the adsorbent is heterogeneous. The effectiveness of chitosan/alumina composite to removal of procion blue MX-R from waste water songket industry is greater compared chitosan ie 85.696 and 60.829 %, respectively.

Acknowledgements
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