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ADSORPTION OF METHYLENE BLUE DYE USING GUARAN/TIO_2 HYDROGEL

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ABSTRACT

Natural polysaccharide, namely guar gum (guaran), was utilized as the raw material for preparing hydrogel adsorbent, TiO_2 was added into the hydrogel to enhance the adsorption capacity. In this work, methylene blue dye was chosen as the adsorbate model to evaluate the adsorption efficiency of the prepared guaran/TiO_2 hydrogel. Several physicochemical characterizations were performed to elucidate the characteristic of the hydrogel, including scanning electron microscopy and Fourier transform infrared spectroscopy. The effect of temperature and pH on the adsorption efficiency of the guaran/TiO_2 hydrogel toward methylene blue was evaluated. The result of the study reveals that the use of guaran/TiO_2 hydrogel allow 69% removal of methylene blue from solution, and the maximum adsorption capacity was found to be 224 mg/g at system pH of 10 and temperature of 303K. The adsorption process was found to fit with the Langmuir model, indicating homogenous surface energy of the adsorption sites. The evaluation on the thermodynamic parameters of the adsorption indicates the spontaneous and exothermic behavior of the adsorption. This study demonstrated the potential of the guaran for preparing an environmentally friendly hydrogel, which can be a good choice of adsorbent for wastewater treatment.

ABSTRAK

Polisakarida alami, yaitu guar guam (guaran(, digunakan sebagai bahan baku untuk pembuatan adsorben berbentuk hidrogel, selanjutnya partikel TiO_2 ditambahkan pada hidrogel dengan tujuan untuk meningkatkan kapasitas adsorpsinya. Dalam studi ini, pewarna metilen biru digunakan sebagai model adsorbat untuk mengevaluasi efisiensi penyerapan (adsorpsi) dari hidrogel guaran/TiO_2 yang telah disiapkan. Beberapa teknik karakterisasi fisikokimia dilakukan untuk mempelajari karakteristik dari hidrogel, antara lain meliputi analisa scanning electron microscope dan Fourier transform infrared spectroscopy. Efek dari suhu operasi, dan pH terhadap efisiensi penyerapan metilen biru oleh hidrogel guaran/TiO_2 dipelajari. Dari hasil studi ini diperoleh bahwa penggunaan hidrogel guaran/TiO_2 mampu menghilangkan 69% pewarna metilen biru dari larutan berair, dan kapasitas adsorpsi maksimum ditemukan adalah sebesar 224 mg/g dari sistem adsorpsi yang dijalankan pada pH 10 dan suhu operasi 303K. Proses adsorpsi ini ditemukan mengikuti model persamaan Langmuir, hal ini mengindikasikan situs-situs adsorpsi yang homogen pada permukaan hidrogel. Evaluasi pada parameter termodinamika dari adsorpsi menunjukkan bahwa proses adsorpsi berjalan secara spontan dan eksotermis. Studi ini mendemonstrasikan potensi penggunaan dari guaran untuk membuat suatu hidrogel yang ramah lingkungan, yang dapat menjadi suatu pilihan yang baik untuk penanganan air limbah.

Keywords: *guaran; guar gum; hydrogel; adsorption; methylene blue*

I. Introduction

Contamination of water by textile dyes is a common environmental problem that frequently occur along with the increasing number of textile industries [1]. Methylene blue is a type of azo dye that is widely used in various industries that involve dyeing processes, such as textiles, yarn, hair dye and colored paper [2]. The content of dyes in industrial wastewater makes wastewater treatment complicated, because dyes are persistent substances [3]. Without an effective treatment, the dye-containing wastewater may cause a serious environmental problem, especially in water bodies [4]. Considering the negative environmental impact that potentially caused by the improper disposal of dye, it is important to develop an effective, economic, and environmental friendly technique to treat the dye content in the wastewater. In this work, a natural polysaccharide based hydrogel is being introduced as an environmental friendly hydrogel for the removal of methylene blue dye, wherein guar gum is used as the polysaccharide.

Guar gum (guaran or galactomannan) is a type of water soluble polysaccharide that can be easily transformed into hydrogel [5, 6]. Guar gum is constituted of the linear chain of galactomannan units ((1→4)-linked β-D-mannopyranosyl) and the side chain of (1→6)-linked α-D-galactopyranosyl. Guar gum is a potential raw material in preparing hydrogel owing to its properties, including swellability,

dissolvability in polar solvent, and ability to form hydrogen bonds [7, 8].

The used of guaran-based hydrogel in the adsorption system has been reported in several studies. For example, Yang et al. (2023) reported that the guaran/cellulose/biochar composite hydrogel can be a potential adsorbent for adsorbing Cu^{2+} and Co^{2+} [9]. In another study, Abdel-Halim and Al-Deyab (2011) demonstrated the use of guaran/acrylamide hydrogel to adsorb Cr^{6+} from aqueous solution [10]. Similarly, in our previous work, we have shown the superiority of the guaran/TiO_2 hydrogel for removal of methylene blue [11] —Nevertheless, the thermodynamic aspect of the adsorption system has not been evaluated, which will be revealed in this study.

The addition of nanoparticles, such as TiO_2, is reported to enrich an adsorbent with photodegradation activity, which can enhance the removal efficiency of dyes [12, 13]. By employing similar strategy, herein, TiO_2 is being integrated into the guar gum hydrogel to improve the removal efficiency toward methylene blue dye. In the preparation of hydrogel, guar gum was first dissolved in a solvent containing urea and sodium hydroxide to obtain a gel-like solution. Subsequently, the TiO_2 particle was suspended in the gel-like solution. Solidification of the mixture into hydrogel was initiated via a crosslinking reaction using epichlorohydrin as the agent.

The adsorption study of the guaran/TiO_2 hydrogel (GTH) was performed against methylene blue as the model adsorbate. The isotherm and kinetic adsorption were performed to determine the maximum adsorption capacity and the adsorption rate, respectively. The thermodynamic aspect of the methylene blue adsorption using GTH is being investigated to reveal the feasibility of the process.

II. Materials and method

II.1. Materials

Guar gum powder (guaran, MW = 535.15 g/mol) and epichlorohydrin (ECH, MW = 92.52 g/mol) were obtained from Sigma Aldrich (Singapore). Sodium hydroxide (NaOH, 97%, MW = 40 g/mol) was obtained from Merck, Germany. Urea (MW = 60.1 g/mol), methylene blue, TiO_2, and sulfuric acid were purchased from a local chemical distributor in Surabaya, East Java, Indonesia.

II.2. GTH preparation and characterization

Solvent for dissolving guaran powder was prepared from the mixture of NaOH and urea at a mass ratio of 7:12. Different amount of guaran powder (1 to 7 g) was dissolved into 100 mL of solvent. After a homogeneous gel-like solution was obtained, 10 mg of TiO_2 and 5 mL of ECH was added and the mixture was stirred for 10 min. Subsequently, the solution was poured into a silicon mold container and being steamed for 30 min at 75°C to obtain the solid hydrogel. The excess chemical reagents were washed with plenty amount of water, and then the hydrogel was dried using freeze drying technique.

Scanning electron microscopy and Fourier transform infrared spectroscopy procedure was perform to elucidate the morphological structure and functional groups of the GTH hydrogel, respectively.

II.3. Adsorption study

The prepared GTH hydrogels were utilized as the adsorbent for the adsorption of methylene blue dye. In a typical isotherm adsorption procedure, 1 g of dried hydrogel was introduced into a 50 mL methylene blue solution at various concentrations from 100 to 1000 mg/L, and the adsorption process was conducted in a shaking water batch at different temperatures of 30 to 50°C for 24h.

The kinetic isotherm was performed using 1000 mL of 100, 300, and 500 mg/L methylene blue solution. The change of methylene blue concentration after the addition of 1 g of dried GTH was determined at various time interval.

The effect of pH was evaluated on 50 mL methylene blue solution prepared at a concentration of 100 mg/L and various pH of 2 to 10. The pH adjustment was done by adding 0.5 M HCl or 0.5 M NaOH solution.

The concentration of methylene blue in the solution was determined by means of spectrophotometric procedure using UV-Vis Spectrophotometer at a wavelength of 663 nm.

III. Results and discussion

III.1. Characterization of GTH

All of the characterization was conducted on the hydrogel prepared using 5 g of guaran powder. Fourier transform infrared (FTIR) analysis was performed to reveal the functional group composition of GTH, and the analysis result is given in Table 1. The FTIR bands of guaran hydrogel without addition of TiO_2 (GH) was also given for comparison. GH and GTH possess similar functional groups as shown by the FTIR bands which detected at similar wavenumbers. The stretching band of the –OH group was observed as a broad band centered at 3444 cm^{-1} and 3323 cm^{-1} for GH and GTH, respectively. The C=O stretching vibration was detected at 1644 cm^{-1} and 1662 cm^{-1} for GH and GTH, respectively. The characteristic bands of galactose/mannose linkage originated from guaran moiety is detected at near 860 cm^{-1} and 920 cm^{-1} for both hydrogels. A new additional band which signifies the presence of TiO_2 particle in GTH

was detected at 566 cm^{-1}, this band was not detected in GH.

Table 1. FTIR bands and the corresponding functional group of the guaran-derived hydrogels

Band wavenumber (cm^{-1})		Corresponding functional group
GH	**GTH**	
3444	3323	-OH stretching vibration
2944	2930	-CH stretching vibration of CH_2
1644	1662	C=O stretching vibration
1153	1090	C-OH stretching vibration from primary alcohol
867, 920	873, 914	Galactose and mannose linkage
	566	Ti-O-O stretching vibration

The SEM imaging was performed on GH and GGH to observe the morphology of the hydrogel. The SEM images are shown in Figure 1. Figures 1a and 1b show the morphology of GH, the agglomerated-like network was observed. Meanwhile, Figures 1c and 1d show the morphology of GTH, the addition of TiO_2 particles induces a rod-like morphology as shown in Figure 1c. An agglomerated network was also observed in GTH (Figure 1d).

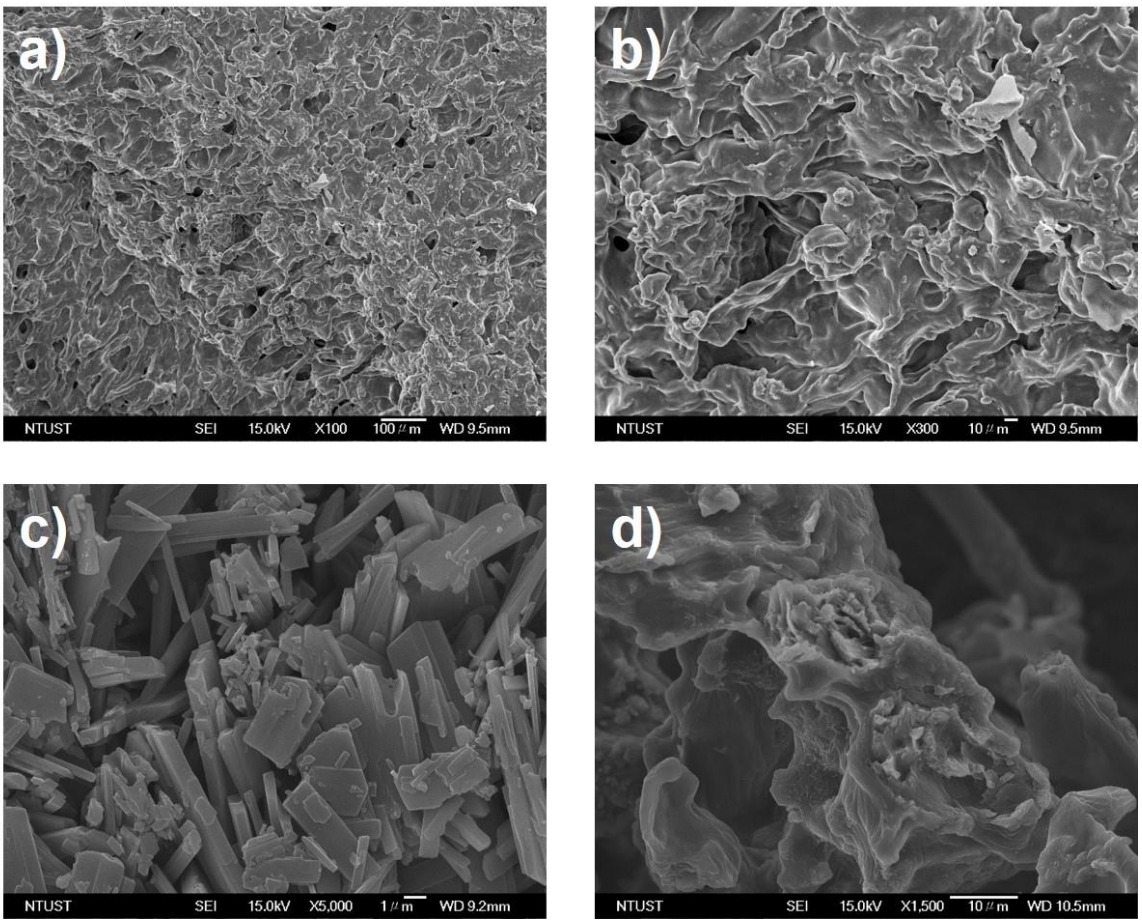

Figure 1. SEM image of (a, b) guaran hydrogel (GH) and (c, d) guaran/TiO_2 hydrogel (GTH)

III.2. Effect of guaran content in the removal efficiency of methylene blue

Figure 2 shows the variation in removal efficiency of GTH prepared using different amounts of guaran powder. It can be seen that the increase in methylene blue removal efficiency by GTH does not increase proportionally with the increase in guaran content. The use of 1% guaran results in the lowest removal efficiency, and the removal efficiency is greatly increased as the guaran content was increased to 5%. However, a further increase of guaran content to 6% is causing a decrease in removal efficiency. The removal efficiency was found to decrease further with the higher content of guaran of 7%. The guaran content is correlated with the density of

the hydrogel, the higher guaran content may result in the higher density of the hydrogel which cause the reduced pore size [14]. According to this result, it can be noted that the use of 5% guaran content produce hydrogel with the highest removal efficiency toward methylene blue.

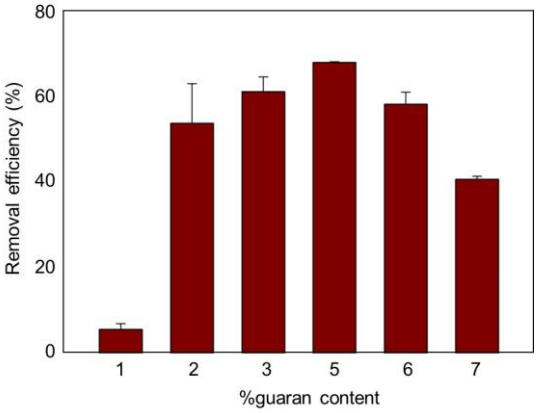

Figure 2. Effect of guaran content variation in the removal efficiency of methylene blue.

III.3. Effect of pH on the removal efficiency of methylene blue

Figure 3 shows the effect of adsorption system pH on the removal efficiency of methylene blue by GTH. The GTH was prepared using 5% guaran, this composition is found to result in the adsorbent with best removal efficiency as revealed from the result in Figure 2. The removal efficiency of methylene blue was found to be very low at acidic pH, and it was significantly increase at pH of 10. The enhancement of removal efficiency at highly alkaline pH can be correlated with the ionization of the hydroxyl functional groups of the guaran moiety in GTH. At alkaline pH the H^+ of the functional groups of guaran is being deprotonated, resulting in the weakening of hydrogen bonds between the polymer chain. This condition facilitates the swelling of the hydrogel, and therefore, more amount of adsorbate molecules in water can diffuse into the internal matrix of the hydrogel [14-16].

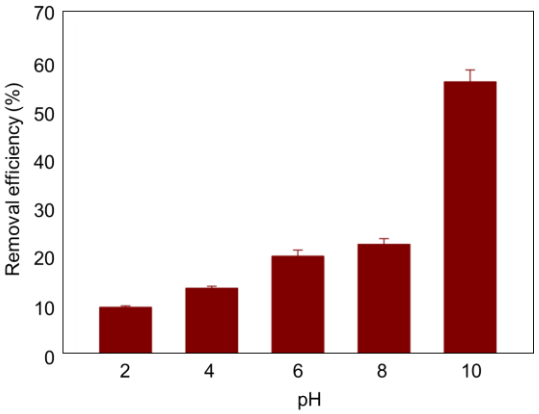

Figure 3. Effect of pH on the removal efficiency of methylene blue.

III.4. Adsorption kinetic

Figure 4 shows the adsorption kinetic curve as constructed by plotting qt vs t, where qt (mg/g) is the amount of methylene blue adsorbed at a specific time (t, min). The parameter qt is calculated according to equation (1).

$$qt = [(C0\text{-}Ct)/m]\times V \quad (1)$$

with, $C0$ and Ct (mg/L) are the concentration of methylene blue at t = 0 and t = t, respectively; m (g) is the mass of the adsorbent; and V (L) is the volume of the system. To find the adsorption rate, Pseudo first-order and Pseudo second-order model were fitted into the data. The mathematical expression of the Pseudo first-order and Pseudo second-order model is shown by equation (2) and (3), respsectively.

$$qt = qe\,(1 - \exp^{-k\cdot t}) \quad (2)$$

$$qt = [qe\,(qe\cdot k\cdot t)]/[1+(qe\cdot k\cdot t)] \quad (3)$$

herein, qe (mg/g) represents the amount of methylene blue in equilibrium; k is the adsorption rate constant with the unit of 1/min (Pseudo first-order) or mg/g·min (Pseudo second-order).

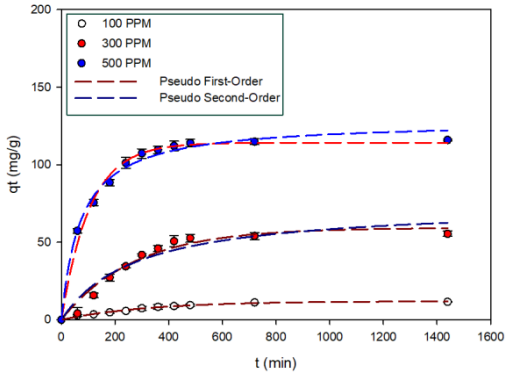

Figure 4. Adsorption kinetic curve showing the adsorption of methylene blue at different concentrations on GTH. PPM is referred to as part per million which is the same as mg/L

It can be noted that the equilibrium time of adsorption does not affected by the concentration of the adsorbate, where the equilibrium time was found to be 400 min for all system as signified by the constant qt. However, the concentration of the methylene blue is affected the rate of adsorption; where the rate of adsorption is faster at higher concentration, as noted from the steeper increase of qt at time close to zero.

The adsorption rate of methylene blue on GTH was calculated by fitting the kinetic data with Pseudo first-order and Pseudo second-order model. The calculated parameters are summarized in Table 2. The fitting using Pseudo first-order gave the best correlation, as indicated by the R^2 value close to 1. And, based on Pseudo first-order model, the adsorption rate (k) is found to increase with the increase of methylene blue concentration, which is in accordance to the experimented kinetic data. On the other hand, the k from Pseudo second-order does not fit the experimented data, as it was found that the k

decreases at the higher methylene blue concentration.

Table 2. Parameters from kinetic data fitting using Pseudo first-order and Pseudo second-order model

Conc. (mg/L)	k × 10^4 (1/min or mg/g min)	qe (mg/g)	R^2
Pseudo-first order			
100	31	11.99	0.97
300	37	59.25	0.96
500	95	114.1	0.99
Pseudo second-order			
100	4	15.13	0.95
300	2	74.58	0.93
500	1	128.3	0.98

III.5. Adsorption isotherm

The adsorption isotherm curve was constructed by plotting the Qe vs Ce. Qe (mg/g) is the amount of methylene blue adsorbed at equilibrium, and Ce (mg/L) is the methylene blue concentration. The value of Qe is calculated according to equation (4).

$$Qe = [(C0\text{-}Ce)/m]\times V \quad (4)$$

To quantify the maximum adsorption capacity (Qmax, mg/g) of GTH toward methylene blue, Langmuir model was employed for the isotherm data fitting. Meanwhile, the Freundlich model was fitted to the data to evaluate the heterogeneous behavior of the adsorption sites of GTH. The mathematical expression of Langmuir and Freundlich model is shown by equation (5) and (6), respectively.

$$Qe = [(Qmax\cdot kL\cdot Ce)]/[1+(kL\cdot Ce)] \quad (5)$$

$$Qe = kF\cdot Ce^{1/n} \quad (6)$$

kL (L/mg) and kF ((mg/g)(mg/L)$^{1/n}$) is the adsorption constant; and n is the constant correlated to the heterogeneity.

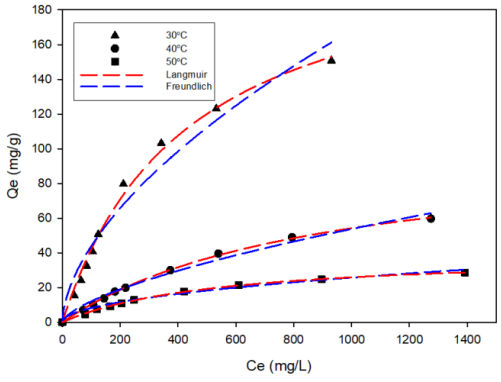

Figure 5. Adsorption isotherm curve showing the adsorption of methylene blue at different temperatures on GTH.

Figure 5 shows the adsorption isotherm curve for the adsorption system at different investigated temperature. It can be noted that the adsorption capacity was decreased with the increase in temperature, indicating the exothermic behavior of the system. This behavior can be an advantage for large-scale applications, as the addition of heat energy does not required for the process.

According to the Langmuir model, the Qmax was found to be 224 mg/g, 103 mg/g, and 40 mg/g for the adsorption system at 30°C, 40°C, and 50°C, respectively. Meanwhile, according to Freundlich model, the heterogeneity of the system is found to be low as the n value is closer to 1 than 10. The calculated parameters of Langmuir and Freundlich model resulted from the data fittings is summarized in Table 3.

Table 3. Parameters from isotherm data fitting using Langmuir and Freundlich model

Conc. (mg/L)	30°C	40°C	50°C
Langmuir			
Qmax (mg/g)	224	103	40
kL (L/mg)	0.0023	0.0011	0.0019
R^2	0.99	0.99	0.99
Freundlich			
kF (mg/g)(mg/L)$^{1/n}$	4.22	0.62	0.68
n	1.88	1.55	1.90
R^2	0.98	0.98	0.98

III.6. Thermodynamic analysis

Thermodynamic analysis was performed to determine the Gibbs energy (ΔG), enthalpy (ΔH), and entropy (ΔS) of the adsorption system. Herein, the ΔG was calculated according to equation (7).

$$\Delta G = -RT\ \ln(kL) \quad (7)$$

where kL value was obtained from the calculated parameter of Langmuir model at different temperature, which are summarized in Table 3. Meanwhile, ΔH and ΔS value is calculated as the slope and intercept of the linear plot between ΔG vs temperature, according to the linear equation (8).

$$\Delta G = \Delta H - T\Delta S \quad (8)$$

As given in Table 4, the ΔG value of the adsorption system at various temperatures is negative, indicating the spontaneity of the process [17-19]. This also signifies the feasibility of the adsorption process. The ΔH is also found to be negative, indicating the exothermic nature of the process which is in accordance to the isotherm data. The ΔS value is found to be negative, indicating the reversible behavior.

Table 4. Thermodynamic parameters derived from Langmuir parameters

Parameter	30°C	40°C	50°C
ΔG (kJ/mol)	-12.8	-10.0	-8.1
ΔH (kJ/mol)		-83.7	
ΔS (kJ/mol K)		-0.23	

IV. Conclusion

This study has demonstrated the use of GTH for adsorption of methylene blue from aqueous solution. The physicochemical

characterization of the GTH reveals that the addition of TiO_2 does not alter the functional group originated from the guaran polysaccharide. The preparation of GTH using higher content of guaran is negatively affect the removal efficiency of methylene blue, which can be correlated to the density of the hydrogel. The adsorption rate of the methylene blue on GTH is dependent on the concentration of methylene blue, however the equilibrium time of adsorption does not change with the change of methylene blue concentration. The adsorption system was found to be exothermic, and the adsorption at lower temperatures is more favorable. Thermodynamic analysis reveals the feasibility of the adsorption process, as indicated from the negative ΔG.

Conflict of interest

The authors declare no conflict of interest.

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