Sorption of malachite green on chitosan bead

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Abstract

Chitosan bead was synthesized for the removal of a cationic dye malachite green (MG) from aqueous solution. The effects of temperature (303, 313 and 323 K), pH of the solution (2–11) on MG removal was investigated. Preliminary kinetic experiment was carried out up to 480 min. The sorption equilibrium was reached within 5 h (300 min). In order to determine the adsorption capacity, the sorption data were analyzed using linear form of Langmuir and Freundlich equation. Langmuir equation showed higher conformity than Freundlich equation. Ninety-nine percent removal of MG was reached at the optimum pH value of 8. From kinetic experiments, it was obtained that sorption process followed the pseudo-second-order kinetic model. This study showed that chitosan beads can be excellent adsorbents at high pH values. Activation energy value for sorption process was found to be $85.6\,kJ\,mol^{-1}$. This indicates that sorption process can be assumed as chemical process. Due to negative values of Gibbs free energy, sorption process can be considered as a spontaneous. In order to determine the interactions between MG and chitosan bead, FTIR analysis was also conducted.
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Keywords: Chitosan bead; Malachite green; Sorption

1. Introduction

Malachite green (MG) is an *N*-methylated diaminotriphenyl-methane dye (Fig. 1) widely used in the fish and dye industries [1]. The used of malachite green in aquaculture industry has a long history, dating back to 1933, when it was first introduced [2]. MG is highly effective against important protozoal and fungal infections [3]. Aquaculture industries have been using malachite green extensively as a topical treatment by bath or flush methods without paying any attention to the fact that topically applied theropeutants might also be absorbed systemically and produce significant internal effects [3]. On the other hand, it is also used as a food coloring agent, food additive, and a medical disinfectant and anthelminthic as well as a dye in silk, wool, jute, and leather cotton, paper and acrylic industries [4]. However, malachite green has now become a highly controversial compound due to the risks it poses to the consumers of treated fish [5] including its effects on the immune system, reproductive system and its genotoxic and carcinogenic properties [6–8].

Due to the these facts, malachite green is on the Food and Drug Administration's (FDA's) priority list for fish drugs that need analytical methods of development [9]. In response to concerns regarding the health risks associated with the use of dyes, adsorption is, by far, the most versatile and widely used technique for the removal of dyes from aqueous solutions [4,10].

Many adsorbents have been tested on the possibility to lower dye concentrations from aqueous solutions, such as activate carbon [7,9], peat [11,12], chitin [13], silica [14], and others [15].

In this study, chitosan was used as adsorbent for the removal of malachite green from aqueous solution, since chitosan is highly abundant natural biopolymer. Chitosan, named poly (β-1,4)-2-amino-2-deoxy-D-glucopyranose, a poly (D-glucosamine) is prepared from chitin by deacetylating its amido groups [16]. Chitosan contains –OH and –NH$_2$ groups that can give rise to hydrogen bonding and the linear molecule express sufficient chain flexibility. It is insoluble in water, alkali and many organic solvent [17].

The aim of this study was to clarify adsorption behavior of chitosan for removal of cationic malachite green from aqueous solution. For that reason, the equilibrium and kinetics of adsorption of malachite green from aqueous solution were investigated.

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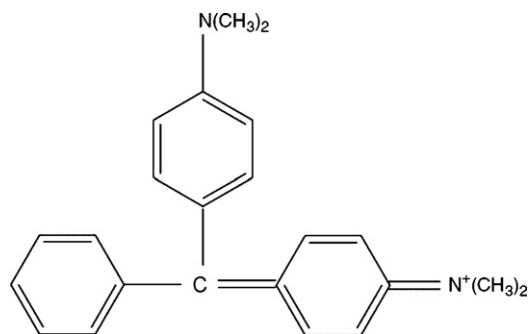*E-mail address:* k.yurdakoc@deu.edu.tr (K. Yurdakoç).

Fig. 1. Chemical structure of malachite green.

Langmuir and Freundlich equations were used to fit the equilibrium isotherms. The kinetics of adsorption was determined by using pseudo first-order and pseudo-second-order reaction and intraparticle diffusion. In addition, the equilibrium thermodynamic parameters were determined for the MG adsorption on the chitosan. The influence of contact time and pH were also studied.

2. Material methods

2.1. Synthesis of chitosan bead

Chitosan is a commercial product supplied from Fluka (Cat no. 48165). Chitosan solution was prepared by dissolving 2.00 g chitosan flakes into 50 mL of 5% (v/v) acetic acid solution. It will take about one night to dissolve chitosan completely. Then the solution is dropped into 0.1 M NaOH by using pipette tips which neutralized the acetic acid within the chitosan gel and there by coagulated the chitosan gel get to special uniform chitosan gel beads. The aqueous NaOH solution was stirred using magnetic shaker. The wet chitosan gel beads were extensively rinsed with distilled water to remove any NaOH, filtered and finally air dried to remove the water from the pore structure. The beads were then ground by using grinder and sieved to constant size before use.

MG used in this study is a commercial product of Fluka (Cat no. 42000). The structural formula of MG was shown in Fig. 1.

2.2. Adsorption study

Adsorption isotherms were determined by using batch equilibrium method. For batch adsorption experiments, 0.05 g of chitosan was added 25 mL of malachite green solution. Concentrations of MG in aqueous solution were between 20 and 240 μM. The solutions were shaken at 150 rpm in a temperature controlled shaking water bath (Memmert) for 5 h to reach equilibrium under experimental conditions. After 5 h, the samples were taken and centrifuged at 5000 rpm for 15 min. Liquid phases were taken and equilibrium concentration of dye in resultant solution was determined by using Shimadzu UV-Visible 1601 model spectrophotometer at $\lambda_{max} = 618$ nm. The amount of MG adsorbed on chitosan was calculated from difference of initial concentration and the equilibrium concentration of MG.

The amount of MG sorbed on chitosan bead was calculated by the following equation:

$$q_e = (C_o - C_e)\frac{V}{m} \qquad (1)$$

where q_e is the amount of MG sorbed (mg g^{-1}), C_o and C_e the initial and equilibrium concentration of MG, V the volume of the solution and m the amount of adsorbent, respectively.

In order to obtain thermodynamic parameters, the same procedures were also performed at the solution temperatures of 303, 313 and 323 K.

2.3. FTIR study

Infrared spectral data obtained from Perkin Elmer FTIR spectrophotometer (Spectrum BX-II) was utilized to determine the interaction between chitosan and malachite green at room temperature. For this reason, pellets were prepared as KBr disks. Chitosan and MG loaded chitosan pellets were prepared using the same ratio of chitosan (1 mg) and MG + chitosan (1 mg) in KBr (100 mg, dried at 383 K). The infrared spectra in the range 4000–400 cm^{-1} were recorded for chitosan and MG + chitosan pellets.

2.4. SEM measurements

The surface morphology of both chitosan and MG loaded chitosan was examined by means of scanning electron microscopy (SEM, Jeol JSM 60) at an accelerating voltage of 20 kV attached an X-ray energy dispersive spectrometer, EDS. The samples were dried and coated with gold before scanning. For SEM, photographs were taken at different magnifications (between 1000× and 10,000×).

3. Results and discussions

3.1. The effect of contact time on adsorption of MG onto chitosan bead

To determine the optimum contact time for adsorption of malachite green onto chitosan, the equilibrium concentrations were measured at certain times and the amounts of malachite green adsorbed were estimated by the equilibrium concentrations which were obtained. Then, the curve that indicated the effect of contact time on adsorption was plotted the amount of malachite green adsorbed (C_s, mg g^{-1}) measured in the certain time intervals versus time. As can be seen from Fig. 2, initial work over 8 h period indicated that equilibrium is almost established within 5 h.

3.2. Adsorption of MG onto chitosan

The adsorption isotherms of MG on chitosan were determined by plotting the amount of MG adsorbed by chitosan (C_s, mg g^{-1}) versus equilibrium concentrations of MG (C_e, mg L^{-1}). Fig. 3 shows the MG sorption isotherms at 303, 313 and 323 K, respectively. In terms of the slope of initial portion of the curves,
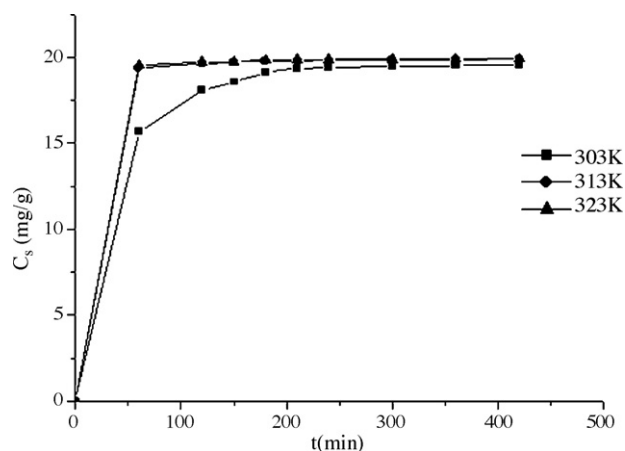
Fig. 2. Effect of contact time of malachite green adsorption onto chitosan for $40\,\text{mg}\,\text{L}^{-1}$ at 303, 313 and 323 K.
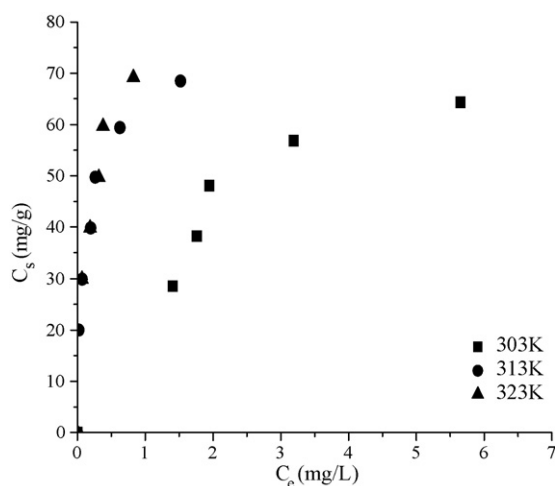

Fig. 3. Adsorption isotherms of MG on chitosan at different temperatures.

the shapes of these isotherms resemble to L type according to the Giles classification [18]. The L curve indicates that there is no strong competition from the solvent for sites on the surface. In that study, it can be easily said that chitosan has a medium affinity for the MG molecules. The curves tend to constant value of C_s and reach a plateau showing the formation of a complete monolayer of MG covering adsorbent surface. The amount of MG adsorbed by chitosan is raised by increasing temperature.

Langmuir Eq. (2) and Freundlich Eq. (3) are applied to evaluate the adsorption data. In order to find sorption capacities of the chitosan, the linear forms of these equations are used.

$$\frac{C_e}{C_s} = \frac{1}{C_m L} + \frac{C_e}{C_m} \qquad (2)$$

$$\ln C_s = \ln K_f + n_f \ln C_e \qquad (3)$$

where C_e is the liquid phase concentrations of adsorbate at equilibrium $(\text{mg}\,\text{L}^{-1})$, C_s the solid phase concentrations of adsorbate at equilibrium $(\text{mg}\,\text{g}^{-1})$, C_m the maximum adsorption capacity (maximum amount that can be adsorbed by adsorbent as a monolayer) $(\text{mg}\,\text{g}^{-1})$, L Langmuir constant regarding the adsorption energy, K_f relative adsorption capacity $(\text{mg}\,\text{g}^{-1})$,

n_f heterogeneity factor (adsorption intensity). Linear regression was frequently used to determine the most fitted isotherm, and the method of least squares has been used for finding the parameters of the isotherms [19]. The Langmuir constant (L) and monolayer capacity were estimated from the intercept and slope of Eq. (2). Table 1 shows the estimated C_m and L values and corresponding linear correlation coefficients at different temperatures. C_m (maximum adsorption capacity) values are $93.55\,\text{mg}\,\text{g}^{-1}$ at $30\,^{\circ}\text{C}$; $72.83\,\text{mg}\,\text{g}^{-1}$ at $40\,^{\circ}\text{C}$; $82.17\,\text{mg}\,\text{g}^{-1}$ at $50\,^{\circ}\text{C}$, respectively. In addition, L values are $0.41\,\text{mg}\,\text{L}^{-1}$ at $30\,^{\circ}\text{C}$; $8.75\,\text{mg}\,\text{L}^{-1}$ at $40\,^{\circ}\text{C}$ and $6.09\,\text{mg}\,\text{L}^{-1}$ at $50\,^{\circ}\text{C}$, respectively. It can be added that although the adsorption of MG onto chitosan bead can be fitted by Langmuir for all studied temperatures, the assumptions of these isotherms may not be purely satisfied.

To determine the adsorption process is favorable or unfavorable, for the Langmuir type adsorption process, the isotherm shape can be classified by a term 'R_L' a dimensionless constant separation factor, which is defined as below:

$$R_L = \frac{1}{1 + a_L C_0} \qquad (4)$$

where a_L is Langmuir isotherm constant, C_0 initial malachite green concentration $(\text{mg}\,\text{L}^{-1})$.

The shapes of the isotherms for $0 < R_L < 1$, $R_L > 1$, $R_L = 1$ and $R_L = 0$ are favorable, unfavorable, linear and irreversible, respectively [20]. The values of R_L (dimensionless separation factor) at different temperatures are reported in Table 1. The values of R_L were between 0 and 1. These values indicated that favorable adsorption for MG occurred.

The Freundlich constant K_f and Freundlich exponent n_f can be obtained from the slope and intercept of the plot between $\ln C_s$ and $\ln C_e$. A graph indicating adsorption of MG onto chitosan which is formed by plotting $\ln C_s$ versus $\ln C_e$ is shown in the Fig. 4. The correlation coefficients are greater than 0.82. The correlation factors (R^2) indicated that better applicability was obtained using linearized Langmuir than Freundlich isotherms.

Freundlich constants were shown in Table 1. As can be seen from Table 1, K_f values are raised by increasing temperature. This result indicates that adsorption capacities of chitosan decrease when temperatures decrease. It can be said that the values of n_f are smaller than 1, reflecting favorable adsorption [21]. The n_f is indicator of heterogeneity factor. If the value of n_f

Table 1
Adsorption Isotherm constants for MG onto chitosan bead

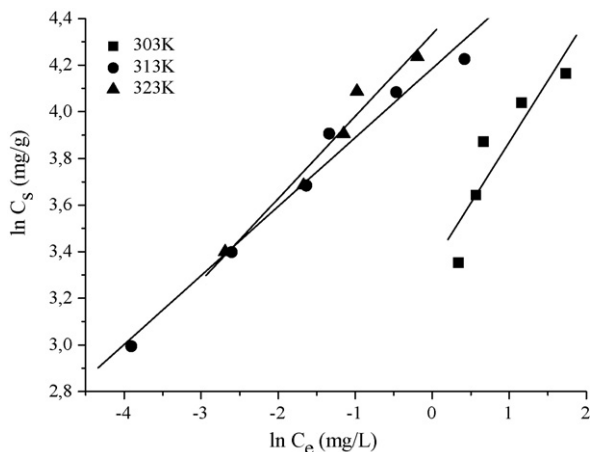|	303 K	313 K	323 K
Langmuir isotherm constants			
C_m $(\text{mg}\,\text{g}^{-1})$	93.55	72.83	82.17
L $(\text{L}\,\text{mg}^{-1})$	0.41	8.75	6.09
R_L	0.058	0.003	0.004
R^2	0.982	0.996	0.982
Freundlich isotherm constants			
K_f $(\text{mg}\,\text{g}^{-1})$	28.38	65.76	76.23
n_f	0.53	0.30	0.35
R^2	0.817	0.977	0.966

Fig. 4. Freundlich plots for adsorption of MG onto chitosan at different temperatures.

is equal unity, the adsorption is linear. It indicates that adsorption sites are not homogeneous in energy. Both these theories suffer from the disadvantage that equilibrium data over a wide concentration range cannot be fitted with single set of constant [22].

3.3. Effect of pH on adsorption of MG onto chitosan

The influence of pH on the MG adsorption onto chitosan was studied while the MG concentration, shaking time and amount of chitosan were fixed at 50 mg L^{-1}, 6 h and 0.05 g, respectively. The variation of dye adsorption onto chitosan over a pH range of 2.1–11.0 is shown in Fig. 5. The result reveals that the adsorption of malachite green increases from 18.80% to 99.38% with an increase in pH of the solution from 2.1 to 11.0. Beyond the pH value of 8, the amount of adsorbed remains almost constant. The adsorption of the charged dye groups onto the chitosan is primarily influenced by the pH of the solution. The chitosan had positive charge in acidic condition.
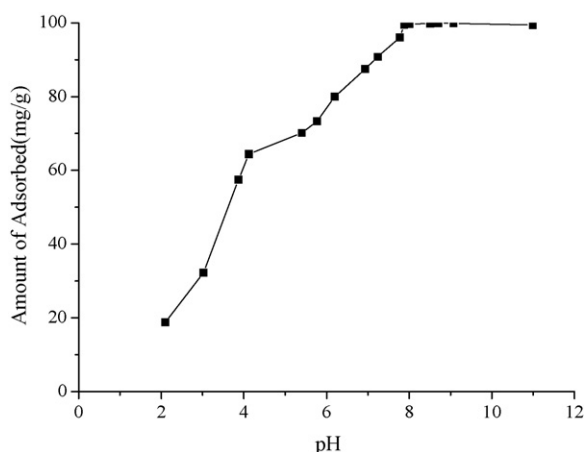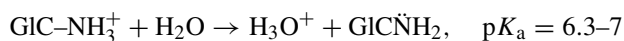
$$GlC-NH_3^+ + H_2O \rightarrow H_3O^+ + GlC\ddot{N}H_2, \quad pK_a = 6.3-7$$

Fig. 5. pH effects on adsorption of MG onto chitosan.

Since the pK_a value of chitosan (GlC–NH$_3^+$) is in the pH range of 6.3–7, the amino groups of chitosan are protonated at low pH values. MG is a cationic basic dye as denoted by the presence of the positive nitrogen ion enters the aqueous solution ensuring that the dye has an overall positive charge. In acidic pH, cationic chitosan repulse the cationic dye, for that reason, the adsorption of malachite green onto chitosan is low in acidic pH. However the pH is increased to basic pH values, the amino groups of chitosan are deprotonated. In this case, the interaction between cationic MG and the pair of electrons of nitrogen present in the structure of chitosan occurs. It is clear that the adsorption of dye onto chitosan at basic pH values is high.

3.4. Adsorption kinetics

To optimize the design of an adsorption system of MG onto chitosan bead, it is necessary to establish the most appropriate correlations for the equilibrium data for each system. Therefore, several kinetic models including the pseudo first order equation, pseudo second order equation, and intraparticle diffusion model were applied to find out adsorption mechanism.

$$\frac{1}{q_t} = \left(\frac{k_1}{q_1}\right)\left(\frac{1}{t}\right) + \frac{1}{q_1} \quad \text{(pseudo-first-order)} \tag{5}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_2^2} + \left(\frac{1}{q_2}\right) t \quad \text{(pseudo-second-order)} \tag{6}$$

$$q_t = k_p t^{0.5} + C \quad \text{(intraparticle diffusion)} \tag{7}$$

where q_t is the amount of MG adsorbed (mg g^{-1}) on chitosan at various time t, q_1 the maximum adsorption capacity (mg g^{-1}) for the pseudo first order adsorption, k_1 the pseudo-first-order rate constant for the adsorption process (min^{-1}), q_2 the maximum adsorption capacity (mg g^{-1}) for the pseudo-second-order adsorption, k_2 the rate constant of pseudo-second-order for the adsorption (g mg^{-1} min^{-1}), k_p the intraparticle diffusion rate constant (mg g^{-1} min$^{-0.5}$), C the intercept for the intraparticle diffusion model (mg g^{-1}). The results were given in Table 2.

The straight-line plots of $1/q_t$ against $1/t$ for the pseudo-first-order reaction and t/q_t against t for the second-order reaction

Table 2
Kinetic parameters for MG adsorption onto chitosan bead at different temperatures for 40 mg L^{-1}

	303 K	313 K	323 K
The pseudo-first-order			
k_1 (min^{-1})	18.89	2.00	1.46
q_1 (mg g^{-1})	20.75	20.00	19.99
R_1^2	0.972	0.987	0.942
The pseudo-second-order			
k_2 (g mg^{-1} min^{-1})	0.006	0.049	0.052
q_2 (mg g^{-1})	19.53	19.49	19.95
R_2^2	0.998	0.999	1.000
Intraparticle diffusion			
k_p (mg g^{-1} min$^{-1/2}$)	0.26	0.04	0.03
C (mg g^{-1})	14.94	19.21	19.41
R_p^2	0.840	0.916	0.898

of the adsorption MG onto chitosan have been investigated to obtain the rate parameters. The k_1, k_2, q_1, q_2 and correlation coefficients R_1^2 and R_2^2 of MG under different conditions were calculated from these plots and are given in Table 2 [23].

As can be seen from Table 2, the coefficients (R_1^2) for pseudo first order kinetic model are between 0.942 and 0.987 and the correlation coefficients (R_2^2) for pseudo-second kinetic model are between 0.998 and 1.000. These results show that the adsorption system obeys the pseudo-second-order kinetic model.

Adsorption kinetics are usually controlled by different mechanisms, of which the most limiting are the diffusion mechanisms, including the initial curved portion, attributed to rapid external diffusion or boundary layer diffusion and surface adsorption, and the linear portion, q gradual adsorption stage due to intraparticle diffusion starts to decrease due to the low concentration in solution as well as fever available adsorption sites.

The rate-limiting step may be due to intraparticle diffusion. The rate constant for the intraparticle diffusion was obtained using Eq. (7).

C gives an idea about the boundary layer thickness. If the intraparticle diffusion is involved in the adsorption process, then a plot the square root of time ($t^{1/2}$) versus the uptake (q_t) would result in a linear relationship and the particle diffusion would be the controlling step if this line passed through the origin. When the plots do not pass through the origin, this is indicative of some degree of boundary layer control and the further show that the intraparticle diffusion is not the only rate-controlling step, but also other processes may control the rate of adsorption, all of which may be operating simultaneously [24].

From Table 2, it is understood that the intraparticle diffusion is not the rate controlling step. Other process may control the rate of adsorption. The correlation coefficients (R_p^2) for the intraparticle diffusion model are between 0.840 and 0.916. The linear portions of curves do not pass through the origin. This indicates that the intraparticle diffusion is not the only rate controlling step for the adsorption mechanism of MG onto chitosan complex. The larger the intercept (C value), the greater is the boundary layer effect. C values are for example; 14.94, 19.21 and 19.41 mg g^{-1} at 303, 313 and 323 K for 40 mg L^{-1}, respectively. C values were found to be 69.36 and 43.35 mg g^{-1} for MG adsorption onto modified rice straw and native rice straw respectively in ref. [25]. C values obtained in this study are rather less than that values. This indicates that boundary layer effect is not so much efficient for the adsorption of MG onto chitosan bead.

3.5. Thermodynamic parameters of adsorption

The thermodynamic parameters of the adsorption process are obtained from experiments at various temperatures. It is essential to clarify the change of thermodynamic parameters. Gibbs energy change, ΔG° are estimated by applying thermodynamic equation [24].
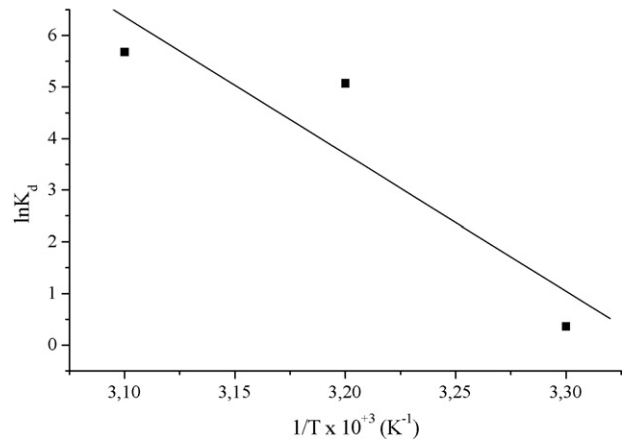
$$\Delta G^\circ = -RT \ln K_d \tag{8}$$

Fig. 6. van't Hoff plot for adsorption of malachite green onto chitosan bead.

where K_d is the equilibrium constant at temperature T, R gas constant (8.314 J mol^{-1} K^{-1}), T absolute temperature (K).

For each temperature, the same t values were selected (360 min) and from this value, firstly q_t and then C_s and C_e values were calculated by using pseudo second order equation. K_d was estimated using the following equation;

$$K_d = \frac{C_s}{C_e} \tag{9}$$

where C_e is the equilibrium concentration, C_s the amount of adsorbed. To determine the values of ΔH° and ΔS°, the van't Hoff equation is used;

$$\ln K_d = \left(\frac{\Delta S^\circ}{R}\right) - \left(\frac{\Delta H^\circ}{RT}\right) \tag{10}$$

ΔH° and ΔS° were calculated the slope and intercept of van't Hoff plots of $\ln K_d$ versus $1/T$ which were presented in Fig. 6. Thermodynamic parameters calculated with the second-order rate constant are presented Table 3.

The Gibbs free energy demonstrates a spontaneous and favorable adsorption process. The higher negative value reflects a more energetically favorable adsorption [26]. The Gibbs free energy value at 323 K is the highest negative value than the values of other temperatures. For that reason, more energetically favorable adsorption is occurred 323 K.

As shown Table 3, the values ΔH° and ΔS° were positive for adsorption of MG onto chitosan. The important thermodynamic function ΔH° is very useful whenever there is a differential change occurs in the system. The positive value of ΔH° indicates that the adsorption process is endothermic in nature and the positive value ΔS° showed the increase in degree of freedom or increases the disorder of adsorption process. The positive value of ΔS° suggests increase randomness at solid/solution interface

Table 3
Thermodynamic parameters for adsorption of MG onto chitosan

Temperature (K)	ΔH° (kJ mol^{-1})	ΔS° (J mol^{-1} K^{-1})	ΔG° (kJ mol^{-1})
303	221.3	738.8	−0.90
313			−13.20
323			−15.25

Fig. 7. The Arrhenius plot for MG adsorption onto chitosan.

3.6. SEM analysis

Fig. 8 shows SEM images of the chitosan beads (at 3000× and 4300× magnifications). As can be seen from Fig. 8 a and b, pores with different size were observed. In addition to this, as shown from Fig. 8, micro-particles are observed. Macroscopically synthesized chitosan beads are generally spherical and adhere to each other and held together. As shown in Fig. 8, pores smaller than 1 μm are observed on the surface of the chitosan bead. Those pores are very suitable places for the sorption of malachite green.

3.7. FTIR analysis

The FTIR spectra of chitosan bead before and after adsorption were shown in Fig. 9. The wide band at 3430 cm^{-1} shown in the spectrum of chitosan bead is attributed to stretching vibration of hydroxyl group of chitosan. This band was shifted to 3423 cm^{-1} when MG was adsorbed. It may indicate a hydrogen bond between malachite green and OH groups of chitosan. The small band at 3748 cm^{-1} is due to stretching vibration of N–H groups. It is not seen exactly in the spectrum of Chit-MG. The band at 2923 cm^{-1} shown in Fig. 9 is assigned to the C–H stretching vibration of polymer backbone. There was significant decrease for that band in the spectrum of malachite green. This band was shifted from 2923 to 2877 cm^{-1}. This can be considered as the evident for the interaction between chitosan and MG cation. The band at 1413 cm^{-1} in the spectrum of chitosan bead is due to C-H bending which was appeared as duplicate at 1419 and 1379 cm^{-1} in the spectrum of chitosan bead after adsorption. The band at 1379 cm^{-1} in the spectrum of Chit-MG is assigned to a symmetrical deformation of the CH$_3$ group. The bands observed at 1640 and 1562 cm^{-1} correspond to N–H bending vibrations. These bands were shifted from 1640 and 1562 cm^{-1} to 1654 and 1589 cm^{-1} when the adsorption of MG occurs. These changes may be owing to weak interactions between MG and chitosan. Presumably it can be claimed that hydrogen bonding occurs between nitrogen and hydrogen of chitosan and MG. As was indicated by Paulino et al. [27], the band
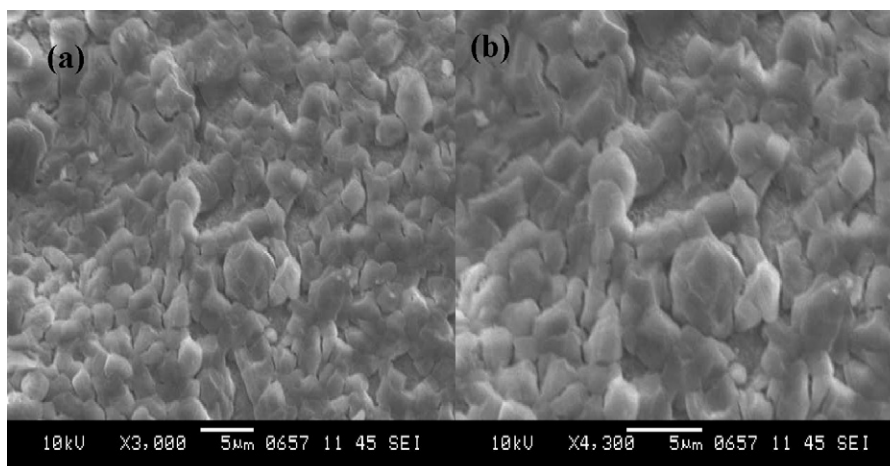
and significant changes occur in the internal structure of the adsorbent through the adsorption of MG onto chitosan [24].

The activation energy, E_a, was obtained from an Arrhenius plot. Arrhenius equation is shown as below;

$$\ln k_2 = \ln A - \frac{E_a}{RT} \qquad (11)$$

where k_2 is the rate constant of pseudo-second order adsorption (g mg^{-1} min^{-1}), A, the Arrhenius factor, R gas constant (8.314 J mol^{-1} K^{-1}), T absolute temperature (K).

The plot of $\ln k_2$ versus $1/T$ in Fig. 7 for the adsorption of MG onto chitosan was applied to obtain the activation energy, E_a from the slope.

Activation energy for MG adsorption onto chitosan is 85.6 kJ mol^{-1}. The significance of E$_a$ is that it is used to determine the type of adsorption. This activation energy value is not between 5 and 40 kJ mol^{-1} values. Since it is high, it is understood that the chemical adsorption mechanism is occurred. It can be easily said that the positive value of E_a represents the nature of chemical adsorption of MG onto chitosan; there is an energy barrier in the adsorption process.

Fig. 8. SEM images showing the surface morphologies of the chitosan beads (at 3000× and 4300× magnifications).
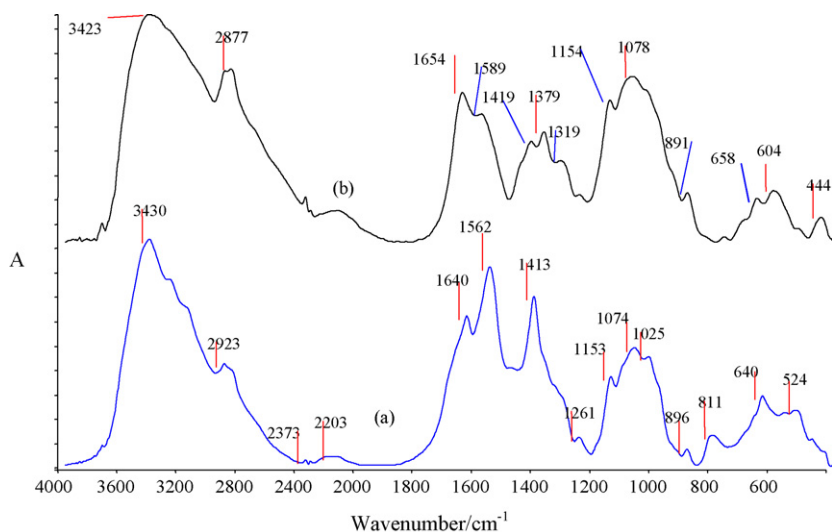
Fig. 9. FTIR spectra of chitosan bead (a) before and (b) after adsorption of MG.

at $1562\,cm^{-1}$ has a larger intensity than at $1640\,cm^{-1}$, which suggests effective deacetylation. Note in the spectrum of chitosan that presence of two bands, one at $1153\,cm^{-1}$ and another at $1074\,cm^{-1}$, probably indicates stretching vibrations of C–O group. The first band did not demonstrate any changes. Besides in the second band, a small change was observed. It can be said that no interaction occurs between C–O groups of chitosan and MG cation.

4. Conclusion

The results in this study showed that highly abundance and low cost biopolymer chitosan can be utilized as an adsorbent for the removal of malachite green from aqueous solution. The initial pH of dye solution did significantly affect the sorption of MG. The optimal pH for the sorption of MG was 8 and above. The sorption data indicate that Langmuir equation provides better fit than Freundlich equation. Thus, it suggests the monolayer sorption of MG onto chitosan bead. The monolayer adsorption capacities (C_m) were found to be $93.55\,mg\,g^{-1}$ at 303 K; $74.83\,mg\,g^{-1}$ at 313 K; $82.17\,mg\,g^{-1}$ at 323 K, respectively. The temperature influenced the adsorption process. The contact time study reveals that the sorption equilibrium was reached at about 5 h. The kinetic experiments imply that sorption process obeys the pseudo-second-order kinetic model. The temperature strongly influenced the adsorption process. It is clear that the q_2 (maximum adsorption capacity for the pseudo-second-order adsorption) values are increased by increasing the temperature. From the thermodynamic study, it is obtained that activation energy value for MG sorption onto chitosan bead is greater than $40\,kJ\,mol^{-1}$. Therefore, the type of adsorption can be considered as chemical adsorption. The ΔH° of 221.3 kJ/mol means that the interaction between malachite green and chitosan is endothermic in nature. ΔG° and ΔS° values suggested that the adsorption of MG onto chitosan is a spontaneous process and it corresponded to an increase in the randomness of adsorbed species.

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