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Synthesis of chitosan-SiO₂ composite for adsorption methyl dyes from solution

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Abstract. Synthesis of chitosan-SiO₂ composite has been done using the precipitation method. The chitosan-SiO₂ composite was applied to removal methyl red dyes from the solution. The chitosan-SiO₂ composite was characterized using Fourier Transform Infrared Spectroscopy (FT-IR), X-ray Diffraction (XRD), and Scanning Electron Microscopy/Energy Dispersive X-Ray Spectroscopy (SEM-EDS). Adsorption by batch method with variables including contact time, weight of adsorbent and initial concentration. The FT-IR spectrum of composite showed the -OH, C-H, C-N, N-H, C-O (ether), C-H asymmetric, C-H symmetric, Si-O-Si, Si-OH and Si-O group. XRD spectra of chitosan-SiO₂ composites showed a widening peak at $2\theta = 19.95$ and amorphous. From SEM-EDS spectra show the morphology of chitosan-SiO₂ composite was rough, porous and inhomogeneous with constituent elements C, N, O, Na and Si. The chitosan-SiO₂ composite has a pH_{pzc} value at pH 7.9. Adsorption data of chitosan-SiO₂ composite for adsorption methyl red dyes followed Langmuir isotherm with maximum adsorption capacity 20.876 mg/g. Adsorption methyl red dye onto chitosan-SiO₂ composites according to pseudo-second order.

Keywords: Chitosan, SiO₂, composite, adsorption, methyl red dye

1. Introduction

Disposal of dyes into the environment, reducing aesthetics, serious damage to biological organisms, human health and ecological [1-2]. The dyes used in the industry generally contain complex aromatic structures and are difficult to degrade such as benzene, toluene, xylene [3]. Industries that produce waste containing dyes such as textiles, printing, paint, plastic, cosmetics, paper, and food. The presence of dyes in the environment causes several problems, including reduced ability to re-oxygenate water, inhibit photosynthetic activity, cause an acute and toxic effect on humans [2]. Synthetic dyes have direct and indirect effects that are related to cancer, irritation, tumors, mutations, and allergies [4].

Various methods can be used to reduce waste containing dyes, for example, biological treatment, electrochemical, oxidation, photocatalytic degradation, ion exchange, coagulation, adsorption, and others. Some literature reports that the adsorption method is an effective, rapid, and inexpensive method for reducing dyes [5-6]. Several types of adsorbents from natural and synthetic materials can be used for the adsorption process. Chitosan is an ideal adsorbent and often used as an adsorbent, including biodegradable, non-toxic, biocompatibility, and bioactivity [7-8]. Chitosan can absorb heavy metal ions and dyes [5-7]. Chitosan has a molecular formula poly- β -(1 \rightarrow 4)-2-amino-2-deoxy-D-glucose. The



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functional groups of -OH and -NH₂ in chitosan is a role group in the adsorption process [9]. However, chitosan has limitations in its use, including dissolving in acid solution, low in chemical resistance, mechanical strength, and surface area [7].

Modifications of chitosan are to be required to increase adsorption capacity. Some researchers have developed several modifications of chitosan including fiber-chitosan [10], bentonite-chitosan [11], chitosan-montmorillonite [12], magnetic-chitosan [13], and cellulose-chitosan [7]. In this study, chitosan was modified with SiO₂ where SiO₂ coating on the surface of chitosan. SiO₂ is a material that has stability in acidic solutions, thermal stability, and resistance to microbes [14]. Chitosan-SiO₂ composites were applied to removal methyl red dyes from aqueous solution. Methyl red is an anionic dye with the molecular formula of (CH₃)₂NC₆H₄N=NC₆H₄CO₂H, and the molecular weight 269.30 g mol [15]. These dyes can irritate the eyes, skin, and respiratory tract when inhaled [16]. Besides that, methyl red dyes are considered mutagenic for living organisms in anaerobic conditions [17]. Therefore, reducing dyes in wastewater is very important before being discharged into the environment.

2. Material and Methods

2.1. Materials

The chemicals used include chitosan from CV Bio Chitosan, Indonesia (95.2 % deacetylation degree), SiO₂, NaOH, C₂H₅OH, NaNO₃, CH₃COOH and HCl from Merck, methyl red dyes from Sigma Aldrich.

2.2. Synthesis chitosan-SiO₂ composites

About 5 g of chitosan was dissolved in 100 mL of 1 M CH₃COOH and stirred using a magnetic stirrer at 150 rpm for 2 hours. Then, 2.5 g of SiO₂ was added to the chitosan solution and stirred for 1 hour until homogeneous. The mixture is stored for 8 hours. NaOH solution (15% in 95% ethanol) as much as 50 mL was added to the mixture using a dropper pipette while stirring using a magnetic stirrer. The mixture stored for 24 hours for composite formation. The composites were separated from the solution and washed with distilled water until pH ± 7. Then, composite dried in an oven at a temperature of 50°C. The composite is crushed and sieved with a size of 100 mesh. The composite of chitosan-SiO₂ powder was characterized using FT-IR (8201PC Shimadzu), XRD (Miniflex 600), and SEM-EDS (Jeol JSM-6335F).

2.3. Determination of pHPZC

Determination of pHPZC obtained by adding 0.2 g of the composite to 20 mL of the KNO₃ solution. The pH of the solution was adjusted from 2-11 by adding 0.1 M of HCl or NaOH solution. By the shaker, the mixture was stirred for 24 hours. Then the final pH is determined using a pH meter.

2.4. Adsorption experiment

The adsorption process was carried out by a batch experiment using a thermostatic shaker. 50 mL of 50 mg/L methyl red dye solution was added 0.05 g of the chitosan-SiO₂ composite. Effect of contact time obtained with variations in contact times of 20, 40, 60, 80, 100, and 120 minutes, stirred using a shaker at 150 rpm at room temperature. The concentration of filtrate was analyzed using a UV-Vis spectrophotometer at wavelength 524 nm (Genesys 10S). The effect of the weight of adsorbent was carried out by the same procedure as the variation in weight of 0.05, 0.10, 0.15, 0.20, 0.25, and 0.3 g. Variations in concentration were observed at initial concentrations of 25, 50, 75, 100, 125, and 150 mg/L. The adsorption ability chitosan-SiO₂ composite compared with chitosan.

3. Result and Discussion

3.1. Characteristic of chitosan-SiO₂ composite

Formation of silica on chitosan can occur through hydrogen bonds or Van der Waals. Chitosan has many hydroxyl groups which can form hydrogen bonds with silanol groups as a result of hydrolysis. Another bonding mechanism between silica and chitosan by electrostatic attraction of chitosan undergoes protonation in an amino group and a hydroxyl group dissociating of silica in solution [18]. The XRD

spectra of chitosan, SiO₂, and chitosan-SiO₂ composites are shown in Figure 1. The XRD spectra of chitosan-SiO₂ composites appear diffracted widened at $2\theta = 5$ to 55° , minor diffraction is detected at 10.32° and the highest peak at 20.72° .

These composite spectra appear to be a combination of SiO₂ and chitosan diffraction. This study is like other studies that chitosan-SiO₂ composites synthesized using ultrasonic batch have diffraction peaks at 10.4 and 23.6° [19]. A widening diffraction peak indicates amorphous silica. The highest peak at $2\theta = 22.52^\circ$. According to JCPDS No. 39-1425 that the silica has a peak at $2\theta = 22.003^\circ$. Amorphous silica is the most reactive and suitable to be applied as an adsorbent [20]. Chitosan also has a widening peak with a sharp peak at $2\theta = 20.321^\circ$ (JCPDS 39-1834). In this study obtained at 20.23° .

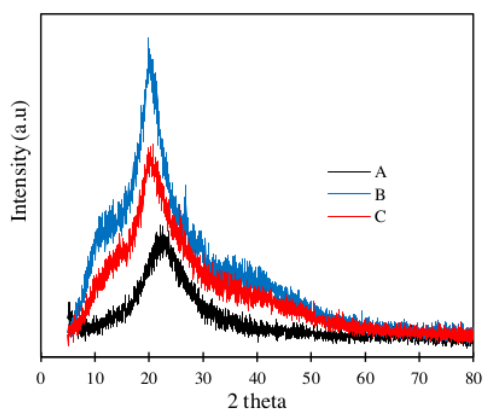


Figure 1. XRD pattern of (A)SiO₂ (B)chitosan (C)chitosan-SiO₂ composite.

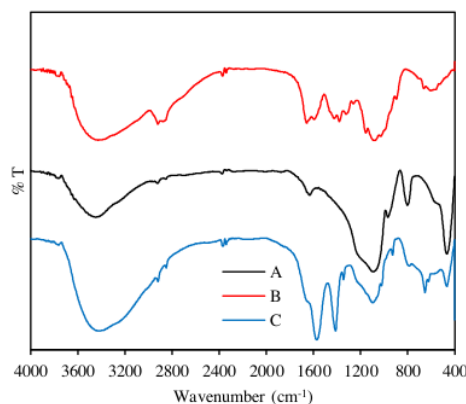


Figure 2. FT-IR spectra of (A)SiO₂ (B)chitosan (C)chitosan-SiO₂ composite.

FT-IR analysis was carried out in the wavenumber range 400 - 4000 cm^{-1} . FT-IR spectra of SiO₂, chitosan, and chitosan-SiO₂ composite displayed in Figure 2. Chitosan has a wide peak at 3421.51 cm^{-1} (overlap between O-H and N-H groups). The peak at 2877.79 cm^{-1} is C-H stretch. Amide groups can be observed at wavenumbers 1656.85 , 1595.13 and 1323.17 cm^{-1} , respectively. C-O stretch is detected at 1083.99 cm^{-1} . The characteristics SiO₂ peak are the hydroxyl O-H of the silanol group and water that appears at wavenumbers 3450.65 and 1631.78 cm^{-1} , Si-O groups at 1095.57 , 970.19 , 802.39 and 466.71 cm^{-1} which show Si-O stretching, Si-OH stretching, Si-O stretching and Si-O-Si bending. The peak in the composite is a combination of SiO₂ and chitosan. The wavenumber at 1413.82 and 1423.47 cm^{-1} shows the presence of C-H groups (asymmetric) on chitosan-SiO₂ composite and chitosan which are not present in SiO₂. This study shows that composite synthesis has been successful.

Figure 3 shows the morphology of chitosan and chitosan-SiO₂ composites. The composite surface appears heterogeneous and dense while the surface of chitosan is more homogeneous and porous. Table 1 indicates the different elements between chitosan and chitosan-SiO₂ composites from EDS data. The main components of chitosan and chitosan-SiO₂ composite are C, N, and O. In the composite, there is the addition of Si elements from SiO₂ (11.76%). The presence of Na on the composite from NaOH for synthesis has not disappeared.

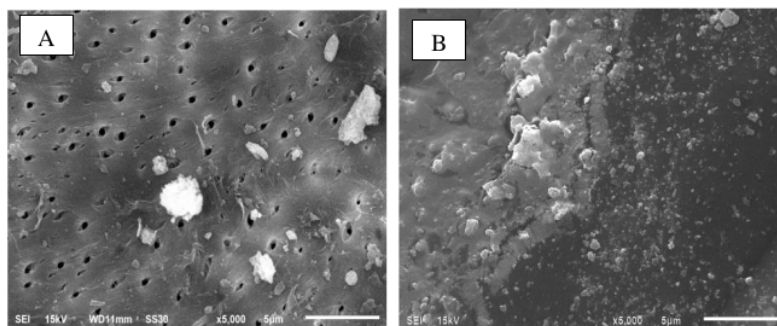


Figure 3. SEM image for (A)chitosan, (B)chitosan-SiO₂ composite.

Table 1. Elements of chitosan and chitosan-SiO₂ composites.

Elements (%)	Adsorbents	
	Chitosan	Chitosan-SiO ₂ composite
C	47.41	17.98
N	48.35	24.63
O	2.64	41.74
Si	-	11.76
Na	-	3.90
Ca	1.60	-

3.2. pH_{PZC} chitosan-SiO₂ composite

pH is one of the parameters that play a role in the adsorption process. The adsorption capacity is influenced by the pH of the solution, correspondent to the electrostatic pull between the adsorbate and the adsorbent. pH_{PZC} chitosan-SiO₂ composite was obtained 7.9 while chitosan at pH 7.7. pH_{PZC} of chitosan-SiO₂ composite and chitosan is shown in Figure 4. The pH of the solution < pH_{PZC} , the adsorbent is positively charged while the pH > pH_{PZC} , negatively charged of the adsorbent. Methyl red dye has pKa 5.1. The effectiveness of the adsorption process at the pH of the dye solution (± 5.1) where there is an electrostatic attraction between negatively charged methyl red dyes and positively charged chitosan or chitosan-SiO₂ composites. Other research, adsorption of methyl red dyes using activated carbon activated from custard apple shell using K₂CO₃, the optimum pH is 5 [15].

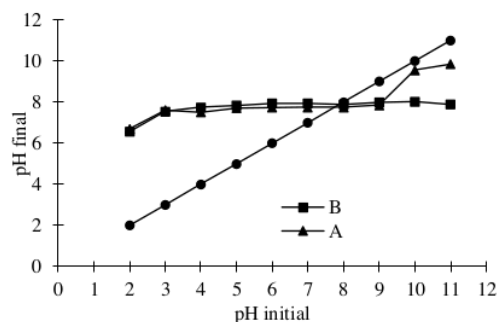


Figure 4. pH_{PZC} (A)chitosan and (B)chitosan-SiO₂ composite.

3.3. Adsorption study

In this study, three variables were used to study the adsorption process, including the effect of contact time, the weight of adsorbent, and the initial concentration of the dye. The effect of adsorption variables on the removal of dyes adsorbed by chitosan-SiO₂ composite and chitosan was illustrated in Figure 5. From Figure 5A, the adsorption equilibrium using chitosan-SiO₂ composites is faster than chitosan. Also, the amount of dyes removal by the composite is greater than chitosan. SiO₂ coating on the surface of chitosan causes the addition of active groups on the surface of chitosan so that more active sites to absorb dye. The adsorption equilibrium was obtained at 40 minutes using a chitosan-SiO₂ composite while chitosan was obtained at 100 minutes.

In Figure 5B, it can be seen that the % removal of methyl red dyes by chitosan, and chitosan-SiO₂ composites increase as the number of adsorbents increases. The increase in weight of the adsorbent is proportional to the increase in the availability of active sites. The limited amount of the dye causes the addition of the adsorbent to not affect the removal of dye. The adsorption capacity of the chitosan-SiO₂ composite is greater than chitosan, as shown in Figure 5C. The presence of SiO₂ in the composite adds to the active site, which can bind to the methyl red dye. Besides that, the addition of silica also improves the mechanical properties of chitosan [21].

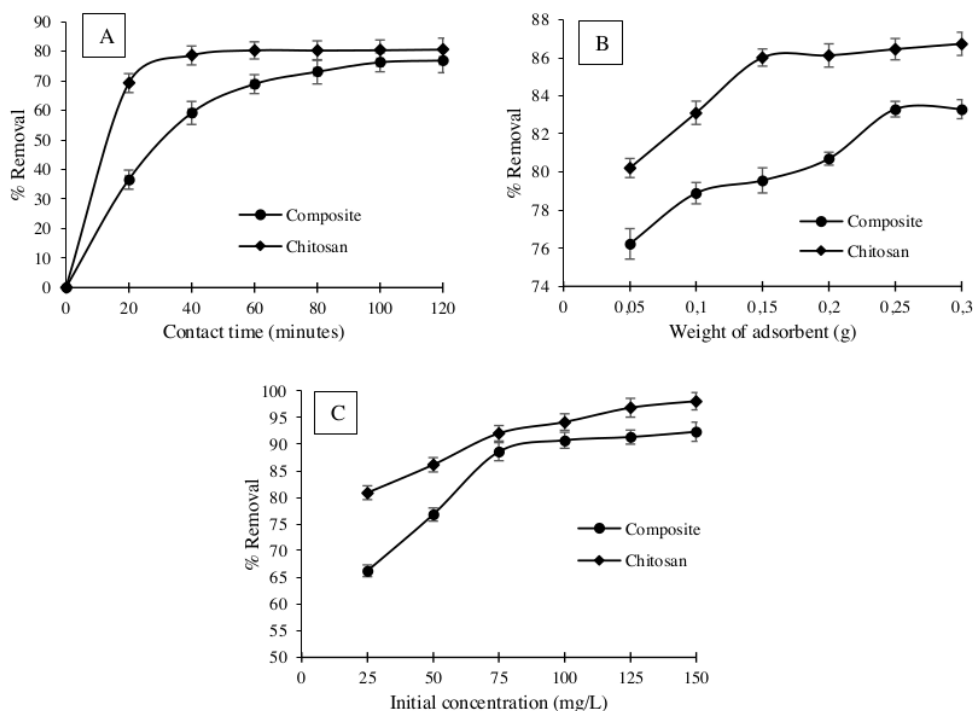


Figure 5. Sorption of methyl red dye onto chitosan and chitosan-SiO₂ composite (A)effect contact time (B)effect weight of adsorbent and (C)effect of initial concentration.

The adsorption isotherm is important to describe adsorbate and adsorbent interactions in solid-liquid adsorption [10]. In this study, adsorption isotherm used the Langmuir and Freundlich isotherm models. The Langmuir isotherm equation illustrates that the surface of adsorbent a monolayer and is homogeneous, whereas for Freundlich's isotherm [7]. The Langmuir and Freundlich equations are expressed in the following formula:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{1}$$

$$q_e = K_F C_e^{1/n} \tag{2}$$

Where q_e is the concentration of the dye at the equilibrium onto adsorbent (mg/g), C_e is the concentration of the dye in the solution (mg/L), q_m is adsorption capacity of adsorbent (mg/g), n is the value associated with the intensity of adsorption, K_L and K_F are the Langmuir (L/mg) and Freundlich (mg/g) constant, respectively. The parameters of adsorption isotherm are shown in Table 2. Suitability of isotherm can be identified from the value of the correlation coefficient (R^2) [22]. The R^2 value of Langmuir and Freundlich isotherm are 0.994 and 0.959, respectively. Therefore, isotherm Langmuir is more suitable for describing the adsorption process of methyl red dye onto chitosan and chitosan-SiO₂ composites. The value of n between 2-5 indicates that it is a favourable process.

Table 2. The Parameters of isotherm adsorption methyl red dye onto chitosan and composite.

Parameters	Langmuir isotherm		Parameters	Freundlich isotherm	
	Chitosan	Composite		Chitosan	Composite
R^2	0.994	0.991	R^2	0.939	0.959
q_m (mg/g)	10.234	20.876	n	2.345	3.213
K_L (L/mg)	1.870	1.349	K_F (mg/g)	2.410	4.782

Adsorption kinetics can be used to describe the adsorption mechanism. The adsorption kinetics depends affected by the chemical or physical characteristics of adsorption. Pseudo-first order and pseudo-second order are often used, kinetics models. The first-order, and second-order are the following:

$$\log(q_e - q) = \log q_e - \frac{k_1}{2.303} t \tag{3}$$

$$\frac{t}{q_e} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{4}$$

Where q_e and q are the amount of dyes absorbed at the equilibrium and time (mg/g), k_1 and k_2 are constant in pseudo-first order and pseudo-second order. Adsorption kinetics data are shown in Table 3. The adsorption of methyl red dye on chitosan and chitosan-SiO₂ composites is more appropriately described using the pseudo-second order based on the value of R^2 . Another study reported that adsorption of methyl red onto banana pseudo-stem fibers and MnFe₂O₄-activated carbon composites and followed a pseudo-second order [22-23].

Table 3. The Parameters of kinetic adsorption methyl red dye onto chitosan and composite.

Parameters	Pseudo-first order		Parameters	Pseudo-second order	
	Chitosan	Composite		Chitosan	Composite
R^2	0.893	0.903	R^2	0.936	0.992
k_1 (min ⁻¹)	0.055	0.072	k_2 (g/mg.min)	0.0025	0.0031
q_1 (mg/g)	8.982	13.421	q_2 (mg/g)	4.112	7.819

4. Conclusions

In this study, chitosan-SiO₂ composite by precipitation method was successfully synthesized. The chitosan-SiO₂ composite has a greater adsorption capacity to methyl red dyes than chitosan. Isotherm Langmuir is more suitable for describing adsorption methyl red dye onto chitosan-SiO₂ composites with adsorption capacity 20.876 mg/g. Kinetic studies show that adsorption was in accordance the pseudo-second order. The adsorbents can be used as an option to removing methyl red dye from the solution.

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