

ADSORPTION OF MALACHITE GREEN ONTO MODIFIED CHITOSAN-SULFURIC ACID BEADS: A PRELIMINARY STUDY

(Penjerapan Malakit Hijau ke atas Manik Kitosan-Asid Sulfurik Terubahsuai: Satu Kajian Awal)

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Received: 2 July 2018; Accepted: 9 July 2019

Abstract

The removal of malachite green (MG) from aqueous solutions by cross-linked chitosan-sulfuric acid (H_2SO_4) beads was investigated. Solubility and swelling tests were performed in order to determine the stability of the chitosan- H_2SO_4 beads in acidic solution, basic solution and distilled water. Different parameters affecting the adsorption capacity such as initial pH (pH 2-12), agitation period (10-60 minutes) and initial concentrations of MG (5-30 mg/L) were studied. In addition, the adsorption capacities of MG onto chitosan- H_2SO_4 beads were determined too. In order to describe adsorption isotherm of chitosan- H_2SO_4 beads, the sorption data were analyzed using linear form of Langmuir and Freundlich equation. It was found that Langmuir isotherm showed higher conformity than Freundlich isotherm ($30.96 > 2.23$). A kinetic study indicated that pseudo-second-order kinetic equation correlates well with the experimental data. FT-IR analysis established there was an interaction between MG and chitosan- H_2SO_4 beads. It can be concluded that chitosan- H_2SO_4 beads were favorable absorbers and could be used as alternate adsorbents for removal of MG in water treatment process.

Keywords: adsorption, chitosan- H_2SO_4 beads, isotherm, kinetics, malachite green

Abstrak

Penyingkiran malakit hijau (MG) daripada larutan akueus oleh manik kitosan-asid sulfurik (H_2SO_4) berangkai-silang telah dikaji. Ujian keterlarutan dan pengembangan dijalankan untuk menentukan kestabilan manik kitosan- H_2SO_4 di dalam larutan asid, larutan alkali dan air suling. Parameter berbeza yang mempengaruhi muatan penjerapan seperti pH awal (pH 2-12), tempoh putaran (10-60 minit) dan kepekatan awal MG (5-30 mg/L) dikaji. Sebagai tambahan, muatan penjerapan bagi MG terhadap kitosan- H_2SO_4 turut ditentukan. Bagi menentukan isoterma penjerapan manik kitosan- H_2SO_4 , data penjerapan telah dianalisis menggunakan persamaan linear Langmuir dan Freundlich. Didapati isoterma Langmuir lebih sesuai berbanding isoterma Freundlich ($30.96 > 2.23$). Kajian kinetik menunjukkan persamaan tertib-pseudo-kedua berhubung baik dengan data kajian. Analisis FT-IR mengesahkan terdapat interaksi diantara MG dan manik kitosan- H_2SO_4 . Dapat disimpulkan bahawa kitosan- H_2SO_4 adalah penjerap pilihan dan boleh digunakan sebagai penjerap alternatif bagi menyingkirkan MG dalam proses perawatan air.

Kata kunci: penjerapan, manik kitosan- H_2SO_4 , isoterma, kinetik, malakit hijau

Introduction

Discharges of various types of waste product and the rapid growth of different chemical industries have become the main causes of environmental contamination and degradation to the country. Dyes, which are widely used in

different industries, can inhibit light penetration into water, retard photosynthetic activity, prevent the growth of biota and have a tendency to chelate metal ions. Dyes are classified according to their chemical properties and solubility. Dyes can be categorized as an acid dye, basic dye, direct dye, mordant dye, disperse dye, reactive dye and vat dye [1]. Basic dyes are the most commonly used in many industries and have become one of the main sources of severe water pollution. Malachite green (MG) is an example of a basic dye used to dye wool, silk, cotton and leather in textile industries and also as a strong anti-fungal, anti-bacterial and anti-parasitic agent in fish farming [1, 2]. Nowadays, MG is considered as a highly controversial compound due to its genotoxic and carcinogenic properties [3].

Adsorption has been found to be the most promising way to remove MG from wastewater because it uses low-cost adsorbents, which could be found in nature or are by-products [4]. Chitosan is one of the unindustrialized adsorption methods for the removal of dyes and heavy metal ions, even at low concentrations [5]. Chitosan is a type of natural polyaminosaccharide composed of poly(β -1–4)-2-amino-2-deoxy-D-glucopyranose and can be produced through deacetylation of chitin. Chitin is the second most abundant polymer in nature after cellulose that can be extracted from crustacean shells such as prawns, crabs and cell walls of fungi [6]. This nontoxic and biodegradable chitosan is an ideal adsorbent due to the presence of the amine ($-\text{NH}_2$) and hydroxyl ($-\text{OH}$) groups that serve as the adsorption sites for many adsorbates [7, 8].

In spite of chitosan's good adsorption capability, it also can be physically and chemically modified [9–11]. Accordingly, the physical modification of chitosan can provide support and increase the availability of the binding sites because the chitosan has low mechanical properties and low specific gravity [12, 13]. Therefore, efforts have been made to improve its chemical stabilities by cross-linking the chitosan to create a very stable and strong chitosan even in acidic and basic solutions.

Many studies have been reported for utilizing modified chitosan for application in MG removal, such as chitosan–ionic liquid beads [14], chitosan nanoparticles [15, 16], chitosan oligosaccharide [17], chitosan composite [18], chitosan–bentonite beads [19] and chitosan foam [20]. These approaches seem to be effective for removing MG but some improvement in existing methods is desirable. All of these modified chitosan's are difficult to prepare, time-consuming and unstable, especially the chitosan foam. Therefore, a simple approach has been taken in this study which is using a modified chitosan with sulfuric acid (H_2SO_4) to remove MG from an aqueous solution. The method to prepare this modified chitosan is relatively straightforward and not expensive.

In this preliminary study, chitosan– H_2SO_4 beads are used to remove MG dye in aqueous solution. The influences of initial pH, agitation time, adsorbent dosage and initial concentrations of MG on the adsorption process were studied. These are the basic parameters to determine the suitability and optimal conditions of the prepared cross-linked chitosan beads as an adsorbent. The pseudo-first-order and pseudo-second-order kinetics models were used to determine the adsorption rate during the adsorption process. The Langmuir and Freundlich isotherm models were used to evaluate the equilibrium adsorption capacity data for the adsorption of MG onto chitosan– H_2SO_4 .

Materials and Methods

Materials

Samples of chitosan flakes (M.W. 100,000–150,000 g/mol) with a degree of deacetylation of 72.55% were supplied by Chito-Chem (M) Sdn. Bhd., Malaysia. MG was purchased from Fluka (Malaysia). Sodium hydroxide pellets, NaOH, hydrochloric acid 37.0%, HCl, acetic acid, CH_3COOH , were purchased from Sigma-Aldrich (Malaysia). All the reagents used throughout the experiments are analytical–reagent grade and used without any further purification. Distilled deionized water was used to prepare all solutions.

Preparations of chitosan beads and chitosan– H_2SO_4 beads

Chitosan beads were prepared by dissolving 2.0 g of chitosan flakes in 60 mL of 5% (v/v) acetic acid. The viscous solution was left overnight before dropping into 500 mL of 0.50 M NaOH solution using a dropper. The aqueous NaOH solution was under continuous stirring with the speed of 300 rpm. The chitosan hydrogel beads were allowed to immerse in 0.50 M NaOH solution for 15 minutes. Then, the formed chitosan beads were filtered with filter paper 2.5 μm of pore size (Whatman 42) and rinsed many times with distilled water. Eventually, the extensively washed

chitosan beads were then added into 100 mL of 0.50 M sulfuric acid solution and were stirred at 200 rpm for 24 hours at room temperature. After 24 hours the solution was filtered and the cross-linked beads were washed several times using distilled water. The chitosan-H₂SO₄ beads were allowed for drying. The beads were then ground using mortar and sieved to a constant size approximately (< 250 µm) before used. The structure of chitosan-H₂SO₄ beads before and after MG adsorption obtained was confirmed by a Perkin-Elmer FT-IR System 2000 Model spectrometer.

Solubility and swelling test of chitosan beads and chitosan-H₂SO₄ beads

The solubility of chitosan-H₂SO₄ beads was tested in 5% (v/v) acetic acid, 0.10 M NaOH and distilled water. Approximately 0.05 g of the beads was weighed and transferred into a 50 mL of these three solutions and were left stirring for 24 hours. After 24 hours, the solubility of the beads in these solutions was observed.

In the swelling test, both chitosan beads and chitosan-H₂SO₄ beads were studied. About 0.05 g of the beads was weighed and transferred into a glass tube with a diameter of 5 mm and a height of 100 mm. Three tubes were prepared. The level of the beads was marked before filling with 1 mL of 5 % (v/v) acetic acid, 0.10 M NaOH and distilled water. They were left for 24 h. After that, the height of the beads in all three solutions was calculated. The percentage swelling was calculated using the following equation:

$$S = \left(\frac{h_t - h_0}{h_0} \right) \times 100 \quad (1)$$

where, S is the percentage of swelling (%), h_t is the height of swollen beads or chitosan-H₂SO₄ beads at time t (cm), h_0 is the initial height of chitosan beads or chitosan-H₂SO₄ beads (cm).

Batch adsorption experiments

A stock solution of 500 mg/L of MG was prepared freshly by dissolving approximately 0.25 g of MG in a 250 mL beaker with distilled water. The solution was transferred into a 500 mL volumetric flask. A series of experiments were conducted in 250 mL beaker using 0.05 g of chitosan-H₂SO₄ beads and left shaking for 30 minutes using Heidolph Unimax 1010 shaker. The absorbance of MG was obtained before and after adsorption at the maximum wavelength of 224 nm using a UV-Vis spectrophotometer (Perkin Elmer Lambda 35).

The effect of initial pH of the solution on the adsorption of MG onto chitosan-H₂SO₄ was performed in the pH range of 2-12. Six sets of 100 mL of MG solutions with concentration of 10 mg/L were prepared.

Adsorption equilibrium analysis was performed at optimum condition where the pH is 6 and the agitation time is 30 minutes for chitosan-H₂SO₄ beads. Isotherm studies were accomplished with a constant amount of chitosan-H₂SO₄ beads and varying the initial concentration of MG in the range of 0-70 mg/L. The adsorption capacity (q_e) at equilibrium was calculated using the following equation:

$$q_e = \frac{C_0 - C_e}{m} v \quad (2)$$

where q_e is the adsorption capacity at equilibrium (mg/g), C_0 is the initial concentration of MG (mg/L), C_e is the final concentration of MG (mg/L), v is the volume of MG (mL), m is the weight of the beads used (g). For batch kinetics studies of MG onto adsorbent was also studied. About 0.05 g of chitosan-H₂SO₄ beads were equilibrated at optimum condition. The beads and 10 mg/L of MG solutions were placed in 250 mL beakers and stirred continuously. The concentration of MG in solution was determined each time based on the differences of MG concentration in the solution before and after adsorption. Three replicates analyses have been done for each adsorption study and the average was reported.

In addition, several parameters were optimized too. Effect of adsorbent dosage (percentage removal) was calculated using the following expression:

$$\% \text{ Removal} = \frac{C_o - C_f}{C_o} \times 100 \quad (3)$$

where C_o is the initial concentration of MG (mg/L) and C_f is the final concentration of MG (mg/L).

Models for adsorption equilibrium isotherms used in this study were Langmuir and Freundlich isotherm models. Langmuir isotherm model used is applicable for monolayer sorption on to a surface with finite number of identical sites and is given by:

$$\frac{C_e}{q_e} = \frac{C_e}{Q} + \frac{1}{Qb} \quad (4)$$

where Q is the maximum adsorption at monolayer (mg/g), C_e is the equilibrium concentration of MG (mg/L), q_e is the amount of MG adsorbed per unit weight of chitosan– H_2SO_4 beads at equilibrium concentration (mg/g) and b is the Langmuir constant related to the affinity of binding sites (mL/mg) and is a measure of the energy of adsorption. A linearized plot of C_e/q_e against C_e gives Q and b .

Freundlich isotherm model is an empirical isotherm for non-ideal adsorption on heterogeneous surfaces as well as multilayer adsorption and is expressed as [21]:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (5)$$

where K_F and n are Freundlich constant that indicates adsorption capacity (mg/g) and intensity, respectively. K_F and n can be obtained from linear plot of $\log q_e$ against $\log C_e$.

The critical features of a Langmuir isotherm can be expressed in terms of dimensionless constant separation factor, R_L which can be expressed as:

$$R_L = \frac{1}{1 + bC_o} \quad (6)$$

where R_L is the separation factor parameter, C_o is the initial concentration (mg/L) and b is the Langmuir constant (L/mg).

Meanwhile adsorption kinetic models used in this study were pseudo-first-order and pseudo-second-order. The linear form of pseudo-first-order rate equation is expressed as Equation 7 [22]:

$$\log (q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (7)$$

where q_e and q_t (mg/g) are the amount of MG absorbed onto adsorbent at equilibrium and at time t (min), respectively and k_1 (min^{-1}) is the rate constant of pseudo-first-order adsorption. The straight-line plots of $\log (q_e - q_t)$ against t will yield the values of rate constant, k_1 and q_e from the slope and intercept, respectively.

The pseudo-second-order equation is based on the assumption that chemisorption is the rate determining step and is expressed as given by Equation 8 [23]:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_e} \quad (8)$$

where $h = k_2 q_e^2$ can be regarded as the initial adsorption rate (mg/g/min) as t approaches to zero, and k_2 (g/min/mg) is the rate constant of pseudo-second-order adsorption.

Results and Discussion

Solubility and swelling test of chitosan and chitosan-H₂SO₄ beads

Chitosan is known for its stability in acidic media. Therefore, physical and chemical alterations were carried out to increase the adsorption capacity and improve the stability of chitosan-H₂SO₄ beads. According to Ngah et al. [10], the primary group of amine causes the chitosan beads to have higher hydrophilicity triggering chitosan to be easily soluble in dilute acetic solution to yield a hydrogel. Based on Table 1, it can be seen that the chitosan beads were insoluble in both distilled water and alkaline solution but completely dissolved in acidic medium giving a viscous solution. The chitosan-H₂SO₄ beads were insoluble in all three media studied. This is due to the ionic cross-linking modification with sulfuric acid greatly reinforcing the chemical stability of chitosan in acidic solution. Both the chitosan beads and chitosan-H₂SO₄ beads do not dissolve in neutral and alkaline media because there is less H⁺ ion present to protonate the amino group of chitosan. The insolubility of the chitosan-H₂SO₄ beads is important because it is the main indicator to determine the optimum pH for the adsorption process and as a sign that it can be used in all media.

Table 1. Solubility effect of chitosan beads and chitosan-H₂SO₄ beads

Adsorbent	Solubility Effect		
	5% (v/v) Acetic Acid	Distilled Water	0.1 M NaOH
Chitosan beads	Soluble	Insoluble	Insoluble
Chitosan-H ₂ SO ₄ beads	Insoluble	Insoluble	Insoluble

The percentage of swelling is the most important to understand the crystalline nature of the adsorbent. From Table 2, the percentage of swelling of chitosan-H₂SO₄ beads was much lower than the percentage of swelling observed for chitosan beads. The swelling ability of chitosan-H₂SO₄ beads depended on the degree of cross-linking. The percentage of swelling will be much lower at a higher cross-linking density [11]. In this study, chitosan beads are soluble in acidic medium but have a higher percentage of swelling in neutral and alkaline medium. However, chitosan-H₂SO₄ beads show the highest percentage in both acidic and neutral medium but a lower percentage of swelling in alkaline medium. This proved that the reduction in the swelling percentage of chitosan can be attributed to ionic linkages formed between the protonated amine groups (-NH₃⁺) of chitosan and SO₄²⁻ ions of sulfuric acid, which increased the chemical stability of the beads in acidic medium.

Table 2. Swelling behavior of chitosan beads and chitosan-H₂SO₄ beads in different medium

Adsorbent	Percentage of Swelling (%)		
	5% (v/v) Acetic Acid	Distilled Water	0.1 M NaOH
Chitosan beads	Soluble	164	104
Chitosan-H ₂ SO ₄ beads	125	81.5	71

Effect of initial pH

Figure 1 shows the effect of different pH for the adsorption of MG onto chitosan-H₂SO₄ beads. It can be seen that dye adsorption was unfavorable at pH < 4. As the pH of the system decreased, the -NH₂ groups that surround the adsorbent surface are protonated. The number of negatively charged adsorbent sites decreased and the number of positively charged surface sites increased, which did not favor the adsorption of positively charged dye cations due to electrostatic repulsion. This would cause repulsion between the -NH₃⁺ groups on the adsorbent surface and the -N⁺(CH₃)₂ groups of MG. Lower adsorption of MG at acidic pH is due to the presence of excess H⁺ ions competing with dye cations for the adsorption sites of chitosan-H₂SO₄ beads [12]. With the increase in pH, the number of H⁺ ions decreased and the adsorbent surface carried more negative charge resulting in greater attraction between the adsorbent and the cationic form of the adsorbate. Therefore, pH 6 was chosen as the optimum condition for following adsorption experiments.

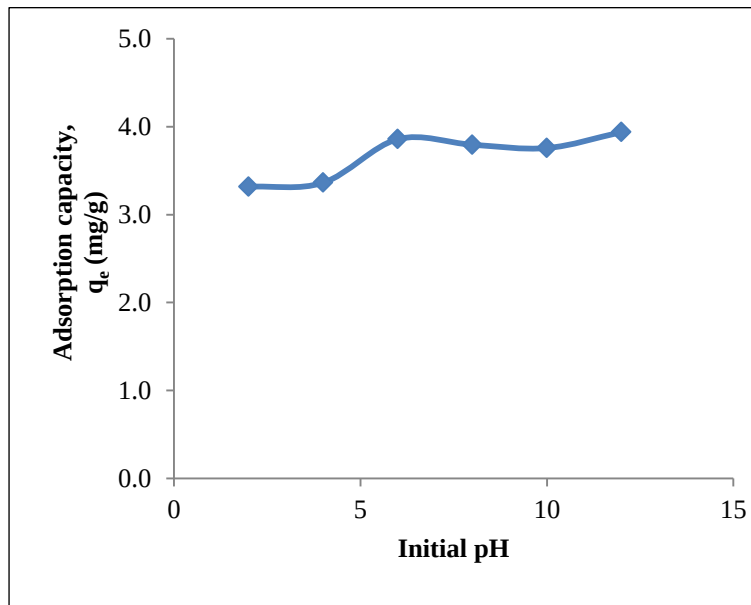


Figure 1. Effect of initial pH on the adsorption of MG onto chitosan–H₂SO₄ beads

Effect of adsorbent dosage

The effect of adsorbent dosage is illustrated in Figure 2. The percentage removal increases with the increasing adsorbent dosage from 8 to 17% for an adsorbent dosage of 0.01 g to 0.10 g. However, the adsorption capacity, which is the amount of MG adsorbed per unit weight decreased with increasing adsorbent dosage. Percentage removal is increased because the availability of adsorption surface is increased yet the decrease in adsorption capacity with increase adsorbent dosage is due to saturation of adsorption sites.

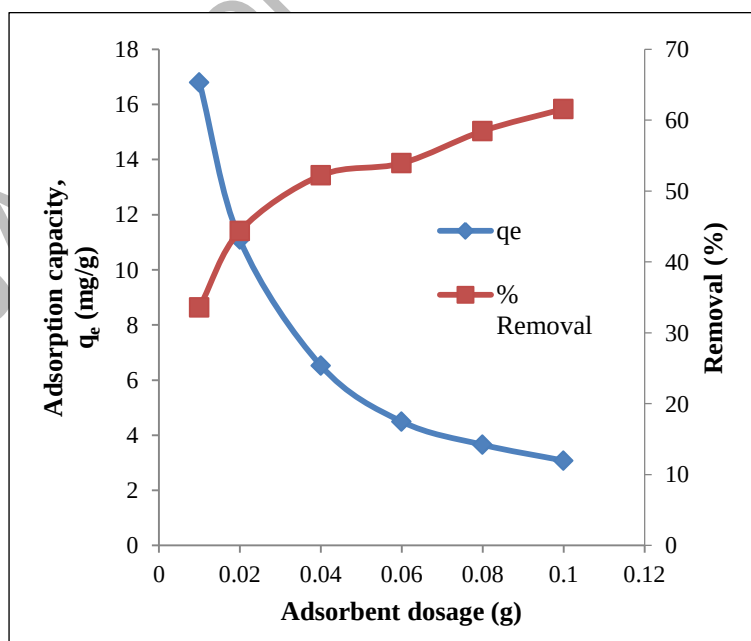


Figure 2. Effect of adsorbent dosage on the adsorption of MG onto chitosan–H₂SO₄ beads

Effect of agitation period

It is necessary to determine the optimum agitation period required for the adsorption of MG because it represented the time required for the adsorbate to reach an equilibrium state after contact with the adsorbent. The optimum period can be observed in Figure 3 by looking at a rapid adsorption capacity within the first 10 minutes, then a decrease before slowly becoming constant at 30 minutes. The initial rapid phase during the first 10 minutes was due to the availability of adsorption sites for the uptake of MG. Meanwhile, after 30 minutes the adsorption became constant because of the quick exhaustion of the adsorption sites [13]. As a result, the equilibrium time of 30 minutes was selected for additional studies.

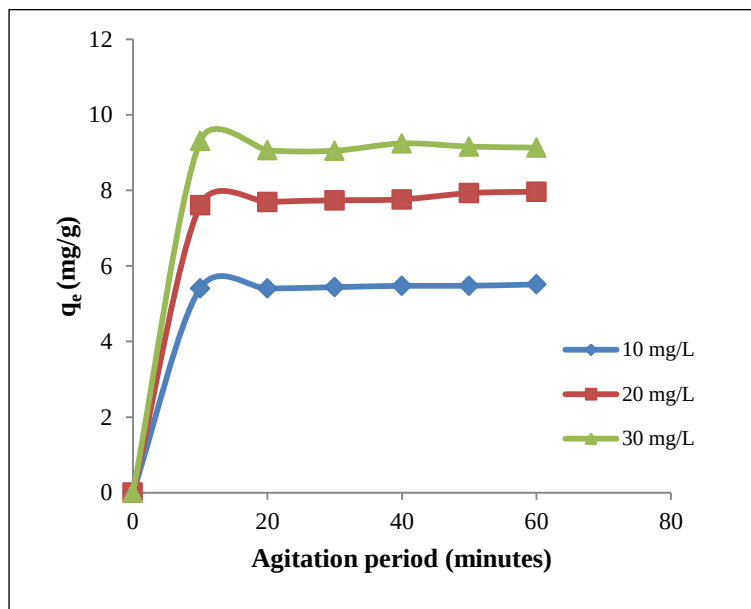


Figure 3. Effect of agitation time on the adsorption of MG onto chitosan-H₂SO₄ beads

Adsorption equilibrium isotherms

An adsorption isotherm is an expression that shows the relationship between the amounts of adsorbate adsorbed per unit weight of adsorbent (q_e , mg/g) and the concentration of adsorbate in the bulk solution (C_e , mg/L) at 300 K under equilibrium conditions. The Langmuir and Freundlich models are often used to describe equilibrium adsorption isotherms. The Langmuir isotherm usually indicates individual chemical adsorption (chemisorption) and reflects a relatively high affinity between adsorbate and the adsorbent within a low concentration range [1].

The Langmuir isotherm also assumes that the adsorbed layer is one molecule in thickness and that all adsorption sites have equal energies and enthalpies of adsorption. The linearized Langmuir and Freundlich models plot at 300 K are shown in Figures 4 and 5, respectively. Table 3 shows the obtained values for the Langmuir and Freundlich isotherms constants and coefficients of determination (R^2). Overall, the experimental data fitted well with the Langmuir isotherm model because the R^2 values were very high. This showed that chitosan-H₂SO₄ beads had homogeneous adsorption sites.

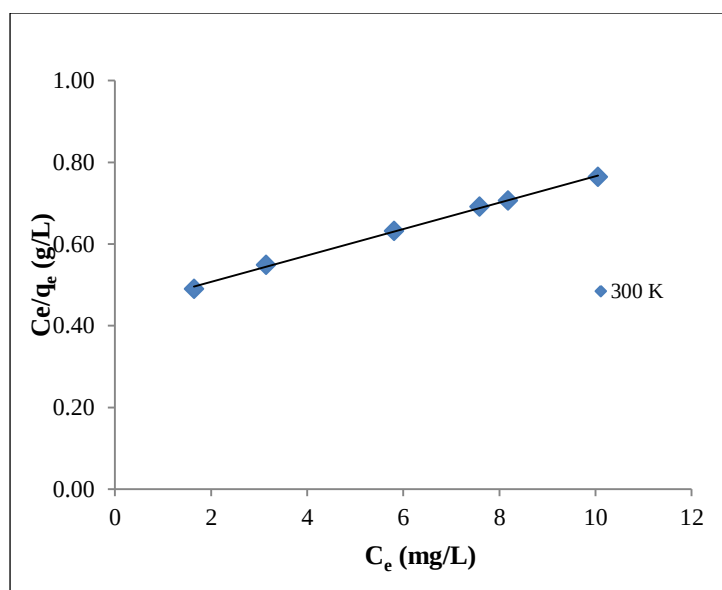


Figure 4. Linearized Langmuir adsorption isotherm of MG onto chitosan–H₂SO₄ beads

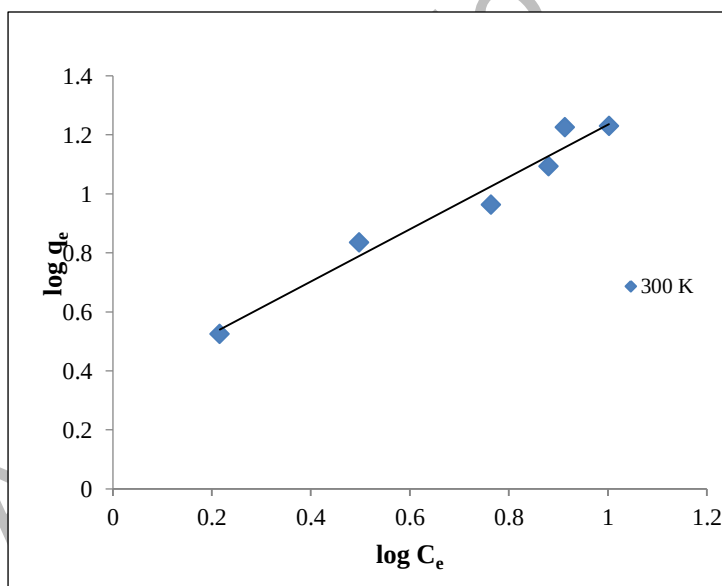


Figure 5. Linearized Freundlich adsorption isotherm of MG onto chitosan–H₂SO₄ beads

Table 3. Langmuir and Freundlich isotherm constants and correlation for the adsorption of MG onto chitosan–H₂SO₄ beads at 300 K

Langmuir			Freundlich		
Q (mg/g)	b (L/mg)	R ²	K _f (mg/g)	n	R ²
30.96	0.0730	0.9985	2.23	1.1287	0.9666

It has been stated that the effect of isotherm shape with a view to predicting if an adsorption system is ‘favorable’ or ‘unfavorable’. It has been established that for favorable adsorption, $0 < R_L < 1$; unfavorable adsorption, $R_L > 1$; linear adsorption, $R_L = 1$; and irreversible adsorption process if $R_L = 0$. Based on Table 4, the R_L values are in the range of $0 < R_L < 1$, which reveals the adsorption of MG onto chitosan- H_2SO_4 beads is favorable.

Table 4. Values of R_L for initial concentrations range from 0 to 30 mg/L at 300 K

Initial Concentration of MG (mg/L)	R_L value
5	0.7326
10	0.5780
15	0.4773
20	0.4065
25	0.3540
30	0.3135

Adsorption kinetics

The kinetics of adsorption is applied to determine the adsorption rate of MG uptake on the beads. The most common kinetic models applied in adsorption studies are pseudo-first-order and pseudo-second-order. Figure 6 represents the pseudo-first-order kinetic plot for chitosan- H_2SO_4 beads.

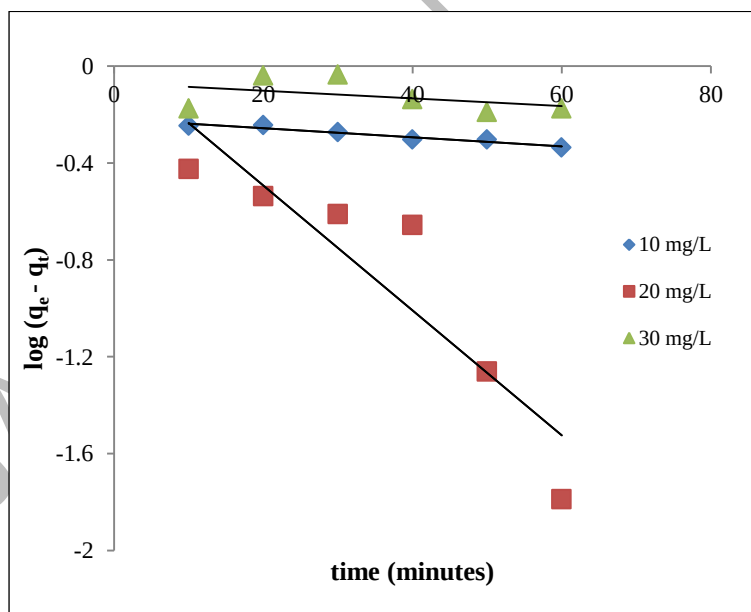


Figure 6. Plot of pseudo-first-order kinetic model for the adsorption of MG onto chitosan- H_2SO_4 beads

The straight-line plots of t/q_t against t were used to determine the rate constant, k_2 and coefficient of determination, R^2 . Figure 7 represents the pseudo-second-order plot for chitosan- H_2SO_4 beads. The results of kinetic parameters of the pseudo-first-order and pseudo-second-order kinetic models for the adsorption of MG are given in Table 5. Based on the R^2 values shown in the table, it can be concluded that the pseudo-second-order kinetic model can be used to represent the adsorption behavior over the whole range of contact time. Moreover, the calculated adsorption

capacity ($q_{e, \text{calc}}$) values were in agreement with the experimental adsorption capacity ($q_{e, \text{exp}}$) value. This showed that the uptake of MG onto chitosan–H₂SO₄ beads was rapid and favorable. The initial adsorption rate, h , of the pseudo-second-order kinetic model increased as concentrations increased. The large number of adsorption sites available on chitosan–H₂SO₄ beads might cause the rapid adsorption of MG at higher concentrations, possibly due to the increase in the driving force for mass transfer, and thus, allowing MG molecules to reach the adsorbent surface in a shorter period of time [24, 25].

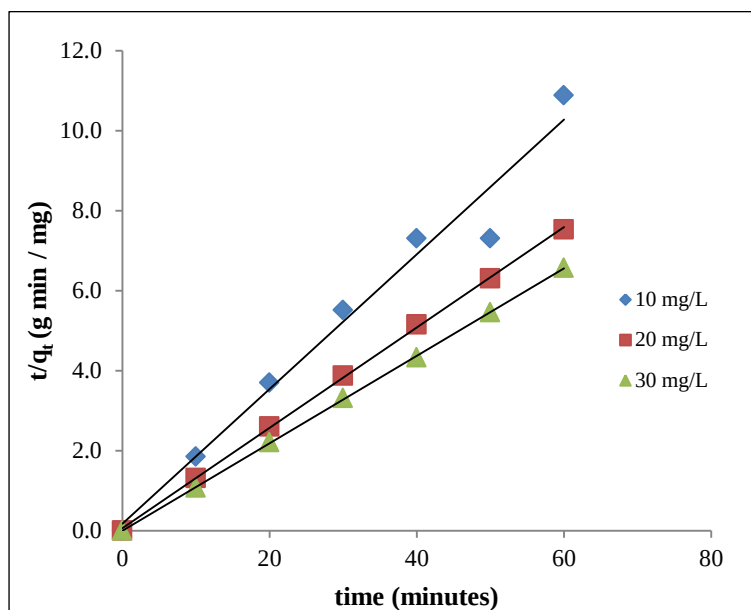


Figure 7. Plot of pseudo-second-order kinetic model for the adsorption of MG onto chitosan–H₂SO₄ beads

Table 5. Kinetic parameters for the adsorption of MG onto chitosan–H₂SO₄ beads based on pseudo-first-order and pseudo-second-order kinetic model

Concentration of MG (mg/L)	Pseudo-First-Order			Pseudo-Second-Order				
	$q_{e, \text{exp}}$ (mg/g)	k_1 (1/min)	R^2	$q_{e, \text{calc}}$ (mg/g)	k_2 (g/mg /min)	h (mg/g /min)	R^2	$q_{e, \text{calc}}$ (mg/g)
10	5.97	4.38×10^{-3}	0.9335	0.61	0.17	5.97	0.9716	5.93
20	7.98	5.94×10^{-2}	0.8227	1.06	0.25	16.10	0.9996	7.97
30	9.97	3.68×10^{-3}	0.1768	0.85	23.89	1999.74	0.9999	9.15

FT-IR analysis

The FTIR spectra obtained for chitosan beads and chitosan–H₂SO₄ beads before and after adsorption were shown in Figure 8. The broad peaks at 3428.58 cm⁻¹ in chitosan beads can be assigned to stretching vibration of hydroxyl group and N–H groups found in chitosan. The adsorption band at 1655.12 cm⁻¹ is the N–H bending in primary amine groups (–NH₂). Other major band observed at 1383.14 cm⁻¹ represents C–N stretching vibration. After the cross-linking process, several changes were observed in the spectra obtained for chitosan–H₂SO₄ beads. The broad peak at 3428.58 cm⁻¹, shifted to 3423.52 cm⁻¹ and eventually become broader. This showed that the –NH₂ groups in chitosan were protonated to –NH₃⁺, as this broader band represented the stretching vibration of –NH₃⁺. The adsorption bands at 1635.05 and 1532.64 cm⁻¹ represented the bending vibration of –NH₃⁺ groups. The involvement

of SO_4^{2-} ions in the cross-linking process was confirmed by the presence of the adsorption bands at 1191.64 cm^{-1} that represented the sulfo groups. The band observed at 1076.47 cm^{-1} also confirmed the presence of S=O stretching found in the SO_4^{2-} ions. This FTIR spectra proved that the formation of chitosan- H_2SO_4 beads was through the ionic interaction between the protonated amine groups ($-\text{NH}_3^+$) of chitosan and the SO_4^{2-} ions of sulfuric acid. The FTIR of chitosan- H_2SO_4 beads after adsorption showed there were no appearances of new bands. However, there were adsorption bands at 887.59 and 855.15 cm^{-1} represented $-\text{NH}_3^+$ rocking vibrations. These spectral changes shown that many amine groups were protonated to form $-\text{NH}_3^+$.

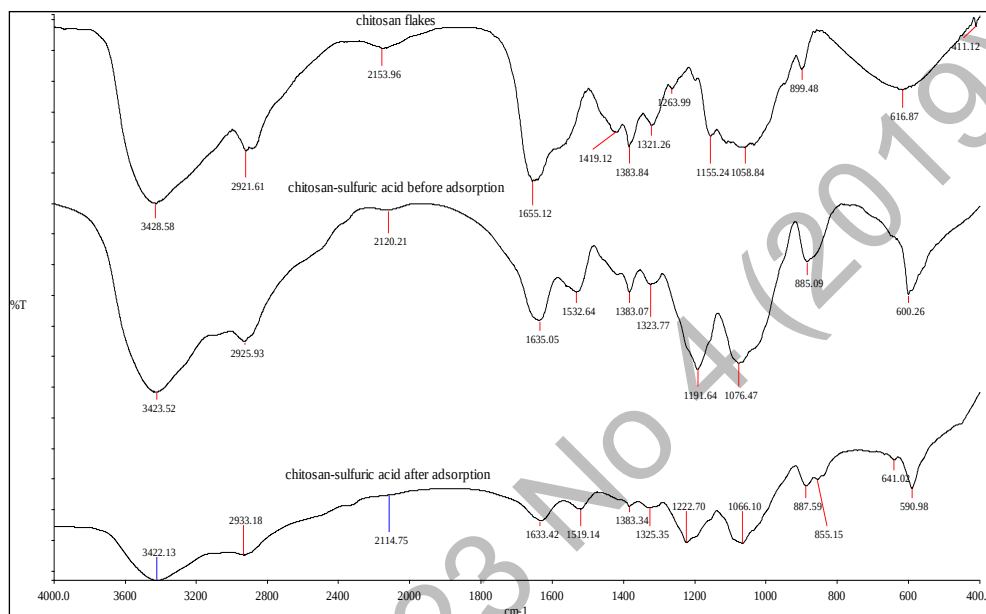


Figure 8. Infrared spectra for chitosan flakes and chitosan- H_2SO_4 before and after adsorption

Conclusion

This study demonstrated that chitosan- H_2SO_4 beads are a promising adsorbent for the removal of MG from aqueous solutions. Chitosan- H_2SO_4 beads show a lower percentage of swelling than chitosan beads. The adsorption isotherm could be well fitted by the Langmuir equation and the MG adsorption followed the pseudo-second-order equation. The interaction between MG and chitosan- H_2SO_4 beads was confirmed by FTIR spectroscopy. Hence, it can be concluded that chitosan- H_2SO_4 beads are effective adsorbents for the uptake of MG sorption studies. Based on these findings, the prepared chitosan- H_2SO_4 beads can be used to remove MG from the wastewater, which is currently being carried out. In addition, the chitosan- H_2SO_4 beads can also be prepared in membrane, microbead and nanoparticle forms. It is expected that the removal of MG shall be increased with the use of different physical shapes of the cross-linked chitosan- H_2SO_4 .

Acknowledgement

Authors would like to thank Universiti Sains Malaysia for providing financial assistances through a bridging grant (304/PKIMIA/6316215) and a short-term grant (304/PKIMIA/6315197).

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