

Kinetic and equilibrium isotherms of removal malachite green from aqueous solution by using $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-CPTS}$ magnetic nanoparticles

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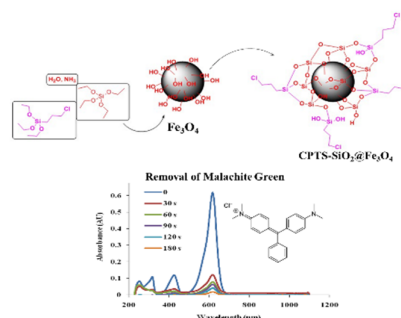
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Abstract

In this report, the kinetic and equilibrium isotherm modeling for removal of malachite green dye with $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-CPTS}$ magnetic nanoparticles in aqueous solutions were investigated. The equilibrium adsorption data were fitted with Langmuir, Freundlich, Redlich-Peterson, Temkin and Dubinin-Radushkevich isotherm models. The adsorption equilibrium data fitted very well to Redlich-Peterson (D-R) isotherm models that predict accurately the adsorption experimental data on solid adsorbents in comparison to other models. Moreover, the adsorption kinetics data were fitted with the pseudo-second order model. Characterization of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-CPTS}$ Magnetic nanoparticles was carried out by using scanning electron microscopy (SEM) and Fourier transform-infrared spectroscopy (FT-IR). The recovery tests were carried out to evaluate the reliability of the NPs for the adsorption and desorption of malachite green dye that showed excellent recoveries in both water solution at pH = 4 (recovery=95%).



Keywords: Kinetics, Malachite green, Isotherm models, $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-CPTS}$ magnetic nanoparticles.

Introduction

Nearly, 80% of all reactive colors are based on azo dyes.¹ Azo dyes are typically used for coloring, texture processing, and paper manufacturing industries. A major amount of azo colors from these sources is discharged into natural waterways that leads to water pollution and human health problems. Therefore, removal of colors from industrial effluent is environmentally important.¹ Nanoparticles (NPs) are known as remarkable species for the removal color pollutants from wastewater. However, the recovery of nanomaterials from a heterogeneous suspension in general is one of the difficulties associated with water and wastewater purification.² Magnetic nanocatalysts can be easily separated from the heterogeneous suspension by the using of a magnetic field. Recently, nanocatalysts with a combination of magnetic and nonmagnetic particles have been utilized for the degradation of organic pollutants in aqueous environment.³ The magnetic nanostructures developed so far contain spinel-type iron oxides (magnetite, Fe_3O_4 or maghemite, $\gamma\text{-Fe}_2\text{O}_3$), black sand, NiFe_2O_4 , ZnFe_2O_4 , CoFe_2O_4 and Co_2O_3 as super paramagnetic cores.⁴⁻⁷ Fe_3O_4 NPs have drawn notable attention because of their remarkable magnetic properties, low toxicity and biocompatibility.⁸⁻⁹ In addition, silica is one of the important widely used inorganic coating materials in the formation of core shell nanostructures. Using silica coating on the surface of

magnetic NPs can prevent their aggregation, correct their chemical stability and provide a range of anchoring sites for the nanocatalytic species using varied silane derivatives.¹⁰

This paper reports on the synthesis of a core-shell magnetic $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-CPTS}$ NPs and its application for the removal and mineralization of an azo dye, Malachite Green.

Experimental

Materials

Tetra ethyl ortho silicate (TEOS), iron (III) chloride .6H₂O, Iron (II) chloride. 4H₂O, Ethanol (98%), ammonia (28%), chloro propyl triethoxy silane (CPTS) all were used as received from Merck. The malachite green dye was provided from Iranian Crepenaz company and distilled water was through all experiments.

Preparation of $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-CPTS}$ NPs

Aqueous solutions of $\text{FeCl}_3.6\text{H}_2\text{O}$ (2.7 g, 10 mmol) and $\text{FeCl}_2.4\text{H}_2\text{O}$ (1 g, 5 mmol) were mixed under nitrogen atmosphere. The resultant solution was left to be stirred for 0.5 h in 80 °C. Then ammoniac (NH_3 , 28% , 11 mol L⁻¹) was added quickly with vigorous stirring to make a black solid product when reaction media reaches pH=10, then the resultant solution was left to be stirred for 1 h in 70 °C. The black magnetite solid product was filtered and washed with ethanol three times and dried at 80 °C to obtain Fe_3O_4 NPs.

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The CPTS-SiO₂@Fe₃O₄ NPs were prepared by a modified Stober method. The Fe₃O₄ (1 g) added to 2 ml tetraethoxysilane (TEOS) and 0.5 ml of CPTS then 30 ml of ethanol add to the solution. This solution was stirred for 0.5 h at room temperature then 1 ml of water was added in a minute. Finally, 2 ml of ammoniac was added during 0.5 h. This solution was stirred for 2 h at room temperature. The prepared silica-coated Fe₃O₄ NPs were separated by a magnet, and were washed with distilled water and ethanol three times and dried at 80 °C for 2 h.

Equilibrium Adsorption Methodology

A series of experiments containing different amounts of CPTS-SiO₂@Fe₃O₄ (3.0 - 7.0 mg) were suspended in 10.0 ml of aqueous solutions of Malachite Green dye (10⁻⁵ M) at pH values ranging from 5 to 8. The samples were mechanically stirred for 1 min at 25 °C and the NPs were separated by magnet. The amount of dyes absorbed by sorbent was calculated as:

$$q = \frac{(C_0 - C)V}{W} \quad (1)$$

where q is the amount of dyes absorbed onto unit amount of the adsorbent (mg g⁻¹), C₀ and C are the concentrations of dye the initial and equilibrium concentrations of the dye in aqueous phase (mg L⁻¹), respectively, V is the volume of the aqueous phase (l), and W is the dry weight of the adsorbent (g).

Characterizations

Fourier transform infrared (FT-IR) spectra of the NPs were obtained using a Bruker Vector 22 spectrometer in the spectrum of 400-4000 cm⁻¹. The morphology of NPs were observed by means of an S-360 Oxford Eng scanning electron microscopy.

Result and discussion

Characterization of CPTS-SiO₂@ Fe₃O₄

The coating of Fe₂O₃ NPs with CPTS-SiO₂ is schematically shown in Figure 1a. The surface morphology of SiO₂@Fe₃O₄ NPs were evaluated by Scanning Electron Microscopy (SEM) techniques before (Figure 1b) and after (Figure 1c) surface modification with CPTS. These images indicated that the average diameter of Fe₃O₄ NPs increased from 56 nm to 95 nm after silica coating. Moreover, the immobilization of CPTS on the surface of SiO₂@Fe₂O₃ NPs can be confirmed through FT-IR spectra. FT-IR spectrum of CPTS-SiO₂@Fe₃O₄ NPs, Figure 1d. The absorption bands at 1050 and 1300 cm⁻¹ are attributed to Si-O-Si and Si-O-Fe bonds, respectively, that confirm the successful silica coating on the surface of Fe₂O₃ NPs.¹¹⁻¹⁴ The characteristic absorption band of Fe-O bond is also observed about 590 cm⁻¹,^{15, 16} and the banding vibration of -CH₂ groups is appeared at 3434 cm⁻¹.

The effect of amount of sorbent and pH on the removal of malachite green dye

The effect of changing the amount of CPTS-SiO₂@Fe₃O₄ NPs from 3 to 7 mg and pH of the solution from 5 to 8 was studied in the presence of a constant concentration of the malachite green (10 ml, 10⁻⁵ M). The solution pH is a major operating parameter affecting malachite green dye removal efficiency. Therefore, the effect of the solution pH on the dye removal efficiency was also investigated in the pH range of 5 to 8. The sample solutions containing NPs were mechanically stirred for a minute, and then absorption of the malachite

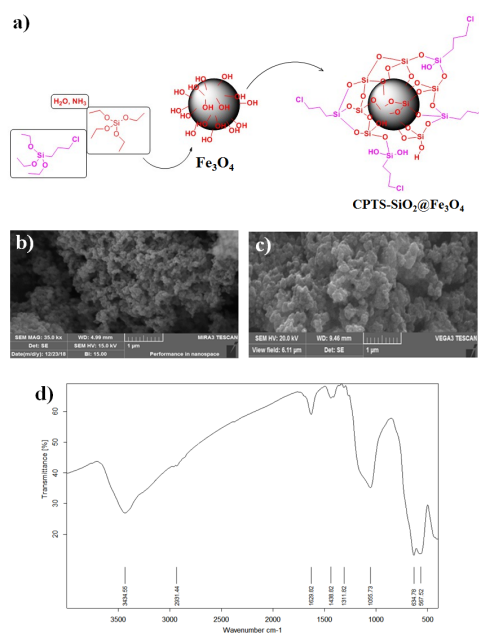


Figure 1. a) A scheme of the preparation process of CPTS-SiO₂ coating on the surface of Fe₃O₄ NPs. b and c) The SEM images of SiO₂@Fe₃O₄ NPs before (b) and after (c) surface modification with CPTS. d) FT-IR spectrum of CPTS-SiO₂@Fe₃O₄ NPs.

green remained in the aqueous solution was measured by UV/vis spectrophotometry. UV-vis spectra for the solutions before and after decolorization under CPTS-SiO₂@Fe₃O₄ NPs are presented in Figure 2. It was found that the most suitable mass of CPTS-SiO₂@Fe₃O₄ NPs for good separation was 5 mg, and the best quantitative removal was achieved at pH 6.4 with a color removal percentage of 98%.

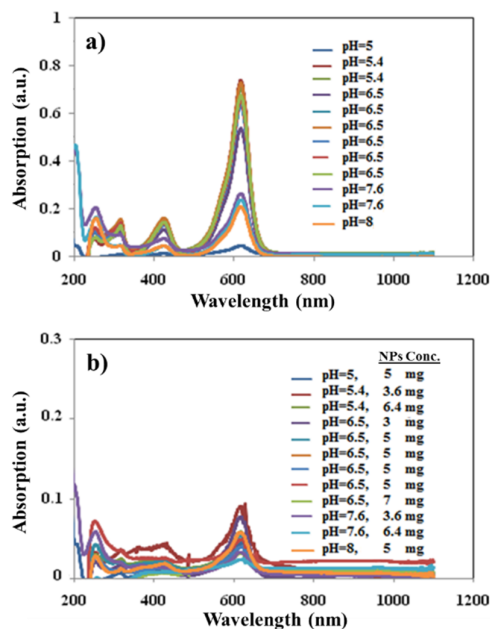


Figure 2. UV-vis spectra for effect of the solution pH and amount of CPTS-SiO₂@Fe₃O₄ NPs on color removal before decolorization (a) and after decolorization under CPTS-SiO₂@Fe₃O₄ NPs (b) (Concentration of malachite green = 10⁻⁵ M and time for time for stirring = 1 min. Some repetitions were also performed).

Adsorption Isotherms Models

Adsorption isotherms are mathematical relation, which are the amount of adsorbate on the adsorbent as a function of concentration at constant temperature, that provide major information on the sorption mechanisms and the surface properties of the adsorbent.¹⁷ Different adsorption isotherms, such as Langmuir, Freundlich, Redlich-Peterson, Temkin and Dubinin-Radushkevich have been used to describe the equilibrium characteristics of adsorption. In this work, the obtained experimental data were fitted to all of these adsorption isotherms models in order to verify which model present the best adjustment. The adsorption phenomena occur because of the specific properties of the solid surface that generally comes from two sources:

1) Discontinuity: That means adsorbent surface properties can be dramatically different from the bulk properties of adsorbents. Actually, atoms on the surface are different from bulk atoms.

2) Unsaturated: Solid surface atoms are unsaturated. Thus, the surface molecules tend to reach saturation.

Each of these adsorption isotherms are based on a set of assumptions.

The Langmuir theory assumes that adsorption occurs at special homogeneous sites on the surface of the adsorbent and suggests the monolayer coverage of the adsorption on the surface of the adsorbent. The Langmuir isotherm model can be represented by the equation (2).

$$\frac{C_e}{q_e} = \frac{1}{K_1 q_m} + \frac{C_e}{q_m} \quad (2)$$

The Freundlich isotherm model assumes that adsorption occurs at heterogeneous surface that is used to describe a multi-layer adsorption with interaction between adsorbed molecules. Freundlich theory is describe by the equation (3):

$$\ln(q_e) = \ln(K_F) + \frac{1}{n} \ln(C_e) \quad (3)$$

Redlich and Peterson isotherm (The R-P isotherm) model can be used in homogeneous and heterogeneous surfaces with a wide concentration range. This theory is describe by the equation (4):

$$\ln\left(K_R \frac{C_e}{q_e} - 1\right) = \ln(R_a) + \beta \ln(C_e) \quad (4)$$

This isotherm assumes that the heat absorption of adsorption of all the molecules due to interactions between the adsorbent and adsorbent decreases linearly with the increasing in coverage of layer. The Temkin isotherm is given by the equation (5):

$$q_e = B_1 \ln(K_T) + B_1 \ln(C_e) , \quad B_1 = \frac{RT}{b} \quad (5)$$

The D-R isotherm model assumes a normal-type distribution mechanism with a normal energy distribution for adsorption on a heterogeneous surface (equation (6)).

$$q_e = q_e \exp(-B \varepsilon^2) \quad (6)$$

q_s is the D-R isotherm constant that depends on temperature through the following equation (equation (7)):

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \quad (7)$$

The mean free energy E of sorbate can be calculated Via B using the equation (8):¹⁸

$$E = \frac{1}{\sqrt{2B}} \quad (8)$$

To study the equilibrium isotherm, in the first stage, UV-vis spectra obtained during dye decolorization with CPTS-SiO₂@Fe₃O₄ NPs at the adsorption concentrations varied from 0.1, 0.4, and 1-7 mg L⁻¹.

In the second stage, by calculating concentrations, the isotherm constants for all the isotherms were determined from the plots of $\ln(q_e)$ versus $\ln(C_e)$ (Freundlich model), C_e/q_e versus C_e (Langmuir model), $K_R C_e/q_e$ versus $\ln(C_e)$ (Redlich and Peterson model), q_e versus $\ln(C_e)$ (Temkin model) and $\ln(q_e)$ versus ε^2 (Dubinin-Radushkevich model), respectively, at 25 °C. The correlation coefficients (R²) with the isotherm constants data are shown in Table 1. As shown, the correlation coefficient for the Redlich-Peterson (D-R) adsorption isotherm model is the highest amount compared to other models. Therefore, this isotherm model was considered to describe the adsorption of malachite green dye with CPTS-SiO₂@Fe₃O₄ NPs.

Adsorption kinetic study

The pseudo-first-order and pseudo-second-order models reaction kinetics were used to study the decolorization kinetics of malachite green dye of the surface of NPs. Figure 3a shows the absorption spectra of malachite green dye after addition of CPTS-SiO₂@Fe₃O₄ NPs with increasing the contact time.

The pseudo-first order is often expressed the following equation (9):¹⁹

$$\frac{1}{q_t} = \frac{K}{q_{max}} \times \frac{1}{t} + \frac{1}{q_{max}} \quad (9)$$

The constants of this equation can be determined by plotting the straight-line $1/q_t$ versus t , Figure 3b. Formula to express the pseudo-second order expressed by the following equation (10):²⁰

$$\frac{t}{q_t} = \frac{1}{K_2 q_{e2}} + \frac{1}{q_e} \times t \quad (10)$$

k_2 : the pseudo-second order constant (g (mg.s)⁻¹) and $k_2 q_{e2} = h$ the initial sorption rate (mg (g.s)⁻¹). The constants of this equation can be determined by plotting the straight line t/q_t versus t , Figure 3c.

Table 1. Isotherm parameters for the removal of malachite green dye by CPTS-SiO₂@Fe₃O₄ NPs (V= 10 mL, 10⁻⁵ M of dye, pH = 6.5, and 5 mg of NPs).

Isotherm model	K _F ((mg g ⁻¹)(mg L ⁻¹) ^{-1/n})	1/n	R ²
Freundlich	22.07 (K _F (mg ⁻¹))	0.8969 (qm(mg g ⁻¹))	0.938
Langmuir	1272 (K _R (g ⁻¹))	142 (aR(mg ⁻¹)/β)	0.989
Redlich-Peterson	12.55 (q _s (mg g ⁻¹))	0.3875 (E(KJ mol ⁻¹))	0.993
Dubinin-Radushkevich	63 (K _R (mg ⁻¹))	0.14 (B1)	0.828
Temkin	37.47	2.355	0.837

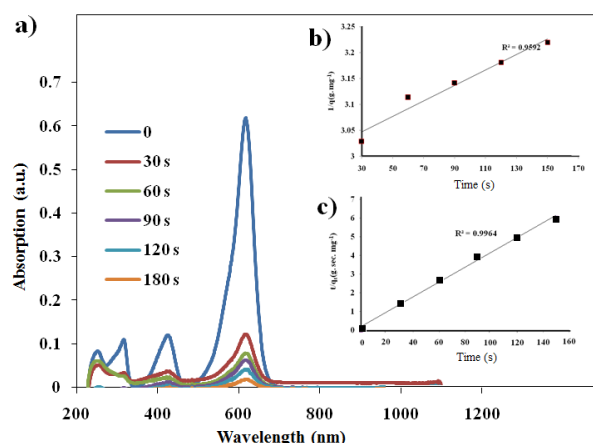


Figure 3. a) UV-vis spectra obtained during dye decolorization with CPTS-SiO₂@Fe₃O₄ at the adsorption time interval of 0–180 second. Insets: b) Fitting of kinetic data to pseudo-first order kinetic model, c) Fitting of kinetic data to pseudo-second order.

Kinetic parameters obtained by pseudo- first- and the second -order kinetic models are calculated and listed in Table 2. Correlation coefficient for the second order kinetics is greater than the first order. In fact, absorption malachite green dye on NPs follows a second-order kinetics.

Table 2. Kinetic parameters for the removal of malachite green dye by CPTS-SiO₂@Fe₃O₄ NPs (V= 10 mL, pH = 6.5, and 5 mg of NPs).

	Pseudo-first order	Pseudo-second order
k (s ⁻¹)	7.35	-
q _{max} (mg g ⁻¹)	25.56	-
q _e (mg g ⁻¹)	-	25.13
h (mg (g.s) ⁻¹)	-	5.583
R ²	0.9582	0.9964

Reusability and recovery of the CPTS-SiO₂@Fe₃O₄

The ability of reusing the adsorbents in several successive adsorption and desorption processes was tested (Figure 4a). The calculated removal percentages for cycles 1-5 were respectively 98.0, 92.5, 80.9, 68.7, and 60.7. These results show that the CPTS-SiO₂@Fe₃O₄ NPs can be reused for three times without a considerable loss in their adsorption efficiency. Moreover, different recovery tests were carried out to evaluate the reliability of the NPs for the adsorption and desorption of the dye. The results showed that excellent recoveries were carried out in present water solution at pH=4 (recovery=95%), Figure 4b.

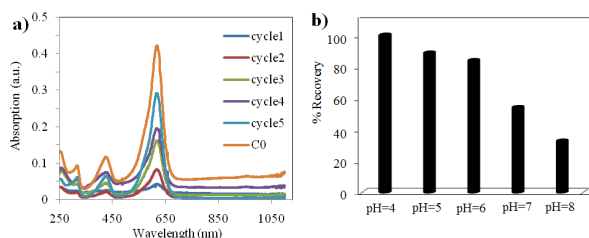


Figure 4. a) UV-vis spectra for malachite green decolorization recycling tests using CPTS-SiO₂@Fe₃O₄ NPs after 1 min reaction time. b) Recovery test of malachite green decolorization at different pH values.

Conclusions

Investigation of equilibrium sorption and reaction kinetics was carried out at 25 °C and pH between 5 and 8. This study shows that the CPTS-SiO₂@Fe₃O₄ NPs are effective adsorbent for the removal of malachite green dye. A higher percentage of malachite green dye removed by these NPs was 98%. The adsorption kinetics was found to follow a second-order rate expression. Equilibrium adsorption data were best represented by the Redlich-Peterson (D-R) isotherm model. The results showed that excellent recoveries were carried out in aqueous solution at pH=4 (95%).

Nomenclature

- a_R: Redlich-Peterson constant in Equation (4) (g mol⁻¹)
- a_R: The R-P isotherm constant
- B: D-R constant defined in Equation (6) (mol²K J⁻²)
- B: Temkin constant in Equation (5) (g.J mol⁻²)
- C_e: The equilibrium liquid phase concentration (mg L⁻¹)
- C_i: Initial dye concentration (mol L⁻¹)
- E: Sorption free energy defined in Equation (7) (kJ mol⁻¹)
- k: The first order rate constant (s⁻¹)
- K_F: Freundlich constant defined in Equation (3) ((mol g⁻¹) (mol⁻¹)ⁿ)
- K_L: Langmuir constant defined in Equation (2) (mol⁻¹)
- K_R: Redlich-Peterson constant defined in Equation (4) (mol⁻¹)
- K_T: Equilibrium binding constant defined in Equation (5) (mol⁻¹)
- m: Mass of the dry chitosan (g)
- n: Sorption intensity defined in Equation (3)
- q_e: Adsorption capacity (mg g⁻¹)
- q_{max}: Maximum adsorption capacity in the monolayer (mg g⁻¹)
- q_s: D-R constant defined in Equation (6) (mol g⁻¹)
- q_i: The amount of dye adsorbed (mg g⁻¹) at time t,
- R: Universal gas constant
- T: temperature (K)
- V: Volume of solution (L)
- β: The exponent which lies between 0 and 1

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