



Application of Magnetic-modified Fe₃O₄ Nanoparticles for Removal of Crystal Violet from Aqueous Solution: Kinetic, Equilibrium and Thermodynamic Studies

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(Received 19 Jun. 2015; Final version received 27 Nov. 2015)

Abstract

The prepared magnetic-modified Fe₃O₄ nanoparticles (Fe₃O₄-TAN) were used as adsorbent for removal of crystal violet (CV) from water solution. The effects of pH, contact time, dye concentration and temperature on adsorption were determined. The experimental data were analyzed using the Langmuir adsorption model. The data fitted well to the model with maximum adsorption capacities 84.0 mg/g under pH=11.0. Also the adsorption kinetics and thermodynamic parameters were studied and evaluated. Adsorption of the CV to nanoparticles reached equilibrium after 15 min. In addition, the external magnetic field could easily separate nanoparticles from water with high separation efficiency.

Keywords: Magnetic separation, Removal, Adsorption, Crystal violet.

Introduction

Dye is one of the most important pollutants in the effluents of textile, paper, plastic, food and cosmetic industries [1]. Many of the industrial dyes are toxic, carcinogenic, mutagenic and teratogenic [2, 3]. It is calculated that, over 100,000 commercially available dyes with more than 7×10^5 tone of dyestuff are produced per year [4-6]. Therefore, there is a huge quantity of colored waste water is generated

from these manufactures. Recently, the removal of dyes from effluent has given much consideration in controlling water pollution. Among a range of techniques available for dye removal from effluent, such as adsorption, flocculation, oxidation and electrolysis [7, 8], adsorption turns to be uncomplicated, effective and economical technique applied for wastewater treatment [9]. In general, adsorbent used are smaller in size since smaller

size adsorbents have increased surface area leading to highest adsorption capacity. But it would be really hard to sort them from water after reaching saturated adsorption. In such conditions, magnetic separation of adsorbents has been one of the promising techniques for wastewater treatment, since no contaminants such as flocculants are produced and large quantity of effluent can be handled within a diminutive period [10, 11].

Magnetic nanoparticles are recognized as efficient adsorbent with large specific surface area and small diffusion resistance [12-14]. Also magnetic nanoparticles are suitable for removal of dyes, because it can be simply recollected from water with magnetic separation. Magnetic nanoparticles are susceptible to air oxidation [15] and easily aggregated in aqueous systems. Recently, some organic substances such as oleic acid (OA), ethylene diamine tetra acetic acid (EDTA) [16] and humic acid (HA) [17] have been used as iron oxides (such as Fe_3O_4) core shell to improve the stability of these nanoparticles. The functional groups of the coated particles also have adsorptive effects.

In this work, we applied magnetic sorbent material that prepared by direct covalent linkage of magnetite nanoparticles to Tannic acid and to remove crystal violet from the aqueous solution. Tannic acid coating of Fe_3O_4 nanoparticles enhances the absorption of crystal violet, because of the negative

charge of tannic acid. The applicability of these modified nanoparticles was evaluated in view of the effects of solution pH, adsorbent dosage, the sorption kinetic and thermodynamic.

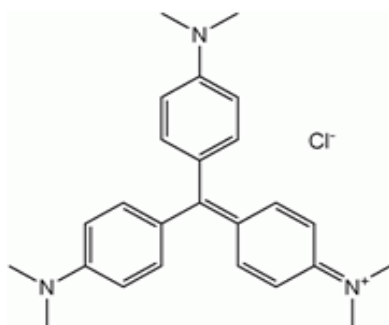
Experimental

Instrumentation

The pH was controlled by Metrohm pH-meter model 713 and Shimadzo λ 25 double beam spectrophotometer was used for the detection of dye concentration in the solution.

Reagents and solutions

All Chemicals were of the reagent-grade and purchased from Fluka and Merck chemical companies. Double distilled water (DDW) was used throughout the study. The pipettes and vessels used for trace analysis were kept in dilute nitric acid for at least 24 h and subsequently washed four times with DDW before usage. The stock solution of dye was prepared by dissolving dye powder in DDW and diluted to prepare the desired concentration of dye solutions. Scheme 1 shows the structure of the crystal violet. CV has quaternary ammonium group and the positive charge is dispersed on the molecule therefore the adsorption of CV on the adsorbent is high.



Scheme 1. The structure of the crystal violet.

Synthesis of magnetic-modified nanoparticles
Tannic acid coating of Fe_3O_4 nanoparticles was prepared by direct covalent linkage of magnetite nanoparticles to Tannic acid according to the literature [18] through a well-known method, as follows: Fe_3O_4 nanoparticles were synthesized via the coprecipitation of Fe^{2+} and Fe^{3+} ions (molar ratio 1:2) in alkali solution. Then, TAN (10 mmol, 3.58g) was added to the as-prepared Fe_3O_4 MNPs (2 gr) which well dispersed in dry toluene (20 mL) and the mixture was refluxed at boiling temperature of toluene (110 °C) for 24 h. Fe_3O_4 -TAN were separated by an external magnet and washed with toluene and acetone repeatedly, and being dried at 80 °C in vacuum for 24. The prepared magnetic nanoparticles (MNPs) were characterized by FT-IR spectroscopy, transmission electron microscopy (TEM), Thermal gravimetric analysis (TGA), and X-ray diffraction (XRD) analyses.

Dyes removal experiment

For each experimental run, ten milligram of

magnetic nanoparticles was added to 20 mL of 20 mgL^{-1} of cationic dye CV solutions with predetermined concentration. The pH was adjusted at 11.0 with 0.1 molL^{-1} NaOH solutions. The mixed solution was gently shaken at room temperature for 15 min. Subsequently, the magnetic nanoparticles with adsorbed dyes were separated from the mixture via a permanent hand-held magnet. The residual amounts of dye in the solution were determined spectrophotometrically at 596 for CV. The adsorption percentage for dye, i.e. the dye removal efficiency, was determined using the following expression:

$$\%R = \left[\frac{(C_o - C_t)}{C_o} \right] \times 100$$

C_o and C_t represent the initial and final (after adsorption) concentration of dye (mgL^{-1}), respectively. All the experiments were performed at room temperature. The effects of pH, contact time, dye concentration and temperature on adsorption were investigated. The adsorption kinetic was determined by analyzing adsorption capacity of the aqueous solution at different time interval. For adsorption isotherm, the dye solution of different concentration in the range of 10-100 mgL^{-1} was agitated until the equilibrium was achieved. The effect of temperature on the adsorption characteristics was studied by determining the adsorption isotherms at 298, 318 and 338 K. The adsorbed amounts (q) of

dye were calculated by the following equation:

$$q = \frac{(C_o - C_e)V}{m}$$

Where C_o and C_e are the initial and equilibrium concentrations of dye in mgL^{-1} , m is the mass of composite (g), and V is the volume of solution

(L). It is clearly shown that the dye adsorbed to the magnetic nanoparticles could be easily separated by a magnetic field, resulting clean water. Figure 1 shows the photographs of magnetic separation of nanoparticles from dye solution.

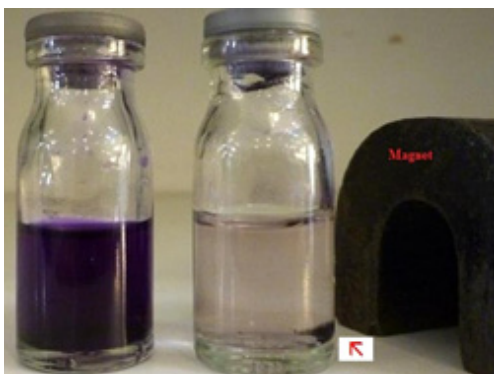


Figure 1. The photographs of the magnetic separation of dye from solution.

Results and discussion

Effect of pH

The effect of pH on the adsorption of dye is shown in Fig.2 from pH 2.0 to 11.0. The pH was adjusted by HCl and NaOH and measured by digital pH meter. The pH may affect both aqueous chemistry and surface binding sites

of the adsorbent. The adsorption of CV was increased at higher pH values. Hence, pH= 11.0 was chosen for subsequent experiments. This phenomenon can be explained on the basis of added the negative charges on the nanoparticles surface, which could enhance the electrostatic interaction of nanoparticles and cationic dye CV.

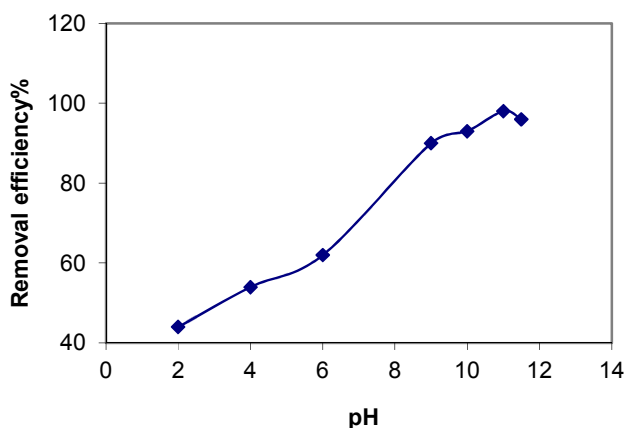


Figure 2. The effect of pH on the adsorption of CV onto the modified nanoparticles.

Effect of the amount of adsorbent

The effect of the amount of modified nanoparticles as adsorbent on the removal of CV was determined at room temperature and at pH 11.0 by varying the adsorbent amount from 0.002 to 0.015 g in 10mL solution of 20 mg L⁻¹ of CV. The results show (Figure 3) that

the removal efficiency of CV was increased by increasing the amount of adsorbent due to the availability of higher adsorption sites. The adsorption reached a maximum with 0.015 g of adsorbent that maximum percentage removal was about 98%.

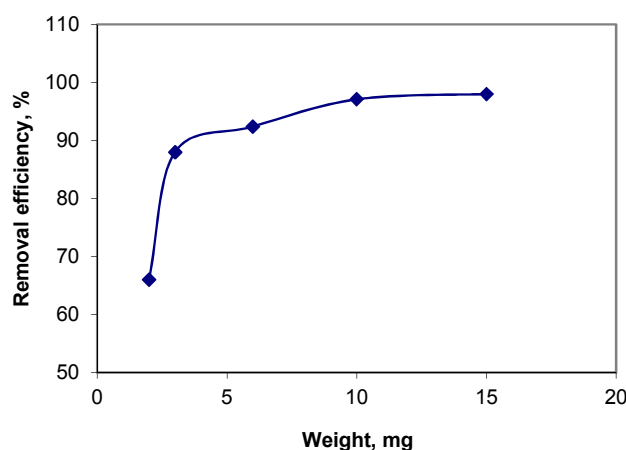


Figure 3. The percentage of dye removal using different amount of modified nanoparticles for CV.

Adsorption kinetics

The effect of contact time on the amount of adsorbed CV was investigated at the initial concentration of 20 mg L⁻¹ at pH 11.0 at room temperature. The concentration of CV was measured using spectrophotometer. The nanoparticles adsorption was measure periodically in 5, 10, 15, 20, and 25 minutes. Figure 4 shows the effect of contact time on the adsorption capacity of CV by the modified nanoparticles. It is clear that the adsorption

capacity increases rapidly during the initial adsorption stage and then continues to increase at a relatively slow speed with contact time and reaches equilibrium point after 15 min. To investigate the adsorption mechanism of CV for modified nanoparticles, two kinetic models, pseudo first-order kinetic model and pseudo-second-order kinetic model, were considered to find the best fitted model for our experimental data.

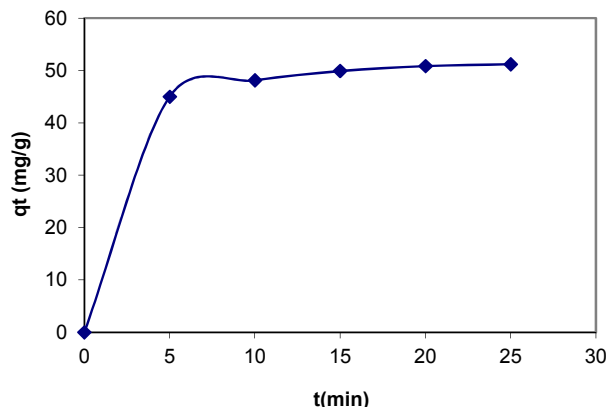


Figure 4. The effect of contact time on the adsorption of CV on modified nanoparticles.

The pseudo-first-order Lagergren equation [19] can be expressed as:

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

Where k_1 is the pseudo-first-order rate constant (min^{-1}), q_e and q_t are amounts of dye adsorbed (mg g^{-1}) at equilibrium and at time t (min). The pseudo-second-order model [20] can be expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

Where, k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) is the rate constant of the pseudo-second-order adsorption.

Kinetic constants obtained by linear regression

for the two models (Figure 5). The results are listed in Table 1. The correlation coefficients (R^2) for the pseudo-first-order kinetic model is relatively low and the calculated q_e values ($q_{e,\text{cal}}$) from the pseudo-first-order kinetic model do not agree with the experimental data ($q_{e,\text{exp}}$), suggesting the adsorption of CV onto the nanoparticles cannot be applied a first order model. For the pseudo-second-order kinetic model, the R^2 value is 0.999 for CV and the $q_{e,\text{cal}}$ values agreed with the $q_{e,\text{exp}}$ values very well. This indicates the applicability of the second-order model to describe the adsorption process of CV onto the modified nanoparticles.

Table 1. Adsorption kinetic parameters of CV adsorption onto the modified nanoparticles.

Pseudo-first order			Pseudo-second order			Experimental data
K_1 (min^{-1})	$q_{e,\text{cal}}$ ($\text{mg g}^{-1} \text{min}^{-1}$)	R^2	K_2 ($\text{g mg}^{-1} \text{min}^{-1}$)	$q_{e,\text{cal}}$ (mg g^{-1})	R^2	$q_{e,\text{exp}}$ (mg g^{-1})
0.189	18.5	0.978	0.018	53.4	0.999	51.2

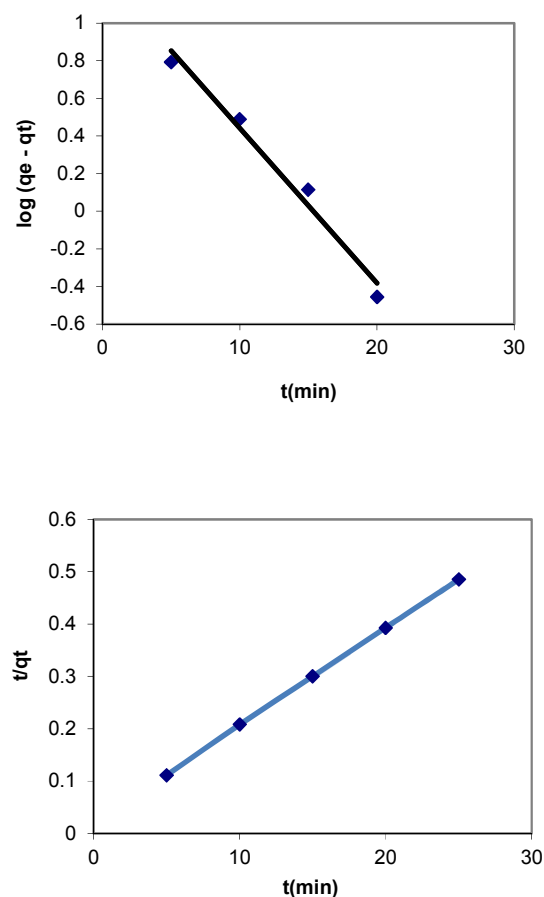


Figure 5. The pseudo-first-order kinetics (a) and the pseudo-second-order kinetics (b) of adsorption CV on the modified nanoparticles.

Adsorption isotherms

In order to optimize the use of modified nanoparticles, it is important to establish the most appropriate adsorption isotherm. The adsorption capacities of the as-obtained modified nanoparticles to dye were measured individually at pH 11.0 with varied CV concentration. The amounts of dyes in the solution were determined after equilibration. The result is shown in Fig.6. The data of the dye adsorbed at equilibrium (q_e , mg/g) and

the equilibrium dye concentration (C_e , mg/L) were fitted to the linear form of Langmuir adsorption model [21].

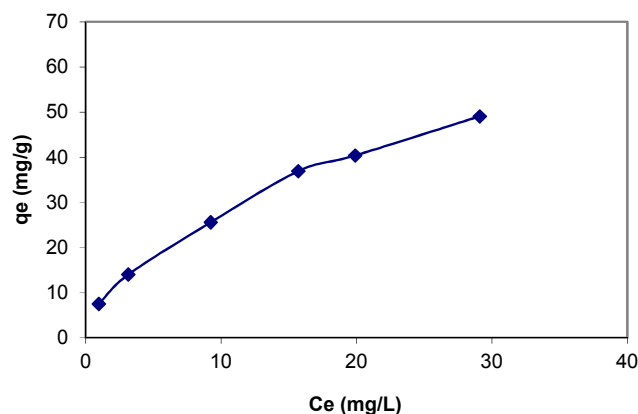


Figure 6. The Langmuir adsorption isotherm of CV for modified nanoparticles.

$$\frac{C_e}{q_e} = \frac{1}{b q_m} + \frac{C_e}{q_m}$$

Where q_m is the maximum adsorption capacity corresponding to complete monolayer coverage and b is the equilibrium constant (L/mg). The data fit well to the model with correlation coefficients (R^2) of 0.995 and the maximum adsorption capacity in the studied concentration range is 84.0 mg/g.

Adsorption thermodynamic

Thermodynamic parameters, such as changes in Gibbs free energy (ΔG° , kJmol⁻¹), enthalpy (ΔH° , kJ mol⁻¹) and entropy (ΔS° , J mol⁻¹ K⁻¹) are the actual indicators for practical applications. Adsorption thermodynamic was evaluated with respect to different temperatures (298, 318 and 338 K). The results are shown

in Fig.7. To obtain the thermodynamic parameters of dyes adsorption, the values of K_d were calculated at different temperature according to the van,t Hoff equation [22], as follows:

$$\Delta G^\circ = -R \ln K_d$$

$$K_d = \frac{q_e}{C_e}$$

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{R}$$

Where K_d is the distribution coefficient, T is the temperature(K), R is the gas constant (8.3145 Jmol⁻¹ K⁻¹), C_e and q_e are the equilibrium concentration in aqueous phase (mg L⁻¹) and the amount of dyes adsorbed per unit mass of the adsorbent(mg g⁻¹), respectively.

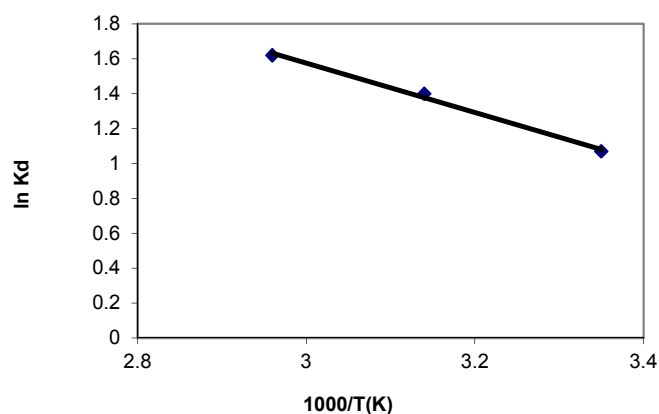


Figure 7. The Van't Hoff plot of $\ln K_d$ versus $1/T$.

The calculated results are listed in Table 2. The negative values of ΔG° indicate that the adsorption process is a spontaneous reaction. The positive values of enthalpy change confirm the endothermic nature of the adsorption process and the positive values of ΔS° reflect an increase in randomness at the solid-solution interface during the adsorption of CV onto the modified nanoparticles.

Table 2. Values of thermodynamic parameters of adsorption of CV adsorption onto the modified nanoparticles.

Temperatures(K)	ΔG° (kJ mol ⁻¹)	ΔH (kJ mol ⁻¹)	ΔS° (J mol ⁻¹ K ⁻¹)
298	-2.65		
318	-3.70	11.75	48.37
338	-4.55		

Conclusions

In this study, the prepared nanoparticles could be well dispersed in the aqueous solution and easily separated from the solution using an external magnet after adsorption. The adsorbent was very effective in removing dye and the adsorption of dye to nanoparticles was fast and agreed well to the Langmuir adsorption model with maximum adsorption capacities of 84.0 mg/g. Further, the cost of magnetic nanoparticles preparation is very

low, the functionalization is easy available, and the process of purifying water pollution is clean and safe using magnetic nanomaterials. Hence, this methodology can be suitable for the large scale removal of the pollutant dyes from water.

Acknowledgments

The financial support to this work by Iran National Science Foundation (INSF 91002199) is gratefully acknowledged.

References

- [1] M. Rafatullah, O. Sulaiman, R. Hashim, A. Ahmad, *J. Hazard. Mater.*, 177, 70 (2010).
- [2] H.A. Mekkawy, M.O. Ali, A.M. El-Zawahry, *Toxicol. Lett.*, 95, 155 (1998).
- [3] D.A. Oxspring, G. Mc Mullan, W.F. Smyth, R. Marchant, *Biotechnol. Lett.*, 18, 527 (1996).
- [4] G. McMullan, C. Meehan, A. Conneely, N. Kirby, T. Robinson, P. Nigam, I.M. Banat, R. Marchant, W.F. Smyth, *Appl. Microbiol. Biotechnol.*, 56, 81 (2001).
- [5] C.I. Pearce, J.R. Lloyd, J.T. Guthrie, *Dyes Pigments*, 58, 179 (2003).
- [6] J.W. Lee, S.P. Choi, R. Thiruvengkatachari, W.G. Shim, H. Moon, *Dyes Pigments*, 69, 196 (2006).
- [7] M. Wawrzekiewicz, *Solvent Extr. Ion Exch.*, 30, 507 (2012).
- [8] G. Crini, *Bioresour. Technol.*, 90, 193 (2003).
- [9] C.D. Shuang, P.H. Li, A.M. Li, Q. Zhou, M.C. Zhang, Y. Zhou, *Water Res.*, 46, 4417 (2012).
- [10] V. Rocher, *Water Res.*, 42 (4-5), 1290 (2008).
- [11] X. Luo, L. Zhang, *J. Hazard. Mater.*, 171, 340 (2009).
- [12] A. Afkhami, R. Norooz-Asl, *Colloids Surf. A*, 346 (1-3), 52 (2009).
- [13] V.K. Gupta, S. Agarwal, T.A. Saleh, *Water Res.*, 45, 220 (2011).
- [14] A.F. Ngomsik, A. Bee, M. Draye, G. Cote, V. Cabuil, *C.R. Chim.*, 8(6-7), 963 (2005).
- [15] D. Maity, D. C. Agrawal, *J. Magn. Magn. Mater.*, 308(1), 46 (2007).
- [16] C. L. Warner, R.S. Addleman, A.D. Cinson, T. C. Droubay, M.H. Engelhard, A.M. Nash, W. Yantasee, M. G. Warner, *Chem. Sus. Chem.*, 3(6), 749 (2010).
- [17] L. Peng, P. Qin, M. Lei, Q. Zeng, H. Song, J. Yang, S. Jihai, B. Liao, J. Gu, *J. Haz. Mater.*, 209-210, 193 (2012).
- [18] Sh. Dehghan Abkenar, M. Khoobi, R. Tarasi, M. Hossieni, A. Shafiee, M.R. Ganjali, *J. Environ. Eng., in press* (2015).
- [19] S. Lagergren, *Handlingar*, 24(4), 1 (1898).
- [20] Y.S. Ho, G. McKay, *Chem. Eng. J.*, 70(2), 115 (1998).
- [21] I. Langmuir, *JACS.*, 38(11), 2221 (1916).
- [22] C. H. Giles, T. H., Macewan, S. N. Nakhwa, D. Smith, *J. Chem. Soc.*, 10, 3973 (1960).