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SYNTHESIS OF CHITOSAN-GRAPHENE OXIDE (GO) COMPOSITE USING THE SOL-GEL METHOD AND ITS APPLICATION IN THE ADSORPTION OF METHYLENE BLUE DYE

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ABSTRACT

Synthesis of chitosan-GO composites using the sol-gel method and its application to methylene blue adsorption has been carried out. This study aims to determine the ability of chitosan-GO composites to adsorb methylene blue. Chitosan-GO composites were made with mass ratios (1:1), (1:3), and (1:5) and characterized by XRD. Material with a ratio (1:1) was chosen to be characterized using BET, SEM-EDS, and used as methylene blue adsorption. Methylene blue adsorption process with several variables including contact time, concentration, and temperature of methylene blue dye. The results of the XRD characterization of the chitosan-GO composite (1:1), (1:3), and (1:5) showed a diffraction peak at an angle of 2θ, namely 25.1°; 26.29° and 19.54°. The surface area of the chitosan-GO composite (1:1) with BET was 145.3505 m2/g. Characterization using SEM showed that the chitosan-GO (1:1) composite had a porous structure and was not homogeneous. Optimum conditions for the adsorption of the chitosan-GO composite on methylene blue were obtained at 50 minutes contact time, concentration of 60 ppm, and at 50°C. The adsorption process of the chitosan-GO composite on methylene blue followed the Freundlich adsorption isotherm with an adsorption capacity of 2.47 mg/g.

Keywords: graphene oxide, chitosan, composite, adsorption, methylene blue, synthesis.

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INTRODUCTION

Dye is known to play an important role in the textile industry of the community. Synthetic dyes are prevalently used, and the resulting waste generated during the procedures presents an environmental issue. Approximately 15% of the textile industry waste is released into the environment, where these residual materials act as contaminants due to their inherent resistance to degradation. Furthermore, one of the most frequently used synthetic dyes in the textile industry is methylene blue (Fajarwati *et al*., 2015), which is an organic compound with the molecular formula $C_{16}H_{18}N_3SCl$ (Fajarwati *et al*., 2015). It is a water-soluble cationic compound with extensive applications in chemistry, biology, processing sciences, and dyeing industries (Riwayati *et al*., 2019). The improper disposal of methylene blue into the environment can lead to damage and harm to humans and other living organisms (Jia *et al*., 2017).

Dye waste can be treated through biological, physical, and chemical methods such as adsorption, biosorption, coagulation, advanced oxidation, ozonation, membrane filtration, and liquid-liquid extraction. Additionally, adsorption is the most commonly used method, effective in removing and reducing water pollutant contaminants (Zhu *et al*., 2020). The method includes the interaction between the analyte or adsorbate as well as the surface of a solid substance or adsorbent.

Chitosan is a deacetylated form of chitin and is the second most important biopolymer compound after cellulose. This is a white, amorphous solid with a fixed crystal structure compared to the initial chitin structure. Moreover, it has shorter chains than chitin, which can be processed and used as an absorbent material. Graphene oxide (GO) can also be used as an adsorbent (Sugiyo *et al*., 2016) and it is a two-dimensional layer of carbon atoms bonded with oxygen, such as carboxyl groups (C=O), produced through chemical oxidation processes. GO is an organic material widely used for various applications due to its excellent properties and mechanics (Taufantri *et al*., 2016). The most common method for synthesizing GO is the modified Hummers, which is cost-effective and suitable for mass production with minimal chemical requirements (Tewatia *et al*., 2020).

Composite materials include combining two or more materials to create properties superior to the original. These properties may include the ability to absorb certain compounds and magnetic properties (Zhu *et al*., 2020). In this study, a composite of chitosan and GO is synthesized using the sol-gel method to produce compounds with a high degree of purity (Liza *et al*., 2016). GO used in the composite is synthesized through the modified Hummers method and characterized using X-ray diffraction (XRD).

The chitosan-GO composite is characterized using XRD, Brunauer Emmett Teller (BET), and Scanning Electron Microscopy Energy Dispersive X-ray spectroscopy (SEM-EDS). Subsequently, the synthesized composite is used to adsorb methylene blue dye with variations in contact time, methylene blue concentration, and temperature.

METHODOLOGY

Material

The equipment used in this study are beakers, burettes, Buchner funnels, erlenmeyer flasks, a furnace, a hotplate, 50 mL volumetric flasks, 100 mL volumetric flasks, a magnetic stirrer, an analytical balance, an oven, a pH indicator, pH meter, vacuum pump, spatula, UV-Vis spectrophotometer brand Orin Aquamate 8000, Brunauer Emmett Teller (BET) brand Micromeritics Tristar type II Plus, Scanning Electron Microscope (SEM) brand FEI type Inspect-S5008.28 and X-Ray Diffraction (XRD) brand PANalytical.

The materials include deionized water, deionized acetone, glacial acetic acid (CH_3COOH), sulfuric acid (H_2SO_4), ice, hydrogen peroxide (H_2O_2), potassium permanganate ($KMnO_4$), filter paper, chitosan, graphite powder, and methylene blue.

Synthesis of Graphene Oxide (GO) (Akhavan et al., 2014)

A total of 1 gram of graphite is placed in a 500 mL beaker and 50 mL of H_2SO_4 is added. The mixture is stirred at 500 rpm using a magnetic stirrer at 80°C for 24 hours. Furthermore, 1 gram of NaNO3 is added to the solution while stirring in a water bath for 1 hour. The slow addition of 6 grams of $KMnO_4$ to the solution is conducted over 4 hours and stirred using a magnetic stirrer. The mixture is heated to room temperature while continuously stirring in the water bath at 35°C for 1 hour.

The prepared solution is diluted with deionized or distilled water, and the solution temperature must be maintained below 60°C during dilution. After 15 minutes, 6 mL of H_2O_2 (30%) diluted with 100 mL of deionized acetone is added to the solution, and centrifuged 10 times at 8000 rpm for 30 minutes. The solution is filtered two to five times while washing with deionized water to obtain a yellow-brown suspension solution. Subsequently, the aqueous suspension is centrifuged at 2000 rpm for 30 minutes and 8000 rpm for 1 hour. The suspension is ultrasonicated for 30 minutes at a frequency of 40 kHz and a power of 150 watts before filtering to dryness to obtain a solid. Finally, the GO solid is dried in an oven at 60°C for approximately 5 hours and the synthesized product is characterized using XRD.

Synthesis of Chitosan-GO Composite (Zhu *et al.*, 2020)

A total of 1 gram of chitosan is dissolved in 100 mL of glacial acetic acid and stirred for 1 hour without heating. Furthermore, 1 gram of GO is dissolved in 100 mL of deionized acetone and mixed with the chitosan solution previously dissolved in acetic acid. Subsequently, the mixture is stirred for 1 hour and filtered using a vacuum pump. The obtained solution is calcined in a furnace at 600°C for 1 hour to obtain a brownish powder and the same process is repeated for ratios of 1:1, 1:3, and 1:5.

Effect of Contact Time

A total of 15 mL of methylene blue solution with a concentration of 20 ppm is placed in an Erlenmeyer flask, and 0.05 g of chitosan-GO composite is added. The mixture is stirred at 200 rpm with various contact times of 10, 20, 30, 40, 50, and 60 minutes. Furthermore, it is analyzed using a UV-Vis spectrophotometer with a wavelength of 664 nm.

Effect of Concentration

A total of 15 mL of methylene blue solution with concentrations of 20, 30, 40, 50, and 60 ppm is placed in a 100 mL Erlenmeyer flask, and 0.05 g of chitosan-GO composite is added. The obtained mixture is stirred at 200 rpm and analyzed using a spectrophotometer at a wavelength of 664 nm.

Effect of Temperature

A total of 15 mL of methylene blue is added to a 100 mL Erlenmeyer flask, and the initial pH is measured. Similarly, 0.05 g of chitosan-GO composite is added with varying temperatures of 20, 30, 40, 50, 60, and 70°C. The mixture is stirred at 200 rpm and analyzed using a UV-Vis spectrophotometer with a wavelength of 664 nm.

Adsorption Isotherm Model Equations

The commonly used adsorption isotherm models are the Langmuir and Freundlich isotherms to determine the adsorption isotherm model on the adsorbent, as shown below:

$$qe = qm.KL\frac{ce}{1+KL.Ce} \quad \text{..... (1)}$$

These equations can be linearized as:

$$\frac{ce}{qe} = \frac{1}{qm.KL} + \frac{1}{qm} \quad \text{..... (2)}$$

Where qm is the maximum adsorption capacity (mg/g), and K_L is the Langmuir adsorption constant (L/mg). Therefore, the values of qm and K_L are obtained from the intersection and slope of the linear plot between Ce/Qe and Ce.

$$Q = K_F.Ce^{1/2} \quad \text{……..…… (3)}$$

These equations can be linearized as:

$$\text{Log } Q = \log K_F + 1/n \log Ce \quad \text{……..... (4)}$$

Where Ce represents the equilibrium concentration of the adsorbate in the solution after adsorption (mg/L), K_F is the Freundlich adsorption constant, n is the empirical constant, and Q is the amount of adsorbate adsorbed per unit weight of adsorbent (mg/g).

Material Characterization

XRD characterization was performed on GO, chitosan, and the synthesized composite. The results were compared with the previous study. The chitosan-GO composite with a mass ratio that exhibited similar diffraction peak patterns to the previous study was further characterized using SEM-EDS, and its surface area was determined using BET. The best-characterized sample was used for the adsorption of methylene blue dye by measuring absorbance values using a UV-Vis spectrophotometer.

RESULTS AND DISCUSSIONS

Characterization of GO and Chitosan by XRD

XRD characterization is conducted to observe diffraction angles, peak intensities, and crystal phases obtained from the synthesis of GO and chitosan, as shown in Figure-1.

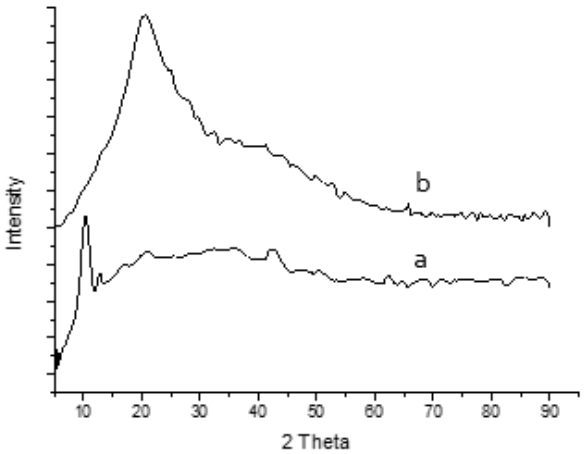

Figure-1. Diffractograms of (a) GO and (b) Chitosan.

In Figure-1(a), the XRD characterization results of GO show diffraction peaks at 28 = 10.12°, which is consistent with the study conducted by Gong *et al* (2018) where the peak is around 2Θ = 10°. This indicates that the synthesized GO has a crystalline solid structure, as shown by the sharp peak in the XRD diffractogram at 2Θ = 10.12°.

Furthermore, the interlayer spacing of GO is increased with a d-spacing of 0.874 and a WHM of 0.118, showing that GO has been successfully synthesized through an oxidation process, as indicated by a sharp peak in the XRD diffractogram. Additionally, the crystal size produced by the synthesized GO is 6.27 nm using the Debye-Scherrer equation.

Figure-1(b) shows the diffractogram results of chitosan. Based on the figure, a peak angle of 2Θ = 19.72° is obtained with a d-spacing of 0.450 and FWHM of 0.87, resulting in a crystal size of 0.90 nm. According to Kumar and Koh (2012), the chitosan peak angle is around 2Θ = 20.3°. The diffractogram results indicate that chitosan forms an amorphous or irregular solid phase, while the synthesized GO has a crystalline solid structure, as shown by the peak angle in the XRD diffractogram at 2Θ = 10.12°.

Characterization of Chitosan-GO Composite with Ratios 1:1, 1:3, and 1:5 by XRD

XRD characterization results for the synthesized chitosan-GO composite with varying mass ratios of 1:1, 1:3, and 1:5 are obtained to observe the shift in the diffraction angle (2Θ), as shown in Figure-2.

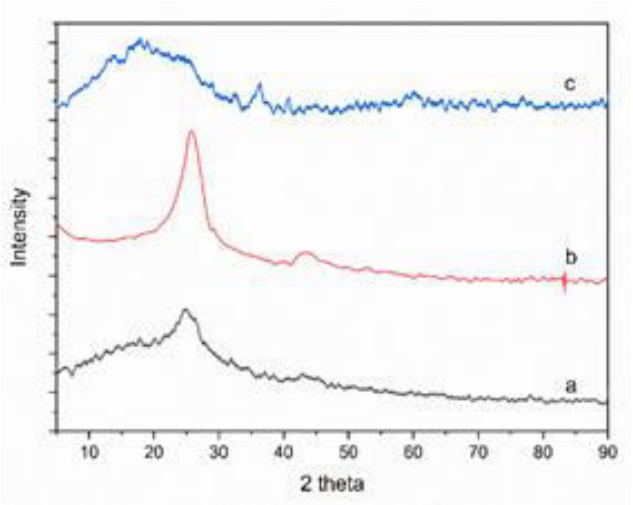

Figure-2. Diffractograms of (a) Chitosan-GO (1:1), (b) Chitosan-GO (1:3), and (c) Chitosan-GO (1:5).

Figure-2(a) is the diffractogram results of the chitosan-GO composite with a ratio of 1:1, showing a peak at an angle of 2Θ = 25.1° with a d-spacing of 0.353 and an FWHM of 0.10. The crystal size produced by the chitosan-GO composite with a ratio of 1:1 is 0.00174.

Figure-2(b) shows the diffractogram results of the chitosan-GO composite with a mass ratio of 1:3, indicating a peak angle of 2Θ = 26.29° with a d-spacing of 0.338 and an FWHM of 0.34, resulting in a crystal size of 2.28 nm. Figure (c) shows the diffractogram results with a mass ratio of 1:5, indicating a peak angle of 2Θ = 19.54 with a d-spacing of 0.455 and an FWHM of 0.83, resulting in a crystal size of 1.02 nm.

The chitosan-GO composite with different ratios shows varying diffraction peak angles. The ratios of (1:1), (1:3), and (1:5) have a peak angle of 2Θ = 25.1°, 2Θ = 26.29°, and 2Θ = 19.54, respectively. The chitosan-GO composite with a ratio of (1:5) has a lower peak angle than the ratios (1:1) and (1:3). This is due to the high temperature (600°C) used during the calcination process, which caused the chitosan to degrade before the addition of aluminum foil during high-temperature calcination, resulting in material contamination.

The diffractogram for the chitosan-GO composite at a 1:1 ratio shows that the peak at an angle of 2Θ = 10.12° and 2Θ = 19.72° indicates the presence of GO and chitosan. In Figure-2, increasing the amount of GO in the composite leads to a shift in the diffraction angle. According to Weizhu *et al*. (2020), the diffractogram

angle is 2Θ = 24°, which can be compared to all ratio peaks closest to 2Θ = 25.1°.

Characterization of the Chitosan-GO Composite with BET

BET characterization of the chitosan-GO composite was carried out to determine the surface area, which is essential for the adsorption process and affects the results. According to Alimano and Mindriany (2014), adsorption is influenced by the surface area. The larger the surface area of an adsorbent, the greater the adsorption capacity. Therefore, the chitosan-GO composite at a 1:1 ratio has a surface area of 145.35 m²/g, suggesting a relatively large surface area.

Characterization of the Chitosan-GO Composite with SEM-EDS

SEM-EDS characterization was conducted to observe the morphological shape of chitosan and the chitosan-GO composite with a 1:1 ratio, as shown in Figure-3.

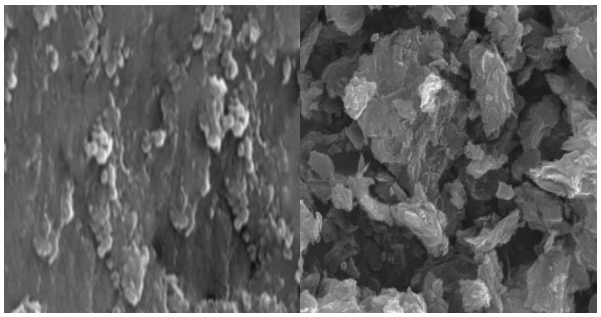

Figure-3. SEM Morphology (a). Chitosan and (b). Chitosan-GO.

According to Leidya (2020), chitosan has a flake or sheet-like shape with a wavy surface and large particle size and interparticle cavities. However, 3(b) shows the morphology of the chitosan-GO composite, indicating a porous and non-homogeneous structure. EDS analysis is performed to determine the elemental composition, as shown in Table-1.

Table-1. Composition of elements in Chitosan and Chitosan-GO composite (% mass).

Material	Element (% massa)			
	C	O	Na	S
Chitosan	53,00	38,64	2,64	1,59
Chitosan-GO	90,8	8,5	0,5	0,1

According to Table-1, the elements present in the composite include carbon (C) and oxygen (O) at 90.8% and 0.8%. Therefore, the chitosan-GO composite was successfully synthesized, as evidenced by the addition of carbon (C) and the reduction of oxygen (O) composition. Meanwhile, nitrogen (N) does not appear in the chitosan-GO composite due to the high calcination temperature, which leads to the degradation of the chitosan.

Effect of Contact Time

The effect of contact time during methylene blue adsorption aims to determine the optimum time with variations of 10, 20, 30, 40, 50, and 60 minutes. The material used is the chitosan-GO composite with a mass of 0.05 g and the graph depicting the influence of contact time on adsorption capacity can be seen in Figure-4.

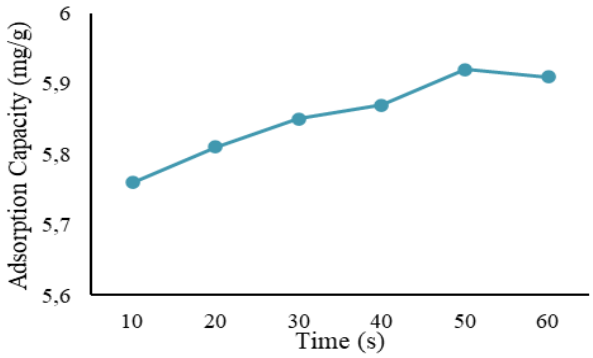

Figure-4. Effect of contact time on adsorption capacity.

Based on Figure-4 above, the adsorption of methylene blue with contact times of 10, 20, 30, and 40 minutes increases. This is because at the beginning of adsorption, all pore surfaces are still empty, and dye molecules adhere and form a layer on the surface, resulting in a faster rate. The optimum adsorption of methylene blue occurs at 50 minutes, with a capacity of 5.92 mg/g and an efficiency of 98.66%. After exceeding 50 minutes, there is a decrease in adsorption capacity. According to Kuntari (2017), the decrease after the optimum time is because the system has achieved equilibrium conditions, and the extension does not increase the percentage. Additionally, when the optimum time is reached, all dye molecules have been adsorbed by the adsorbent.

Effect of Concentration Variation

The effect of concentration on methylene blue adsorption was studied with variations of 20, 30, 40, 50, and 60 ppm, and the material used is the chitosan-GO composite with 0.05 g. The influence of concentration variation was conducted to determine the adsorbed concentration of the dye, as shown in Figure-5.

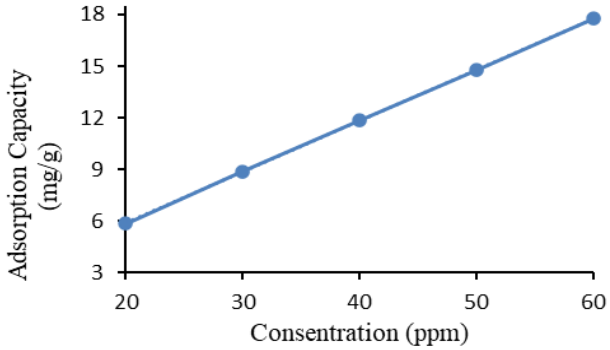

Figure-5. Effect of concentration on adsorption capacity.

Based on Figure-5, the curve shows that the adsorption of methylene blue increases with the concentrations used. The adsorption capacity also increases when the initial concentration is increased from 20 ppm to 60 ppm. According to Zein *et al.* (2019), adsorption capacity increases with the concentration of the dye due to increased electrostatic interactions between active sites on the adsorbent surface and the dye molecules. The optimum adsorption capacity occurs at a concentration of 60 ppm, with an adsorption capacity of 17.41 mg/g. Rahayu *et al*. (2021) stated that concentration was directly proportional to adsorption capacity. This is because the number of methylene blue ions bound to the active sites of chitosan-GO adsorbent increases. The adsorbed ions are proportional to the number of active sites available on the adsorbent.

Effect of Temperature

The effect of temperature on methylene blue adsorption was investigated at various temperatures of 20, 30, 40, 50, 60, and 70°C using 0.05 g of the chitosan-GO composite. Temperature variation tests aim to observe the decrease in adsorption capacity with the chitosan-GO composite and the occurrence of decreased adsorption capacity. Furthermore, the composite adsorbing methylene blue occurs at an optimum temperature of 50°C with a capacity of 5.97 mg/g and an efficiency of 99.56%, as shown in Figure-6.

According to Pari (2004), the increase in temperature is directly proportional to the adsorption of methylene blue. This is because there is a shift in the adsorbed particles, which pushes the dye out of the solution when adsorbed. Meanwhile, the adsorption ability may decrease after reaching the optimum temperature. The adsorption capacity decreases as the temperature increases.

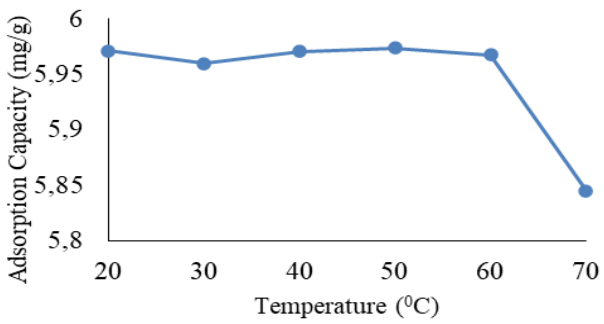

Figure-6. Effect of Temperature on Adsorption Capacity.

Adsorption isotherm models

The adsorption process is expressed using the Langmuir and Freundlich adsorption isotherm equations, as shown in Table-2.

Table-2. Adsorption isotherm parameter data for Chitosan-GO composite adsorption of methylene blue.

Isoterm Models	Parameter	Chitosan-GO Composite
Langmuir	qm (mg/g)	17.241
	K_L (L/mg)	1.331
	R^2	0,374
Freundlich	K_F (mg/g)	2.471
	1/n	3.428
	R^2	0.716

Table-2 shows the results of the two adsorption isotherm models. The Langmuir isotherm obtained the coefficient of correlation (R) value, while the Freundlich isotherm resulted in a correlation coefficient (R) value of 0.7106 and an adsorption capacity of 2.47 mg/g. Therefore, the adsorption of methylene blue by the chitosan-GO adsorbent followed the Freundlich isotherm, which obtains a higher correlation coefficient (R) value. The Langmuir and Freundlich isotherms suggest that monolayer and multilayer adsorptions occur on homogeneous and heterogeneous adsorbent surfaces, respectively (Maylani et al., 2016)

CONCLUSIONS

In conclusion, the chitosan-GO composite with ratios of 1:1, 1:3, and 1:5 were successfully synthesized. XRD characterization results showed that the 1:1, 1:3, and 1:5 ratios obtained a diffractogram peak at 2Θ=25.14°, 2Θ=26.29°, and 2Θ=19.54°, respectively. The chitosan-GO composite had a surface area of 145.3505 m/g and the morphology had smaller and non-homogeneous particles. Furthermore, the ability to adsorb methylene blue occurred at a contact time of 50 minutes, with a maximum concentration of 60 mg/L and a temperature of 50°C. The

adsorption process of the chitosan-GO composite followed the Freundlich isotherm with a capacity of 2.47 mg/g.

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