Kinetic Study of Adsorption of Malachite Green Dye on Poly Aniline-Formaldehyde/Chitosan Composite

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Abstract. Poly aniline-formaldehyde/chitosan composite (PAFC) was prepared by the in situ polymerization method. It was characterized by FTIR spectroscopy in addition to SEM, EDS and TGA techniques. The adsorption kinetics of malachite green dye (MG) on (PAFC) were studied for various initial concentrations (20, 30 and 40) mg/L at three temperatures (308, 313 and 318) K. The influence factors of adsorption; adsorbent dose, contact time, initial concentration and temperature were investigated. The kinetic studies confirmed that adsorption of MG obeyed the pseudo-second-order model and the adsorption can be controlled through external mass transfer followed by intraparticle diffusion mass transfer. A study of the temperature effect was indicated that the adsorption process was endothermic. The activation energy value for each concentration of the dye was calculated, it is observed that it decreases with increasing initial dye concentration.

Keywords: Adsorption, Kinetic, Malachite green, Poly aniline-formaldehyde, Chitosan.

Introduction

In recent years, the textile industry produces a large amount of dyed wastewater, this causes serious environmental problems [1]. These effluents hinder the light penetration in water bodies and may affects negatively on the biological processes [2]. Additionally, dyes are toxic to most organisms and harmful to aquatic animals. Also, some dyes are very carcinogenic hence the removing of dyes before elimination of wastewater is extremely important [3].

Malachite green (MG) is one of the most dyes is utilized in the textile industry [4-6]. The exposure to MG can have teratogenic, mutagenic and carcinogenic effects on humans [7].

Various chemical and physical processes are used to remove MG dye from wastewater [8-12]. Adsorption is an effective and versatile process as a result to its easy operation [13-15].
Poly aniline-formaldehyde (PAF) is widely employed as an adsorbents for dyes removal from wastewater. It is a functional polymer containing amine group (NH$_2$) which can act coordination bond with the cationic species as a result of the presence of the electronic lone pair in sp$^3$ hybridized amine nitrogen.

Currently, biopolymer such as chitosan has been applied as one of the most emerging adsorption methods to remove dyes, even at low concentrations [16]. Different materials were used to form a composite with chitosan such as polyvinyl alcohol, polyurethane and montmorillonite [17-19]. This work aims to develop the adsorption capacity of chitosan by modifying it with poly aniline-formaldehyde resin to adsorb malachite green and to explain the adsorption processes and assess the probability of using the modified chitosan as an adsorbed in the practical removal of the dye. To predict the kinetics of the adsorption process; pseudo-first-order model, pseudo-second-order model and intra-particle diffusion model have been examined for several initial concentrations of dye and temperatures.

**Experimental**

**Chemical materials**

Chitosan, aniline, formaldehyde (37%) and malachite green dye were obtained from Sigma Aldrich Company. Acetic acid was purchased from Merck Company. All this chemical materials have been used without purification processes.

**Preparation of poly aniline-formaldehyde/ chitosan composite (PAFC)**

9 g of aniline and 0.5 g of chitosan were mixed slowly with continuous stirring then 10 drops of concentrated acetic acid were added to the mixture with constant stirring in a thermostatic water bath 353 K for two hours. After that the product was cooled then formaldehyde solution 5 mL was added to it and heated to 353 K for two hours with continuous stirring. The product was collected and washed with distilled water to remove the acid residue, then dried in an oven at 363 K for 6 hours. The resulted polymer composite has been grind and sieved by a sieve ≤100 µm. Hence it was characterized and kept for adsorption experiments.

**Adsorbate**

The concentrations of malachite green dye were observed by using double beam UV-Vis spectrophotometer PG Instrument T80. The absorbance was determined at $\lambda_{\text{max}}$ =610 nm. The chemical structure of MG dye is shown in Figure 1.

![Fig. 1. The chemical structure of Malachite Green dye.](image)

**Adsorption experiments**
The studies of adsorption kinetic were performed by adding 0.006 g (particle size ≤100 µm) of adsorbent to 20 mL of MG dye solutions for specific concentrations (20, 30, and 40) mg/L. The adsorbent dose, contact time, initial concentration and temperature were examined using a shaking water bath Laptech LSB-015S with a shaking speed 60 rpm. These samples were withdrawn from the water bath shaker at specific time periods and the dye solution has been separated from the adsorbent by a centrifuge at 90 rpm for 2 min. The remaining dye concentration was determined by spectrophotometer. The adsorption studies were conducted at different temperatures (308, 318 and 328) K to determine the effect of temperature on the kinetics of adsorption process.

The amount of absorbed dye \( q \) (mg/g) was estimated as follows:

\[
q = \frac{(C_o - C)V}{w}
\]  

(1)

where \( C_o \) is the initial dye concentration (mg/L), \( C \) is the remaining dye concentration (mg/L), \( V \) is the dye solution volume (L) and \( w \) is the adsorbent mass (g).

**Results and discussion**

**Infrared spectroscopy**

Infrared spectrum of polymer composite (PAFC) was obtained by a FT-IR spectrophotometer Shimadzu 8400S. It was recorded using KBr pellet method with a spectrum range 4000-400 cm\(^{-1}\).

FTIR spectrum of the prepared polymer composite (PAFC) was shown in Figure 2. A broad band was observed at 3410 cm\(^{-1}\) due to the stretching vibrations of O-H groups of the polymer composite. The stretching vibrations of C-H groups appeared at 3030 cm\(^{-1}\) and 2883 cm\(^{-1}\). The C-N groups axial deformation 1369 cm\(^{-1}\), including the characteristic bands of polysaccharide at (1070-1028) cm\(^{-1}\). So, there is a strong absorption band appeared at 1662 cm\(^{-1}\) attributed to the characteristic vibrations of of azomethine C=N [20], which is not observed in chitosan. The bands at 1500 cm\(^{-1}\) and 810 cm\(^{-1}\) were attributed to the stretching of C=C and C-H groups in the aromatic ring, respectively.

**Fig. 2.** FTIR spectrum of poly aniline-formaldehyde/chitosan (PAFC).

**SEM technique**
Figure 3 shows the SEM micrographs of the grinded powder of poly aniline-formaldehyde/chitosan composite surface which were performed using a scanning electron microscope Zeiss SEM EVO18. There are many particles fragments are observed that have irregular structure.

![Fig. 3. SEM micrograph of poly aniline-formaldehyde/chitosan (PAFC).](image)

**EDS technique**

In order to confirm the components and purity of the prepared polymer composite (PAFC), the energy dispersive X-ray spectroscopy (EDS) was done using a spectrometer EDS Oxford Xmax50. Figure 4 show only three characteristic signals attributed to the main constituents C, O, and N with composition ratio 78.5%, 14.3% and 7.2% respectively.

![Fig. 4. Energy dispersive spectrum of poly aniline-formaldehyde/chitosan (PAFC).](image)

**TGA technique**

The TGA thermograms of polymer composite (PAFC) was shown in Figure 5, which was recorded by a thermogravimetric analyzer PerkinElmer TGA8000. The thermogravimetric analysis shows that the mass loss has occurred in four stages. A mass loss is ~10% at range 70-170 °C related to the loss of moisture that adsorbed on the surface of polymer composite. So, a mass loss is ~10% at 170-250 °C and ~35% at 250-350 °C due to the degradation of (PAFC) composite. Final, a mass loss is ~20% at around 350-700°C due to the degradation in polymer composite chains. Additionally, there is no mass loss was observed when the temperature was increased to 800 °C, which confirms the higher thermal stability of prepared polymer composite. So, the residue ratio of (PAFC) was 25%.
**Adsorption experiments**

**Influence of adsorbent dose**

The effect of adsorbent dose was examined to determine the adsorption optimization. The experiments of adsorption were performed by various masses of the prepared polymer composite (PAFC) (0.002, 0.004, 0.006, 0.008 and 0.01) g (particle size ≤100 µm), 20 mL of MG dye concentration 20 mg/L at 308 K and 30 min. The results are illustrated in Figure 6. The adsorbed amount increases until it reaches the highest value at 0.006g. As a result of the increase in the number of active adsorption sites that increases by increasing the adsorbent mass [21].

**Influence of contact time**

The effect of contact time for the adsorption of MG dye on 0.006 g (particle size ≤100 µm) of poly aniline-formaldehyde/chitosan composite surface was investigated at 20 mL of initial concentrations (20, 30, and 40) mg/L and 308 K as shown in Figure 7. Obviously, the time has a great effect on the studied adsorption system. It was noted that the adsorbed quantity of MG dye molecules from aqueous solution increases gradually with the time and reaches to up 10.619 mg/g within 15 min. Then, it increases slowly through 45 min to reaches 10.852 mg/g. After that the adsorbed quantity becomes steady, this is due to the saturation state of surface adsorption capacity.
Fig. 7. Effect of contact time on the adsorption of MG dye on (PAFC).

**Influence of initial concentration**

To determine the optimum initial concentration of malachite green dye MG, the concentrations (20, 30, and 40) mg/L with a volume 20 mL were examined at adsorbed mass 0.006 g (particle size ≤100), contact time 45 min and 308 K. Figure 8 refers to the initial concentration effect on the adsorbed dye by the prepared composite (PAFC). It is clear the adsorbed quantity of MG dye decreases with increase in the concentration, it possibly due to the saturation of active sites of the adsorbent surface when the concentration is increasing.

Fig. 8. Effect of initial dye concentration on the adsorption of MG dye on (PAFC).

**Influence of temperature**

The effect of temperature for the adsorption of MG dye on the surface of prepared composite (PAFC) was investigated within temperatures (308, 313 and 318) K on the adsorption of initial dye concentration (20, 30 and 40) mg/L with volume 20 mL and 0.006 g of adsorbent, results are shown in Figure 9. It was observed that the adsorption amount of MG dye increases with increasing temperature that related to the increasing of kinetic energy of dye molecules then increasing their ability to pass the energy barrier.
Adsorption kinetics

The kinetics of adsorption is essential to investigate the solute adsorption rate which is determining the adsorbent efficiency and adsorption mechanism. Therefore, different models of kinetic the pseudo-first-order, pseudo-second-order and intra-particle diffusion have been used. Pseudo-first-order equation can be applied in the following formula [22]:

$$ln(q_e - q_t) = lnq_e - k_1t$$  \hspace{1cm} (2)

where $q_e$ is the adsorbed capacity in the equilibrium (mg/g), $q_t$ is the adsorbed quantity at time $t$ (mg/g), $k_1$ is the pseudo-first-order rate constant (min$^{-1}$) and $t$ is the time (min). The results of fitted are presented in Table 1 with the values of correlation coefficient. The plot of $ln(q_e - q_t)$ versus $t$ at the studied temperatures represents the fitted of pseudo-first-order equation, Figure 10.
Fig. 10. Pseudo-first-order model fitted for adsorption of MG dye on (PAFC).

Table 1. Pseudo-first-order model constants and correlation coefficients for adsorption of MG dye on (PAFC).

| C (mg/L) | T (K) | $q_{e\,\text{cal.}}$ (mg/g) | $q_{e\,\text{exp.}}$ (mg/g) | $k_1$ (min$^{-1}$) | $R^2$ |
|----------|-------|-----------------|-----------------|-------------------|------|
| 20       | 308   | 2.191           | 10.774          | 0.082             | 0.798|
|          | 313   | 2.589           | 17.053          | 0.079             | 0.631|
|          | 318   | 2.439           | 17.906          | 0.078             | 0.719|
| 30       | 308   | 2.320           | 7.131           | 0.094             | 0.802|
|          | 313   | 1.793           | 6.976           | 0.063             | 0.638|
|          | 318   | 1.989           | 8.681           | 0.057             | 0.689|
| 40       | 308   | 2.218           | 10.543          | 0.067             | 0.746|
|          | 313   | 2.827           | 15.271          | 0.082             | 0.803|
|          | 318   | 3.594           | 16.667          | 0.111             | 0.706|

It was found that difference in the experimental and theoretical values of ($q_e$). In addition to low correlation coefficient values. This supports the suggestion that the adsorption of MG dye on (PAFC) does not obey the kinetic of pseudo-first-order model.

On the other hand, the pseudo-second-order model was applied in the linear form [23], as following:

$$\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \left(\frac{1}{q_e}\right)t \quad (3)$$

where $k_2$ is the pseudo-second-order rate constant (g/mg.min). A plot of $t/q_t$ versus $t$ was drawn, Figure 11. The adsorbed amount at equilibrium $q_e$ and the pseudo-second-order constant $k_2$ were estimated from the slope and intercept respectively. The $k_2,$ $q_e$ and correlation coefficient values are showed in Table2. It was observed that there is a good agreement between the calculated and experimental values of adsorbed quantity. So, the correlation coefficient values indicate the adsorption of MG dye on (PAFC) composite agree with the pseudo-second-order model for all studied temperatures.
Fig. 11. Pseudo-second-order model fitted for adsorption of MG dye on (PAFC).

Table 2. Pseudo-second-order model constants and correlation coefficients for adsorption of MG dye on (PAFC).

| C (mg/L) | T (K) | \( q_{e\, cal.} \) (mg/g) | \( q_{e\, exp.} \) (mg/g) | \( k_2 \) (min\(^{-1}\)) | \( R^2 \) |
|----------|-------|----------------|-----------------|----------------|-------|
| 20       | 308   | 11.155         | 10.691          | 0.130          | 0.997 |
|          | 313   | 16.810         | 16.588          | 0.402          | 0.997 |
|          | 318   | 16.981         | 16.598          | 0.458          | 0.997 |
| 30       | 308   | 7.934          | 7.131           | 0.063          | 0.996 |
|          | 313   | 7.137          | 6.821           | 0.132          | 0.996 |
|          | 318   | 9.528          | 8.991           | 0.148          | 0.996 |
| 40       | 308   | 10.801         | 10.465          | 0.085          | 0.998 |
|          | 313   | 14.342         | 15.271          | 0.117          | 0.999 |
|          | 318   | 15.659         | 15.891          | 0.132          | 0.999 |

Continuously, the adsorption rate of dye increases when the temperature rises, which means that the adsorption process is endothermic and there is a diffusion in addition to the adsorption.
The activation energy value $E_a$ is estimated from the slope of plot $\ln k$ versus $1/T$, Figure 11 according to the following Arrhenius equation [24]:

$$\ln k = \ln A - \frac{E_a}{RT} \quad (4)$$

where $k$ is the rate constant, $A$ is the pre-exponential factor, $E_a$ is the activation energy, $R$ is the universal gas constant 8.314 J/mol.K and $T$ is the absolute temperature in kelvin.

The values of activation energies $E_a$ and Arrhenius factor $A$ were estimated from the slope and intercept respectively of the straight line. The calculated values of activation energy was reported in Table 3. It was founded that an increase in the concentration of the initial dye concentration leads to a decrease in the activation energy value, can be due to increase in the mobility of dye molecules that may occur at a high concentration that needs a lower activation energy to pass the energy barrier hence adsorbed on the adsorbent surface.

![Fig. 12. Arrhenius equation fitted for adsorption of MG dye on (PAFC) composite.](image)

**Table 3.** Kinetic energy values for adsorption of MG dye on (PAFC).

| C (Mg/L) | $E_a$ (kJ/mol) | $A$     |
|---------|----------------|---------|
| 20      | 107.518        | 2.503x1017 |
| 30      | 86.133         | 3.872x1013 |
| 40      | 36.095         | 1.166x105   |

Additionally, intra-particle diffusion is an alternative method to express the kinetic and predict the mechanism of the adsorption process. This kinetic model depends on the transfer of the target species from their aqueous solutions to the adsorbents through intra-particle diffusion according to Weber’s equation [25]:

$$q_t = k_id t^{1/2} + C \quad (5)$$

where $k_id$ is intra-particle diffusion constant (mg/g.min$^{1/2}$) and $C$ is the influence secondary layer. The plot of $q_t$ values versus $t^{1/2}$ represented in Figures 13, 14, and 15. The value of $k_id$ and $C$ were estimated from the slope and intercept the drawn straight line. The calculated values of intra-particle diffusion coefficient are listed in Table 4.
It is worth mentioning, the plots of $q_t$ against $t^{1/2}$ had two lines part and the intraparticle diffusion rate constant $k_{id}$ was calculated directly from the slope of the second line.

If the straight line of $q_t$ against $t^{1/2}$ passes through the all points that mean the intraparticle diffusion is the limiting-controlling step, but if the line does not pass through all the original points that indicate the intra-particle diffusion is not a specific rate-controlling step. Hence, the line plot of all concentrations could not pass through the origin. This suggests that the intra-particle diffusion was not the only rate-controlling step.

So, the adsorption happens on the outer surface and ends at time (15) min as a first step then the step of intra-particle diffusion control begins and continues until time (45) min where the equilibrium is start. All this can be deduced that the adsorption process of MG dye involves more than one process and the intraparticle diffusion is not a rate-controlling step.

The intra-particle diffusion plots are curved throw small time, this may be due to the mass transfer effect. Thus, can be separate the curve into two regions. The first part represents the effect of boundary layer diffusion and the second part refers to the effect of intra-particle diffusion.

Generally, the correlation coefficients of intra-particle diffusion were smaller than of pseudo-second order model. This confirms the adsorption process mostly followed by intra-particle diffusion process. So, the line which does not pass through the origin that refers to some degree in the boundary layer control.
**Fig. 13.** Intra-particle diffusion model fitted for adsorption of 20 mg/L MG dye on (PAFC) at studied temperatures.

**Fig. 14.** Intra-particle diffusion model fitted for adsorption of 30 mg/L MG dye on (PAFC) at studied temperatures.
Fig. 15. Intra-particle diffusion model fitted for adsorption of 40 mg/L MG dye on (PAFC) at studied temperatures.

Table 4. Intra-particle diffusion model constants and correlation coefficients for adsorption of MG dye on (PAFC).

| C (mg/L) | T (K) | First part | R² | Second part | R² |
|---------|-------|------------|----|-------------|----|
|         |       | kᵢ (mg/g.min⁻¹/²) | C  | kᵢ (mg/g.min⁻¹/²) | C  |
| 20      | 308   | 0.282 | 9.513 | 0.994 | 0.174 | 9.651 | 0.889 |
|         | 313   | 0.233 | 15.893 | 0.994 | 0.119 | 16.342 | 0.862 |
|         | 318   | 0.282 | 16.490 | 0.994 | 0.081 | 17.368 | 0.802 |
| 30      | 308   | 0.261 | 5.649 | 0.443 | 0.165 | 6.189 | 0.701 |
|         | 313   | 0.327 | 5.601 | 0.975 | 0.117 | 6.368 | 0.714 |
|         | 318   | 0.110 | 7.899 | 0.216 | 0.118 | 7.962 | 0.719 |
| 40      | 308   | 0.282 | 7.899 | 0.994 | 0.100 | 9.893 | 0.765 |
|         | 313   | 0.380 | 13.500 | 0.995 | 0.091 | 14.679 | 0.931 |
|         | 318   | 0.331 | 15.151 | 1.000 | 0.099 | 16.134 | 0.450 |
Conclusion

This study illustrated the use of poly aniline-formaldehyde/chitosan composite (PAFC) as an adsorbent surface to MG dye from their aqueous solutions. It was prepared by the in situ polymerization method by the condensation reaction of aniline and chitosan with formaldehyde. The produced polymer composite was characterized by FTIR, SEM, EDS and TGA techniques before the adsorption experiments. The adsorption kinetic of MG dye from the aqueous solution was investigated. The experimental results show that (PAFC) an effective adsorbent to remove MG dye from water. So, the obtained results were described using three kinetic models; pseudo-first-order, pseudo-second-order and intra-particle diffusion. It was found from that the adsorption data is more suitable with the pseudo-second-order model. Thus, the adsorption process is mostly followed by intra-particle diffusion process.

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