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Study of Congo Red Adsorption by Chitosan-Graphene Oxide (Chitosan-GO) Composite Synthesize with Hydrothermal Synthetic Method: Optimization and Determination Condition

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Abstract

This research aims to synthesize chitosan-graphene oxide (chitosan-GO) material using the hydrothermal method at varying material ratios and adsorption studies on Congo red. Chitosan-GO composites were synthesized with mass ratios of (1:1), (1:3) and (1:5). The synthesized chitosan-GO composite was applied to adsorb Congo red dye. The adsorption process is carried out by varying pH, contact time, concentration and temperature. The chitosan-GO composite was characterized using XRD, BET and SEM-EDS. The results of XRD characterization of the chitosan-GO composite with a ratio of 1:1 showed a diffractogram of 2θ = 22.3°, at a ratio of 1:3 the diffractogram angle was 2θ = 22.1°, while the ratio (1:5) of the diffractogram peak obtained was 2θ = 22.8°. The surface area obtained in chitosan-GO composite was 11.60 m^2/g. The morphology of the chitosan-GO composite (1:5) is in the form of crystalline lumps with the constituent elements C (65.98%), O (32.68%), Na (0.22%) and S (0.09%). Adsorption of Congo red dye using chitosan-GO composite obtained optimum conditions at pH 7, contact time 50 minutes, Congo red concentration 45 mg/l and temperature 50°C. The adsorption isotherm is in accordance with the Langmuir isotherm model and the maximum adsorption capacity (Qm) is 10.245 mg/g.

Keywords: *Chitosan-GO composite, hydrothermal, graphene oxide, adsorption studies, congo red*

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Abstrak (Indonesian)

Penelitian ini bertujuan untuk mensintesis bahan kitosan-oksida grafena (kitosan-GO) menggunakan metode hidrotermal dengan rasio bahan yang bervariasi dan studi adsorpsi pada Congo red. Komposit kitosan-GO disintesis dengan rasio massa (1:1), (1:3), dan (1:5). Komposit chitosan-GO yang disintesis diterapkan untuk menyerap pewarna Congo red. Proses adsorpsi dilakukan dengan memvariasikan pH, waktu kontak, konsentrasi, dan suhu. Komposit kitosan-GO dikarakterisasi menggunakan XRD, BET, dan SEM-EDS. Hasil karakterisasi XRD dari komposit kitosan-GO dengan rasio 1:1 menunjukkan difraktogram pada 2θ = 22,3°, pada rasio 1:3 sudut difraktogramnya adalah 2θ = 22,1°, sementara rasio (1:5) puncak difraktogram yang diperoleh adalah 2θ = 22,8°. Luas permukaan yang diperoleh pada komposit kitosan-GO adalah 11,60 m^2/g. Morfologi komposit kitosan-GO (1:5) berbentuk gumpalan kristalin dengan unsur-unsur penyusunnya C (65,98%), O (32,68%), Na (0,22%) dan S (0,09%). Adsorpsi pewarna Congo red menggunakan komposit kitosan-GO diperoleh pada kondisi optimum pada pH 7, waktu kontak 50 menit, konsentrasi Congo red 45

mg/l dan suhu 50°C. Isoterm adsorpsi sesuai dengan model isoterm Langmuir dan kapasitas adsorpsi maksimum (Qm) adalah 10,245 mg/g.

Kata Kunci: Komposit Kitosan-GO, hidrotermal, oksida grafena, studi adsorpsi, congo red

INTRODUCTION

Dyes are a combination of unsaturated organic substances that are classified into molecules such as benzene, toluene, phenol, and others [1] According to Ambika *et al.* [2], synthetic dyes have a structure that is included in the complex group and is stable so that it will not fade easily and is also difficult to degrade in waste. In general, textile dyes contain azo compounds and benzene groups. If azo compounds are contaminated with the environment for a long time, they will cause disease [3]. Azo compounds are carcinogenic and mutagenic. Once formed, the aromatic amines undergo metabolic activation in the body. This process involves N-hydroxylation and N-acetylation, followed by O-acylation, which results in the formation of highly reactive electrophilic intermediates. These intermediates can bind to DNA, leading to mutations and potentially cancer [4].

One of the synthetic dyes that is widely used in the textile industry is Congo red, which is included in the group of azo dyes and has a chromophore group so it is widely used in fabric dyeing. The Congo red dye is highly toxic, posing significant risks to aquatic life when it contaminates water systems. Therefore, effective measures are necessary to mitigate the environmental impact of its waste [5]. Several methods can be used to minimize the content of color substances in industrial waste, namely biological methods, coagulation, electrocoagulation, adsorption, ozonation and chlorination [6]. The adsorption or adsorption method can reduce soluble or insoluble organic compounds. Therefore, adsorption can be used for the treatment of a number of organic and inorganic contaminants [7].

The adsorption method includes the interaction between the analyte or adsorbate and the surface of a solid substance or adsorbent. One type of adsorbent is a composite in the form of a new material derived from two or more different materials, that combined produces better properties than the original material [8]. Composite is a material formed from a combination of two or more constituent materials to obtain better mechanical properties from the constituent materials [9]. One of the composite materials that can be combined with other materials that can increase the effectiveness of good adsorption is chitosan [10]. Chitosan is a compound resulting from the deacetylation of chitin and is composed of units such as *n*-acetyl glucosamine and n-glucosamine [11]. Chitosan is widely used as a preservative for marine products and as a color stabilizer for food products. The use of chitosan as a composite material, both as a compound adsorbent and catalyst, is promising research as the latest environmentally friendly synthetic material product [12]. Chitosan can also be combined with carbon materials such as graphite and graphene with increased adsorption effectiveness compared to just one material alone [13].

Graphene is a two-dimensional nanomaterial sheet consisting of a hexagonal lattice structure and formed by the stacking of single carbon atoms. Graphene has been widely applied in various biomedical fields, such as electronic components and semiconductors, biosensors, nanocomposites, and drug carriers [14]. Graphene oxide (graphene oxide) is a graphene oxidation product which has a structural composition similar to graphene except that there are a number of surface oxygen functional groups such as hydroxyl (C-OH), epoxy (C-OC), carboxyl groups (COOH), and carbonyl groups (C=O) [15]. Research on the use of chitosan combined with graphene oxide has been widely used in the world of material synthesis both as a means of adsorbing metals and other toxic materials [16–17]. Previous methods for synthesizing chitosan-graphene oxide (GO) composites, such as coprecipitation method has several limitations, for examples; low adsorption capacity, high synthesis costs and complexity and time-consuming processes [18]. Moreover, the use of the hydrothermal synthesis method for combining materials and the effectiveness of adsorption studies and isotherm models on the synthesized material on the adsorption of Congo Red have never been used before. The method used in the synthesis of chitosan-GO composites is hydrothermal using a certain temperature and high pressure in an autoclave. This method is used because it is more environmentally friendly which allows controlling the size of the crystals to be purer than other methods, besides that the manufacturing process is easy because it only involves temperature and synthesis time. Based on this description, this research aims to see the adsorption of Congo red dye in synthetic materials using the hydrothermal method at the best variation of several material ratios used.

MATERIALS AND METHODS

Materials and instrumentation

The materials used in this research are demineral aqua p.a (Bratachem), distilled water (technically), acetic acid glacial (Merck), hydrochloric acid 37% (Merck), sulfuric acid 98.9% (Merck), Congo red (Merck), hydrogen peroxide 30% (Merck), potassium permanganate p.a. (Merck), chitosan (Merck), sodium hydroxide p.a. (Merck), graphite powder (Merck), and sodium nitrate (Merck). Instrumentation was used in this research include: UV-Vis Spectrophotometer (Orion Aquamate 8000), X-Ray Diffraction/ XRD (PANalytical), Brunauer Emmett and Teller/BET type Micromeritics (Tristar II Plus), Scanning electron microscopy with energy dispersive X-ray spectroscopy/ SEM-EDS (JEOL JSM-6510LA), and Sonificator (Biobase UCD-250).

Procedures

Synthesis of graphene oxide (GO)

A total of 1 g of graphite was put into a 500 mL beaker and 50 mL of H_2SO_4 was added and stirred at a speed of 500 rpm using a magnetic stirrer at 80 °C for 24 hours, then 1 g of $NaNO_3$ was added to the solution while stirring in a water bath for 1 hour, then slowly added 6 g of $KMnO_4$ to the solution for 4 hours and stirred using a magnetic stirrer, after which it was warmed to room temperature while stirring continuously in a water bath at 35 °C for 1 hour. The prepared solution is then diluted using distilled water. The temperature of the solution should be maintained at less than 60 °C during dilution. After 15 minutes, 6 mL of H_2O_2 (30%) was added to the solution which had been diluted with 100 mL of distilled water and centrifuged 10 times at a speed of 8000 rpm for 30 minutes. The solution was filtered two to five times while washing with distilled water to obtain a brownish yellow suspension solution. The aqueous suspension was centrifuged at 2000 rpm for 30 minutes and 8000 rpm for 1 hour, then the suspension was ultra sonicated for 30 minutes with a frequency of 40 kHz and a power of 150 watts, then filtered the suspension using a vacuum pump until dry, thus obtaining a solid. Next, the graphene oxide solid was dried using an oven at 60 °C for approximately 5 hours [19]. The synthesis results were characterized using XRD.

Synthesis of chitosan-GO composite [20]

A total of 1 g of chitosan was added to 100 mL of 1% acetic acid solution, and ultra sonicated for 2 hours to completely dissolve the chitosan and a transparent viscous liquid was produced, then 1 g of GO powder was dissolved using 100 mL of distilled water. The two solutions were mixed then put into a hydrothermal autoclave and reacted at a temperature of 120 ºC for 12 hours, then filtered the suspension using a vacuum pump until dry. The solid is obtained on filter paper, dry the solid using an oven at 120 ºC until dry, then the composite is crushed to form powder. Composite synthesis was carried out with chitosan: GO mass ratios of 1:1, 1:3 and 1:5.

Adsorption of Congo red solution

For the pH effect on adsorption, chitosan-GO composite 0.05 g of were added with 15 mL of 25 ppm conga red solution. The pH of the five solutions was adjusted to 5, 6, 7, 8 and 9 using 0.1 M NaOH or 0.1 M HCl [20]. Then the absorbance was measured using a UV-Vis spectrophotometer at a wavelength of 499 nm. The procedure is carried out in the same way on the effects of concentration, temperature and contact time with each effect carried out at varying concentrations (20, 25, 30, 35, and 40 mg/L), varying temperatures (40, 50, 60, and 70 °C) as well as variations in contact time (30, 60, 90, and 120 minutes).

Data analysis

The results of each characterization of various instruments will be the spectral patterns. SEM acts as a provider of information regarding the morphology and characteristics of the surface. XRD plays a role in checking the size of the crystals present and EDX is used to determine the band gap or energy band gap. Crystallite size can be calculated using the Debye Scherrer equation:

$$d = \frac{K\,\lambda}{\beta \cos\theta} \qquad (1)$$

Where d is crystallite size (nm), K are dimensionless shape factor constant (0,9), λ are length of the X-ray wave gel used, β are FWHM (full width at half maximum) of the diffraction peak, and θ are Bragg diffraction angle.

To determine the band gap, it can be determined using the Wood Tauc plot relationship. This method involves extrapolating a graph of the relationship between photon energy ($h\upsilon$) in the form of the abscissa or x-axis and $(\alpha h\upsilon)^2$ in the form of the ordinate or y-axis. The value comes from the derivation of the Max Plank formula, while the $(\alpha h\upsilon)^2$ comes from the derivation of the Lambert Beer formula. The results obtained are in the form of a graph obtained from the intersection of the abscissa and ordinate which can be said to be the energy band gap. Wood Tauc plot similarities include using the Equation 2:

$$(\alpha h\upsilon)^2 = A\,(h\upsilon - Eg) \qquad (2)$$

Where *h* is Planck constant, α is the adsorption coefficient corresponding to the frequency ν, A is proportionality constant, Eg is an optical band gap of a semiconductor, and ν is frequency. The absorbance value obtained from measuring the absorbance of the Congo red solution after adsorption is used to calculate the concentration of Congo red that is not adsorbed. The concentration of adsorbed Congo red can be calculated using the equation 3:

$$C_{ads} = Co - Ce \quad (3)$$

where C_{ads} is the concentration of adsorbed Congo red (mg/L), Co is the initial concentration of Congo red (mg/L) and Ce is the concentration of Congo red that is not adsorbed (mg/L). Based on equations 4 and 5, the adsorption capacity value can be calculated using equation 4:

$$Q_e = \frac{(Co-Ce)\ V}{W} \quad (4)$$

Where W is weight of adsorbent used (g), V is volume of adsorbate to be adsorbed (L), Co is Initial concentration of Congo red solution (mg/L), Ce is Residual concentration of Congo red solution (mg/L), Qe is adsorption capacity (mg/g). Based on equations 3 and 4, the percent adsorption efficiency (%R) can be calculated from equation 5:

$$\%R = \frac{(Co-Ce)\ V}{Co} \times 100\% \quad (5)$$

Where Co is initial concentration of Congo red solution (mg/L), Ce is residual concentration of Congo red solution (mg/L), %R is percentage of adsorption efficiency (mg/g).

RESULTS AND DISCUSSION

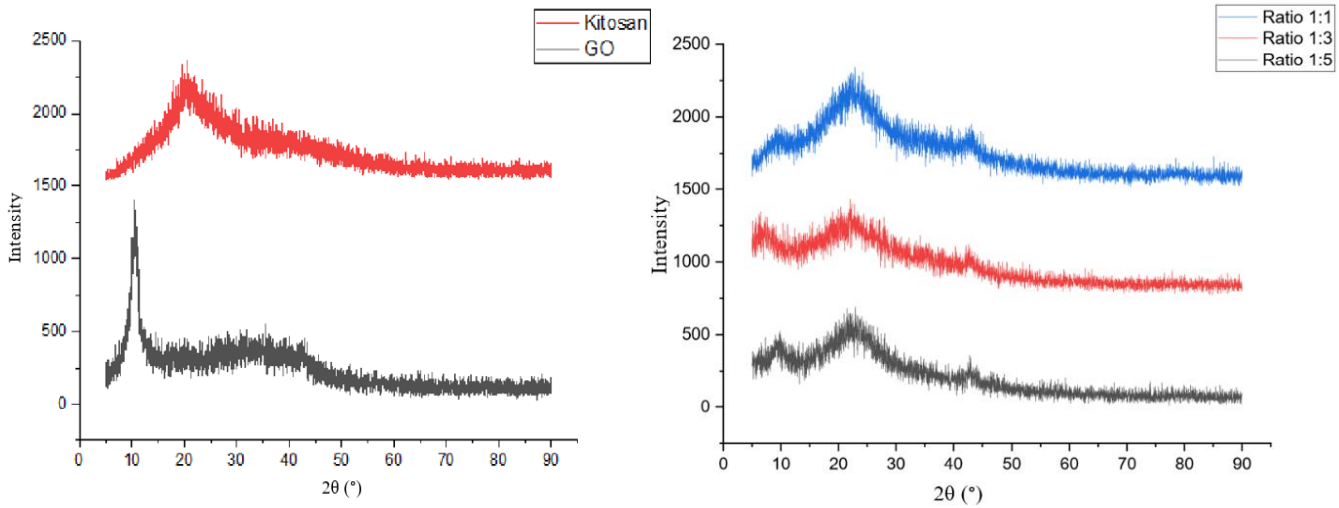
Process synthesis and characterization chitosan-graphite oxide

The synthesis of graphene oxide uses the Hummer method which is carried out using graphite by adding sulfuric acid (H_2SO_4) with the aim of keeping the graphite in an acidic state. Sodium nitrate ($NaNO_3$) is added, followed by the addition of potassium permanganate ($KMnO_4$), which functions as a strong oxidizer in an acidic environment so that it can facilitate the oxidation process. That process can make graphene oxide become hydrophilic and easily peel off in water [21]. The hydrophilic of graphene oxide can affect by pH of the solution. At low pH there will be protonated carboxyl groups such as graphene sheets becoming less hydrophilic so that aggregates are formed, whereas at high pH conditions the carboxyl groups will be deprotonated to form very hydrophilic groups like separate sheets so that graphene oxide can dissolve in water. This process takes place exothermically or releases heat energy into the environment, so this process is carried out in a container containing ice cubes to reduce the exothermic process. The oxidation process was stopped by adding hydrogen peroxide (H_2O_2) which indicating that the mixed solution changed color to brownish green with the presence of white bubbles. In the oxidation process of graphene oxide synthesis, functional groups are formed in the form of epoxide, ketone, phenol, carboxyl and carbonyl which are bound to the carbon structure [22].

Graphene oxide is ultra sonicated, which aims to make the resulting graphene oxide form a solution using ultrasonic frequencies. This method also functions to exfoliate graphite layers in water where exfoliation in this method occurs due to the frictional force of ultrasonic waves and the cavitation process that occurs in the water medium on graphite oxide. This cavitation effect creates strong and repetitive forces that can damage the bonds between particles in the graphite layer [23]. There is a pressure difference during the ultrasonic process, causing a peeling process called the cavitation process [24]. Chitosan-graphene oxide was synthetized with hydrothermal have a benefit which can makes the material a three-dimensional structure form, many holes and a large specific surface area [20]. Chitosan-graphene oxide that was successfully synthesized with three variations in the weight ratio of chitosan and graphene oxide was then continued with material characterization using XRD, SEM-EDX and BET. The XRD of Chitosan-graphene oxide, graphene oxide and chitosan were presented in **Figure 1**.

The XRD characterization results of GO can be seen in **Figure 1(a)**, there is one sharp peak with an angle of 2θ = 10.36°. The peak of GO that has been characterized shows similarities to the peak of GO characterized in the research of Ghosh *et al*. [25] where the peak is around 2θ = 10.5°, enhanced by d-spacing of 0.834 and FWHM of 0.144. This shows that graphene oxide was successfully synthesized in this study through a perfect oxidation process as indicated by the sharp peak in the XRD diffractogram in **Figure 1(a)**. in the same figure, XRD characterization results of chitosan be seen that the peak is 2θ = 19.72° with d-spacing 0.450 and FWHM 0.87. This shows similarities to the XRD characterization results research conducted by Podgorbunskikh *et al*. [26] with a diffractogram peak of 2θ = 20°. The XRD diffractogram shows that the chitosan used in this study has an amorphous solid structure. In contrast to chitosan, graphene oxide in this study has a crystalline solid structure which can

be seen from the sharp peak in the XRD diffractogram at 2θ = 10.36°.



(a) (b)

Figure 1.XRD pattern of material (a) chitosan and graphene oxide, (b) chitosan-graphene oxide material in all variation synthesized.

Based on **Figure 1**, there are three diffraction patterns located at almost the same angle 2θ, but what differentiates them is the adsorption intensity. There are 3 ratios of chitosan-GO composites in this study, including 1:1, 1:3 and 1:5. In the chitosan-GO composite with a ratio of 1:1, the diffractogram result was 2θ = 22.3° with d-spacing 0.398 and FWHM 0.927, while at a ratio of 1:3 the diffractogram angle was shown at 2θ = 22.1° with d-spacing 0.402 and FWHM 0.90 and at a ratio of 1:5 which shows 2θ = 22.8° with d-spacing 0.390 FWHM 0.76. The results of the diffractogram at a ratio of 1:5 can be seen that the characteristic peak 2θ = 10.36° indicates the presence of graphene oxide, while the peak 2θ = 19.72° indicates the presence of chitosan. It can be said that the more graphene oxide added to the composite, the greater the shift in the diffractogram angle. According to research conducted by Zhu *et al*. [20], the diffractogram angle of the chitosan-GO composite is 2θ = 24°, so it can be compared with all peak similarity ratios which are close to a ratio of 1:5.

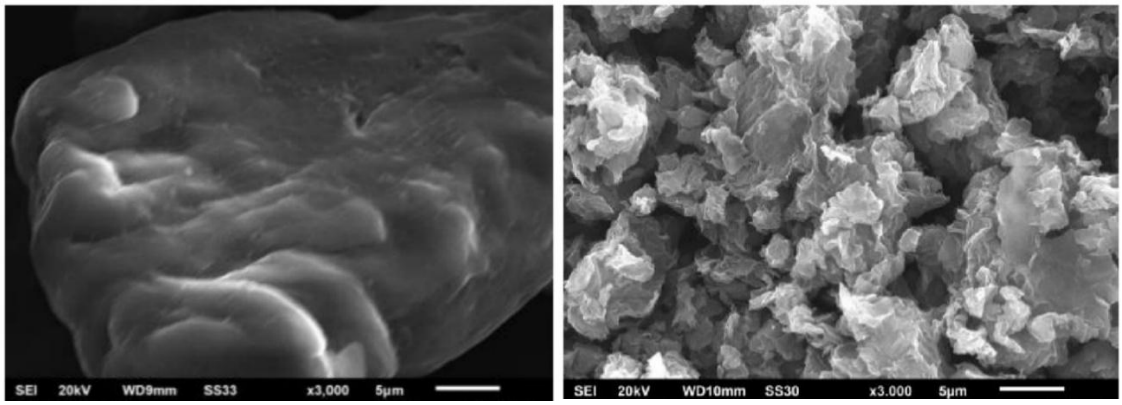
The BET surface area of the chitosan-GO composite with a mass ratio of 1:5 can be seen in **Table 1**. Based on **Table 1**, it can be seen that the chitosan-GO composite is 11.60 m^2/g, which indicates that the chitosan-GO composite has a relatively small surface area. However, the chitosan-GO composite has a lot of surface area that can interact with molecules or other substances such as in the adsorption process. Chitosan generally has a very low specific surface area ranging from 2-30 m^2/g [27]. Adsorption is influenced by the surface area. The greater the surface area of an adsorbent, the greater its efficiency, the greater its adsorption capacity. This causes more adsorbate to be adsorbed [28].

Table 1. Comparison of the surface area of Chitosan-GO composite

Adsorbent	BET (m^2/g)	Total pore volume (cm^3/g)	Pore size (nm)
Chitosan-GO	11.60	2.665	2.67
Chitosan-GO [29]	37.37	-	13.67
Chitosan-GO [30]	54.71	0.044	-

Characterization on chitosan-GO composite for surface morphology structure was done using SEM-EDX and can be seen in **Figure 2**. Based on **Figure 2(a)**, it can be seen that chitosan has a morphology similar to chips or sheets which have a wavy surface and have a large particle size and large voids between particles, while **Figure 2(b)** shows the morphology of the chitosan-GO composite in the form of aggregates. Guo *et al*. [31] from their research said that a graphene oxide sheet was distributed in or on the adsorbent which attach in the composite, provides a larger surface area and nanoscale roughness for the textile effluent to attach, which is one of the advantages of composites to adsorb dyes. EDS analysis which can be seen in **Table 1** in the chitosan-GO (1:5) composite contains the elements C, O, Na and S. The most abundant element in the composite is C at 65.98% compared to the O element at 32.68%.

This indicates that the chitosan-GO composite was successfully synthesized, marked by an increase in the composition of C and a decrease in the composition of the O element.



(a) (b)

Figure 2. SEM morphology (a) Chitosan and (b) chitosan-GO at 3000× magnification.

Study adsorption of Congo red by chitosan-GO

Effect of solution pH

The effect of pH variations on Congo red dye using a pH range of 5, 6, 7, 8 and 9 with a concentration of 25 mg/L for 15 mL. A graph of the effect of pH variations can be seen in **Figure 3(a)**. In **Figure 3(a)**, optimum pH for the adsorption capacity of Congo red dye in the chitosan-GO composite is pH 7, with an adsorption capacity of 7.21 mg/g. This indicates that the more H^+ ions contained, the more acidic it is with the reaction of oxide radicals, thus indicating that there are many hydroxyl radicals to oxidize the Congo red dye. This can increase the effectiveness of reducing the concentration of Congo red. According to Alves *et al*. [32] the surface of the adsorbent will be positively charged due to the protonation of the chitosan functional groups. The NH_2 group undergoes protonation to become $–NH_3^+$ so that it tends to occur electrostatically and then the adsorption process occurs. Protonation of $-NH_2-$ to $-NH_3^+$ causes a reduction in the number of active sites on the adsorbent surface [33].

Effect of contact time

Time variations are used to determine the optimum time for the chitosan-GO composite, where the contact time greatly influences the adsorption performance. The graph of the influence of variations in contact time on adsorption capacity can be seen in **Figure 3(b)**. Based on the graph of the optimum contact time for Congo red dye adsorption, it is at 50 minutes with an adsorption capacity of 7.2 mg/g and an adsorption percentage of 96.05%. Apart from that, there is also an increase in adsorption capacity with increasing variations in contact time. This can be said that on the surface of the adsorbent there are still empty pores, so there will be a tendency for the dye solution to be adsorbed into the adsorbent [34]. Congo red in the chitosan-GO composite has reached the optimum contact time, there will be a decrease in the adsorption capacity. The equilibrium point occurs when the adsorption capacity has decreased on the surface of the adsorbent, which indicates that the adsorbent is filled with dye [35]. That phenomenon makes the adsorbent is saturated and adsorption of the dye can no longer occur.

Effect of dye initial concentration

The effect of varying concentrations was carried out to determine how much concentration of dye would be adsorbed by the chitosan-GO composite. A graph of the effect of variations in concentration on adsorption capacity can be seen in **Figure 3(c)**. Based on **Figure 3(c)**, it can be stated that the greater the concentration of Congo red will result in a large amount of Congo red being collected on the adsorbent, thereby increasing the adsorption capacity of the chitosan-GO composite in adsorbing Congo red. At low concentrations, the number of adsorption sites available on the solid surface is not completely filled, so that increasing the concentration of Congo red dye tends to increase the amount of dye adsorbed on the solid surface [36]. The higher the concentration of Congo red, the higher the adsorption saturation on the surface of the solid. According to Iryani *et al*. [37], an increase in dye concentration can cause an increase in the adsorbate thrust so that more dye molecules will be adsorbed. So it can be said that the higher the concentration of dye, the active sites on the surface of the adsorbent will be fully occupied by dye molecules, causing the adsorption ability to decrease [38].

Effect of temperature variation in adsorption study

The effect of temperature variations was carried out to determine the effect of temperature on the adsorption system carried out by chitosan-graphene oxide on Congo red dye. Based on **Figure 3(d)**, it can be stated that there is an increase in the adsorption capacity value to optimum conditions, and then there is a decrease in the adsorption capacity value. Chitosan-GO composite adsorbs Congo red dye at an optimum temperature of 50 °C with an adsorption capacity of 7.06 mg/g and an efficiency of 94.25%. According to Gil [39], the higher the temperature used, the more adsorption rate will occur, so that more adsorbate will be adsorbed. Adsorbates that have been adsorbed can be released again by the adsorbent when the temperature increases.

Apart from that, as the temperature increases, the kinetic energy of the substance particles in the solution will move faster, which will reduce the interaction between the adsorbent and adsorbate so that a decrease in adsorption capacity will occur [40,41].

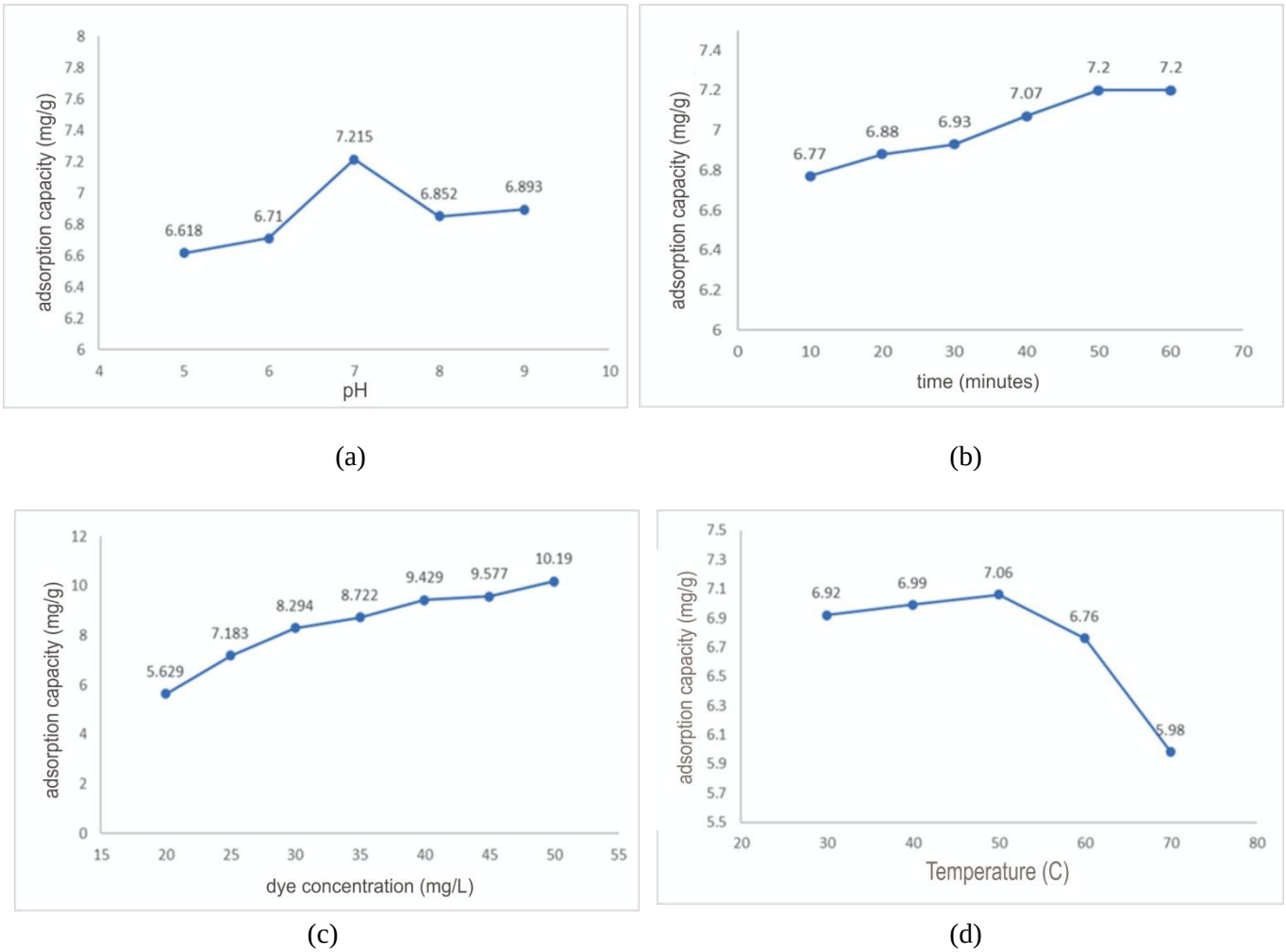


Figure 3. Parametric analysis effect of Congo red adsorption capacity on (a) pH, (b) contact time, (c) dye concentration, and (d) temperature effect.

Isotherm adsorption model

Adsorption isotherm model was represented as the number of adsorbate molecules per unit mass of adsorbent as a function of equilibrium concentration in bulk solution at a constant temperature [42]. Adsorption isotherms are useful for understanding the mechanism of the adsorption. Langmuir and Freundlich isotherm models were chosen in this study for evaluating the relationship between the amounts of Congo red adsorbed by chitosan-GO equilibrium concentration in aqueous solution. The Langmuir model assumes that adsorption takes place

at specific homogeneous sites on the surface of the adsorbent and also, when a site is occupied by an adsorbate molecule, monolayer adsorption, and the energy of the adsorption is constant. Langmuir isotherm model can be presented in linear equation by as Eq. 6:

$$\frac{1}{Q_e} = \frac{1}{K_L Q_m} C_e + \frac{1}{Q_m} \quad (6)$$

where C_e is the equilibrium concentration of the adsorbate ions (mg/L); qe is the amount adsorbed (mg/g); and Q_m and K_L are Langmuir constants correlated to the maximum monolayer adsorption capacity (monolayer capacity) (mg/g) and energy of adsorption (L/mg), respectively. The maximum adsorption capacity (Q_m) is calculated by plotting the curve 1/qe vs 1/Ce which gives the maximum adsorption capacity as well as the Langmuir constant which relates to the energy of adsorption. The essential features of the Langmuir isotherm model can be expressed in terms of "R_L" a dimensionless constant, separation factor or equilibrium parameter with equation represented by Eq. 7:

$$R_L = \frac{1}{(1+C_0 K_L)} \quad (7)$$

where Co (mg/L) is the initial amount of adsorbate and b (L/mg) is the Langmuir constant described above. The R_L parameter is considered as more reliable indicator of the adsorption. There are four possibilities for the R_L value which is $0 < R_L < 1$ (favourable adsorption), $R_L > 1$ (unfavourable adsorption), $R_L = 1$ (linear adsorption), and $R_L = 0$ (irreversible adsorption). The Freundlich isotherm model is valid for multilayer adsorption on a heterogeneous adsorbent surface with sites that have different energies of adsorption. This model explains both mono- as well as a multilayer adsorption process, it also explains that the adsorbent has surfaces of varied affinities or adsorption on heterogeneous surfaces. Freundlich isotherm model can be presented in linear equation by as Eq. 8:

$$\text{Log } Q_e = \text{Log } K_F + \frac{1}{n} \text{Log } C_e \quad (8)$$

Where K_F (mg/g) is the constant related to the adsorption capacity and n is the empirical parameter related to the intensity of adsorption. The n number varies with the heterogeneity of the adsorbent and for favorable adsorption process the value of n should be less than 10 and higher than unity, while the values of K_F and 1/n are determined from the intercept and slope of linear plot of log Qe versus ln Ce, respectively. Data on the adsorption isotherm parameters of the Chitosan-GO composite on Congo red dye can be seen in **Table 2**.

Based on **Table 2**, it can be seen that the correlation coefficient (R^2) value of the Langmuir equation is 0.9956 while in the Freundlich equation it is 0.4459. Therefore, it can be said that the adsorption equation follows the Langmuir isotherm model because the value of the correlation factor (R^2) of the Langmuir equation is greater than the Freundlich equation [43]. The Langmuir isotherm suggests that a homogeneous adsorbent surface occurs in monolayer adsorption, while the Freundlich isotherm suggests that a heterogeneous adsorbent surface occurs in multilayer adsorption [44].

Table 2. Data on the adsorption isotherm parameters of the Chitosan-GO composite on Congo Red

Isoterm Models	Parameters	
Langmuir	Qm (mg/g)	10.245
	K_L (L/mg)	1.666
	R^2	0.9956
Freundlich	N	2.17
	1/n	0.4604
	K_f (mg/g)	3.619
	R^2	0.4459

CONCLUSION

Chitosan-GO composites were successfully synthesized with a ratio of 1:1 being the best ratio (the morphological condition of the chitosan-GO composite was in the form of aggregates with the constituent element C (75.98%), O (32.68%), Na (0.22%) and S (0.09)). The ability of the Chitosan-GO composite to adsorb Congo red dye obtained optimum results at pH 7, contact time 50 minutes and concentration of Congo red dye 45 mg/L at a temperature of 50 °C with the adsorption isotherm model which corresponds to the Langmuir isotherm.

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