

[Research]

Removal of reactive black 5 dye from aqueous solutions by Fe₃O₄@SiO₂-APTES nanoparticles

Bozorgpanah Kharat Z.¹, Mohammadi Galangash M.^{1*}, Ghavidast A.², Shirzad-Siboni M.³

1. Department of Environmental Sciences and Engineering, Faculty of Natural Resources, University of Guilan, Sowmeh Sara, Guilan, Iran and Dept. of Water Eng. and Environment, University of Guilan, Rasht, Iran

2. Department of Chemistry, Faculty of Science, University of Guilan, Rasht, Iran

3. Department of Environmental Health Engineering, School of Health, Guilan University of Medical Sciences, Rasht, Iran and Research Center of Health and Environment, Guilan University of Medical Sciences, Rasht, Iran

* Corresponding author's E-mail: m_mohammadi@guilan.ac.ir (Received: Feb. 06. 2018 Accepted: May 31. 2018)

ABSTRACT

In this study, Fe₃O₄@SiO₂-APTES nanoparticles were successfully synthesized via a one-pot route in order to remove reactive black 5 dye from aqueous solutions. To obtain optimal conditions on the dye removal efficiency, the effects of various parameters were investigated including solution pH, initial dye concentration, and adsorbent dosage. According to the experimental results, the removal efficiency of the dye decreased with increasing in pH and initial dye concentration, as well as with decreased adsorbent dosage. In fact, about 100.00 % of reactive black 5 was removed from aqueous solution using Fe₃O₄@SiO₂-APTES NPs at the adsorbent amount of 0.4 g L⁻¹ and pH = 3 in 90 min. The kinetics were found well match with pseudo-second-order equation. The isotherm analysis indicated that the equilibrium data were well fitted to the Langmuir isotherm model, showing a monolayer adsorption manner of the dyes on homogeneous surface of nanoparticles. Also, the results of adsorbent recycling showed that this nanoparticle could be reused up to 6 times with high efficiency.

Key words: Fe₃O₄@SiO₂-APTES nanoparticles, Reactive Black 5, Kinetic, Isotherm.

INTRODUCTION

Due to limited availability of fresh water resources and growth of industrial development, large quantities of effluents are generated and wastewater treatment became as one of the main priorities for preservation of the aquatic ecosystems (Agarwal *et al.* 2016). Among the various industries, paper, food, pharmaceutical, leather and especially the textile industries, are producing high volume of colored wastewater and have to be specific treated before released into the environment (Madrakian *et al.* 2013). The most of the dyes which are used in the industries are of organic origin and can cause allergy, skin irritation and genetic mutations for humans and animals (Gholivand *et al.* 2015). By the growing production of these dyes, the

discharge of dye effluents at high concentration and strong color has caused serious environmental pollution, because many of these dyes are toxic and unruly to biodegradation. Due to the chemically and light stable characteristics of dye wastes, a wide range of techniques have been developed for management of related issues. So far, various physical, chemical and biological methods have been investigated for the treatment of colored wastewater, such as coagulation and flocculation, chemical oxidation, membrane filtration, electrochemical purification, advanced oxidation, enzymatic decomposition, ultrasonic waves and electrochemical degradation (Karadag *et al.* 2007; Zhang &

Kong 2011). Beside the several methods of purification, absorption technology is one of the most effective methods for removing dye from textile sewage due to its simplicity, high efficiency, flexibility, low cost, insensitivity to toxic compounds and the availability of a wide range of adsorbents (Robinson *et al.* 2011). The results of studies on neutral red (Qu *et al.* 2008; Iram *et al.* 2010), methylene blue (Yang *et al.* 2008 ; Zhang & Kong 2011), methyl orange (Zhu *et al.* 2010), reactive blue 19 and reactive red 198 (Moussavi & Mahmoudi 2009), reactive orange 16 (Ramachandran *et al.* 2011), acid orange 7 (Sheshmani *et al.* 2014) and acid red 18 (Zhang *et al.* 2014) have illustrated that adsorption methods especially by nanomaterial are increasing for the efficiency purification systems. Among different nanostructure materials, magnetic nanoparticles (NPs), as compared with other materials, have a widespread use in removing dye from industrial wastewater. Magnetic NPs have high thermal, mechanical stability, easy separation of NPs from the dye and the reusability of these NPs are another advantage of their use in absorbing industrial dyes (Mohagheghian *et al.* 2015). Iron oxide NPs are eco-friendly materials that have been investigated in recent years as effective adsorbents in adsorption of dye pollutants from wastewater (Zhang & Kong 2011). Ease to use, affordable, rapid absorption response, the high surface-to-volume ratio of magnetic NPs and their adequate level to trap components of dye contaminants have led to a wide application of these materials (Ghoreishian *et al.* 2014).

The reactive black 5 (RB-5) as an azo-reactive dyes is the most varied of water-soluble artificial dyes and because of easy to use and low energy consumption is used extensively in the textile industries (Demirbas & Nas 2009). High resistance to aerobic decomposition and water solubility of RB-5 has made it difficult to treat by conventional biological treatment processes (Vijayaraghavan & yan 2008; Shirzad-Siboni *et al.* 2014). In recent years, various adsorbents such as activated carbon

(Choi *et al.* 2008), chitosan (Chen & Huang 2010), fly ash (Eren & Acar 2007), modified zeolite (Karadag *et al.* 2007) and graphite oxide (Travlou *et al.* 2013) have been used to remove RB-5 dye. Regarding the high volume of dye sewage production in Iran and its harmful effects, this study was conducted to synthesis magnetic amino-coated silica iron oxide NPs of Fe₃O₄@SiO₂-APTES NPs to remove RB-5 dye from water. In order to achieve the highest absorption efficiency, the effects of some parameters were studied such as, pH, RB-5 concentration and adsorbent dosage. In addition, the adsorption isotherm, kinetics, thermodynamics feature and the reusability of the adsorbents are also analyzed to evaluate the economic values.

MATERIALS AND METHODS

The following reagents were purchased (Merck, Germany) and used without further modification: ferric chloride hexahydrate (FeCl₃.6H₂O), ferrous chloride tetrahydrate (FeCl₂.4H₂O), ammonia (NH₃, 25 wt %), tetraethyl orthosilicate (TEOS) and 3-Aminopropyl triethoxysilane (APTES). The RB-5 dye was supplied from Alvan Sabet Co., Iran. The properties of RB-5 dyes are shown in Table 1. In the experiment, deionized water was used for all sample preparation process. The initial pH of solution was adjusted by the addition of 0.1 M NaOH or HCl and also using a pH meter device (WTW, Germany). The external magnet was used to remove NPs from the aqueous solution. The X-ray diffraction (XRD) patterns were recorded in air at ambient temperature by Phillips (pw-1840) X-ray diffractometer with Cu-K α radiation source ($\lambda = 1.54056 \text{ \AA}$) at 40 KV voltage and 25 mA current in a wide angle range ($2\theta = 20-70$).

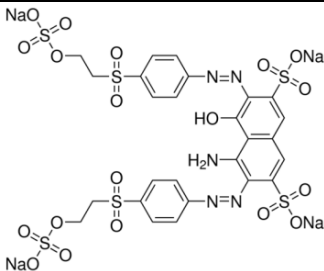
The synthesis of Fe₃O₄@SiO₂-APTES NPs

Firstly, the synthesis of iron oxide NPs (Fe₃O₄ NPs) was carried out using co-precipitation method in alkaline conditions. So that, 1.08 g FeCl₃.6H₂O and 0.39 g FeCl₂.6H₂O were dissolved with deionized water in three necked bottom flask and stirred heavily under argon gas at 80 °C. Then, the ammonia was

added dropwise via a dropping funnel under mechanical stirring. The reaction was refluxed at 80 °C for 5 h at argon atmosphere. Then, black precipitate Fe₃O₄ was formed and separated from the reaction medium using an external magnet of 1.4 T (Mohagheghian *et al.* 2015) and washed with deionized water. Then, 1 g of synthesized Fe₃O₄ NPs was dispersed with 50 mL of deionized water under argon atmosphere for 10 min. After reaching the temperature to 80 °C, 1 mL of TEOS was added in 20 mL of EtOH, and the reaction was continued for 24 h in inert conditions. Thereafter, the black powder Fe₃O₄@SiO₂ NPs formed and separated from the reaction

medium using the external magnet, then was washed with H₂O and EtOH three times. Subsequently, this achieved NPs suspended in 10 mL of EtOH and stirred heavily for 15 min under N₂ gas. Then, 0.37 mL APTES in 25 mL EtOH was added drop-wise to resulting mixture under mechanical stirring. The reaction was refluxed at 80 °C for 8 h at argon atmosphere. The resulted mixture was cooled and the solid was separated magnetically and then washed with EtOH and H₂O several times (3 × 50 mL). The precipitate was then dried in oven at 50 °C for 8 h and the black nanopowder Fe₃O₄@SiO₂-APTES NPs was obtained.

Table 1. The properties of RB-5 dye.

Chemical structure	Molar mass	Color index number	λ_{max}
	991.82 g mol ⁻¹	20.505	597

Removal efficiency

The effect of parameter changes such as pH, absorbent dose and dye concentration was investigated on absorption efficiency. To evaluate the effect of pH on the dye removal efficiency of RB-5, we examined different values, ranging 3-9 with RB-5 concentration 20 mg L⁻¹ and adsorbent dosage 0.3 g L⁻¹. After reaching pH 3 as optimum pH, the adsorption of dye on Fe₃O₄@SiO₂-APTES NPs was examined by changing the quantity of adsorbent range from 0.1 through 0.4 g L⁻¹, with the dye concentration of 20 mg L⁻¹, room temperature (25 ± 1 °C) and pH = 3, hence, 0.4 g L⁻¹ was obtained as an optimum dose of adsorbent. Finally, the effects of initial dye concentrations on the rate of adsorption by Fe₃O₄@SiO₂-APTES NPs were studied in different initial RB-5 concentrations of 20-80 mg L⁻¹ under the 0.4 g L⁻¹ adsorbent and pH = 3 at different times (Ballav *et al.* 2015). The removed amount of dye by Fe₃O₄@SiO₂-

APTES NPs and removal efficiency were calculated by Eqs. 1 and 2, respectively (Eren & Acar 2007), where q is the adsorption capacity (mg g⁻¹), C_i , C_0 and C_e are the initial, outlet, and equilibrium concentrations of dye (mg L⁻¹), V (L) is the volume of dye solution and M (g) is the total amount of Fe₃O₄@SiO₂-APTES NPs.

$$q = \frac{(C_0 - C_i)V}{M} \times 100 \quad (1)$$

$$\text{Removal efficiency (\%)} = \frac{(C_i - C_0)}{C_i} \times 100 \quad (2)$$

The efficiency of recycled Fe₃O₄@SiO₂ APTES NPs

After performing the parameters optimization tests, all the used adsorbent to dye removal experiments were collected and regenerated with 0.1 M sodium hydroxide solution (NaOH). The adsorption-desorption experiments were carried out under optimal conditions (pH = 3, initial RB-5 concentration

= 20 mg L⁻¹, adsorbent dose = 0.4 g L⁻¹). The result showed the recovered adsorbent reused for at least six successive removal processes with removal efficiency higher than 80%, displaying the stability of adsorbent (Mohagheghian *et al.* 2015).

Kinetic studies

The kinetic experiments of the adsorption process were carried out at different concentrations of RB5 (20-80 mg L⁻¹), 0.4 g L⁻¹ NPs, pH = 3 and at different contact times. The pseudo-first order and pseudo-second-order kinetic models were applied in order to find an efficient model for the description of adsorption mechanism (Liu & Liu 2008). In adsorption kinetics equations, q_e is the adsorption capacity at equilibrium (mg g⁻¹), q_t is the adsorption capacity at different time (mg g⁻¹), K_1 is equal to the speed coefficient (min⁻¹) and K_2 is the velocity coefficient (g mg⁻¹min⁻¹) (Samarghandi *et al.* 2011). Kinetic equations are presented in Table 2.

Equilibrium studies

To evaluation of adsorption isotherms, the adsorption experiments of RB-5 on the Fe₃O₄@SiO₂-APTES NPs with 20 mg L⁻¹ RB-5

as an initial concentration using various adsorbent dosages (0.005 - 1 g L⁻¹) at pH = 3 for 24 h and also at 20, 30 and 45 °C are given in Fig. 6. The equilibrium adsorption data were evaluated according to the renowned models Langmuir and Freundlich isotherms (Sadaf & Bhatti 2014).

Isothermic equations are presented in Table 2. In isotherm models, C_e is equal to the equilibrium concentration (mg L⁻¹), q_e is the equivalence of adsorption capacity at equilibrium time (mg g⁻¹), K is the equation of equation (L mg⁻¹) and q_m is the equal to the maximum adsorption capacity (mg g⁻¹) (Geetha *et al.* 2014). The adsorption isotherm process favorability was also evaluated using the dimensionless separation factor (R_L) that were calculated using the following equation [67]:

$$R_L = \frac{1}{1 + k_1 C_0} \quad (3)$$

The adsorption process can be defined as favorable ($0 < R_L < 1$), unfavorable ($1 < R_L$), linear ($R_L = 1$) and irreversible in nature ($R_L = 0$) (Ballav *et al.* 2015).

Table 2. The equations of isotherm and kinetic used in this study.

Isotherm equations	Kinetic models
Freundlich isotherm	Pseudo-first order
$\log q_e = \log k + \frac{1}{n} \log c_e$	$\ln \left(1 - \frac{q_t}{q_e} \right) = -k_1 t$
Langmuir isotherm	Pseudo-second order
$\frac{c_e}{q_e} = \frac{1}{q_m K} + \frac{1}{q_m} c_e$	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$

RESULTS

Adsorbent characterization

The FT-IR spectrum of prepared Fe₃O₄@SiO₂-APTES (red line) compared with Fe₃O₄ NPs (black line) and Fe₃O₄@SiO₂ NPs (violet line) is shown in Fig. 1. The typical absorption peaks at 567 is related to the stretching vibration of

Fe-O bond and also overlap with stretching bonds of Si-O-Fe. The characteristic absorption bands at 1000, 3417 and 2869-2906 cm⁻¹ are corresponded to C-N, N-H and C-H stretching modes of the alkyl chain, respectively and the N-H bending mode appeared at 1627 cm⁻¹ that

confirm the successful coating of APTES on Fe₃O₄@SiO₂ surfaces. Fig. 2, shows the X-ray diffraction (XRD) patterns of Fe₃O₄@SiO₂-APTES. The sharp diffraction peaks with 2θ at 30.3° (220), 35.6° (311), 43.3° (400), 53.9° (422), 57.2° (511) and 62.5° (440) are observed, indicating that the Fe₃O₄@SiO₂-APTES NPs have highly crystalline cubic spinel structure of the magnetite.

The average crystallite size *D* was determined by the Scherrer formula, $D = K\lambda/(\beta\cos\theta)$, where $\lambda = 1.54 \text{ \AA}$ is the wavelength of Cu-K α radiation used, β is the full width at half-maximum (FWHM) intensity of the diffraction line, θ is the Bragg angle for the measured *hkl* peak and *K* is a constant equal to 0.94. The particle sizes of the magnetite calculated using the Scherrer equation was 15.7 nm.

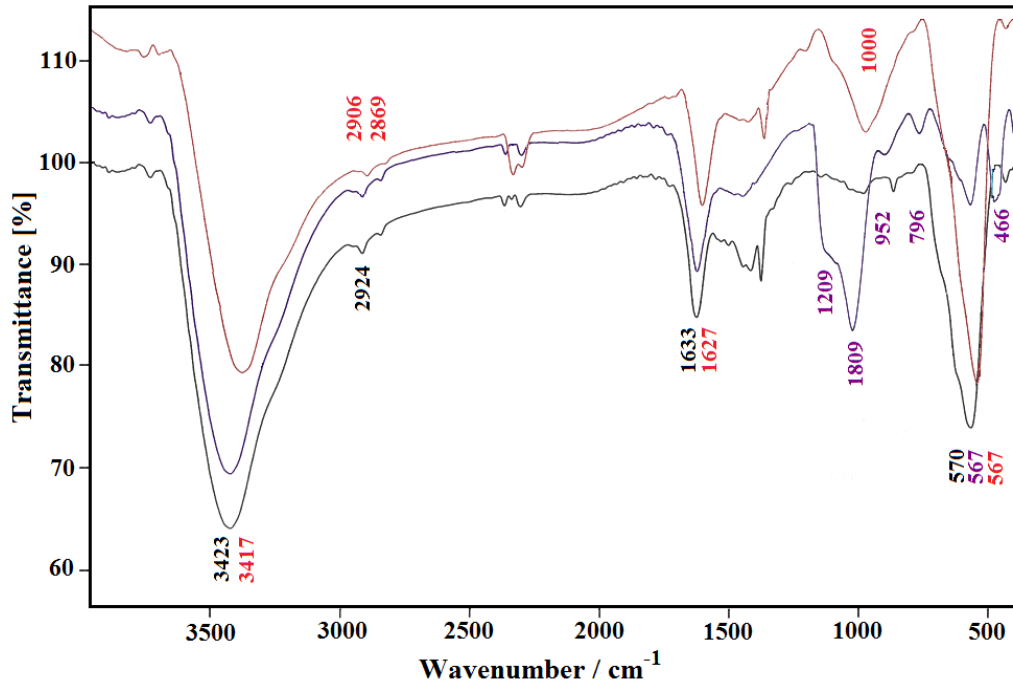


Fig. 1. The FT-IR spectra of Fe₃O₄@SiO₂-APTES (red line), Fe₃O₄@SiO₂ NPs (violet line) and Fe₃O₄ NPs (black line).

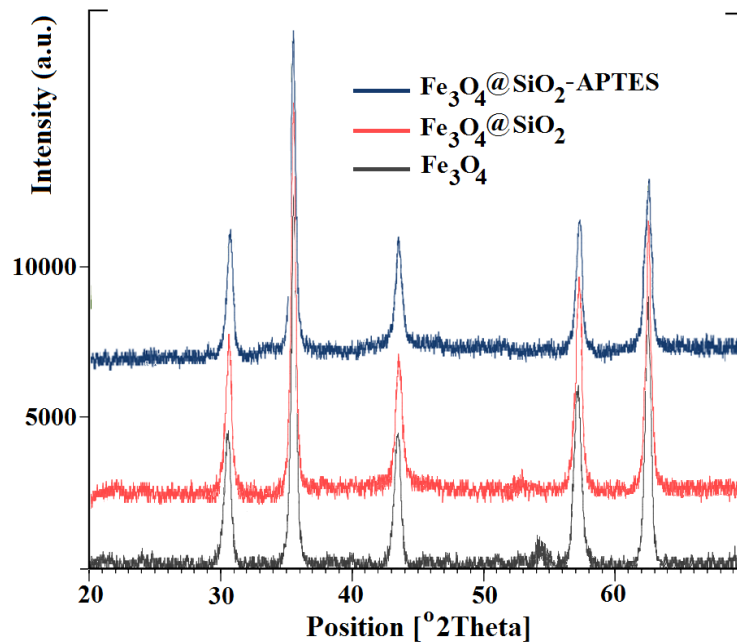


Fig. 2. The XRD image of Fe₃O₄@SiO₂-APTES NPs.

Fig. 3 shows the transmission electron microscopy (TEM) images of the $\text{Fe}_3\text{O}_4@\text{SiO}_2$ -APTES microspheres. The TEM images obviously show that the functional group (with light color) is immobilized on the surface of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ NPs (with dark color). The

synthesized $\text{Fe}_3\text{O}_4@\text{SiO}_2$ -APTES NPs showed a spherical shape with an average diameter of about < 20 nm, however, the NPs tended to aggregate to large particle. This value is in good agreement with that obtained from XRD patterns (Scherrer equation = 15.7 nm).

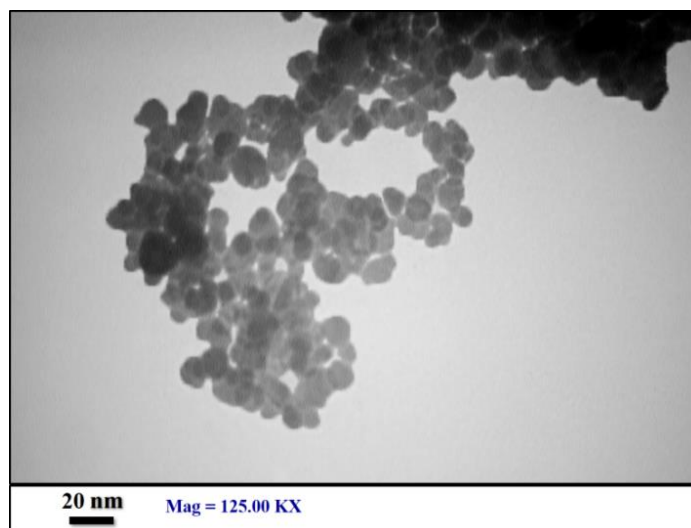


Fig. 3. The TEM micrographs of synthesized $\text{Fe}_3\text{O}_4@\text{SiO}_2$ -APTES NPs.

The effect of solution pH

The effect of pH on the RB-5 (20 mg L^{-1}) adsorption onto $\text{Fe}_3\text{O}_4@\text{SiO}_2$ -APTES NPs (0.3 g L^{-1}) was investigated between pH 3 to 9, and the results are depicted in Fig. 4.

The removal efficiency decreased from 96.45 to 29.14% by increasing the solution pH from 3 to 9. The interactions between $\text{Fe}_3\text{O}_4@\text{SiO}_2$ -APTES NPs and RB-5 dye are shown in Fig. 4b.

The effect of adsorbent dosage

The influence of adsorbent dosage on the removal efficiency for RB-5 was investigated at various amounts of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ -APTES NPs in the range of 0.1 - 0.4 g L^{-1} at pH 3 (Fig. 5). Indeed, the removal efficiency increased from 43.9 to 100% by increasing the adsorbent dosage from 0.1 to 0.4 g L^{-1} over the entire reaction time (1-120 min).

The effect of initial RB-5 concentration

The effect of initial RB-5 concentration on the removal efficiency was studied by varying the initial RB-5 concentration ($20, 40, 60, 80 \text{ mg L}^{-1}$)

at constant adsorbent dosage (0.4 g L^{-1}) and at pH 3 (Fig. 6). By increasing initial RB-5 concentration from 20 to 80 mg L^{-1} , the RB-5 removal efficiency decreased from 100 to 54.7%.

The recovery of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ -APTES NPs

While RB-5 dye adsorption on the $\text{Fe}_3\text{O}_4@\text{SiO}_2$ -APTES is a reversible process, it is possible for regeneration or activation of adsorbent to reuse (Fig. 7).

The desorption ability of NaOH 0.1 M was found higher than the other solvents.

The results showed that desorption efficiency higher than 80% after six cycles can be attained in a short time of 1 min and in a one-step elution using 3 mL of NaOH 0.1 M , as shown in Fig. 7. Furthermore, after seven cycles of the desorption-adsorption process, the high magnetic sensitivity of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ -APTES still retained and was collected from the solution using a magnet of 1.4 T. Therefore, the $\text{Fe}_3\text{O}_4@\text{SiO}_2$ -APTES can be potentially used as a magnetic adsorbent for further dye adsorption from water.

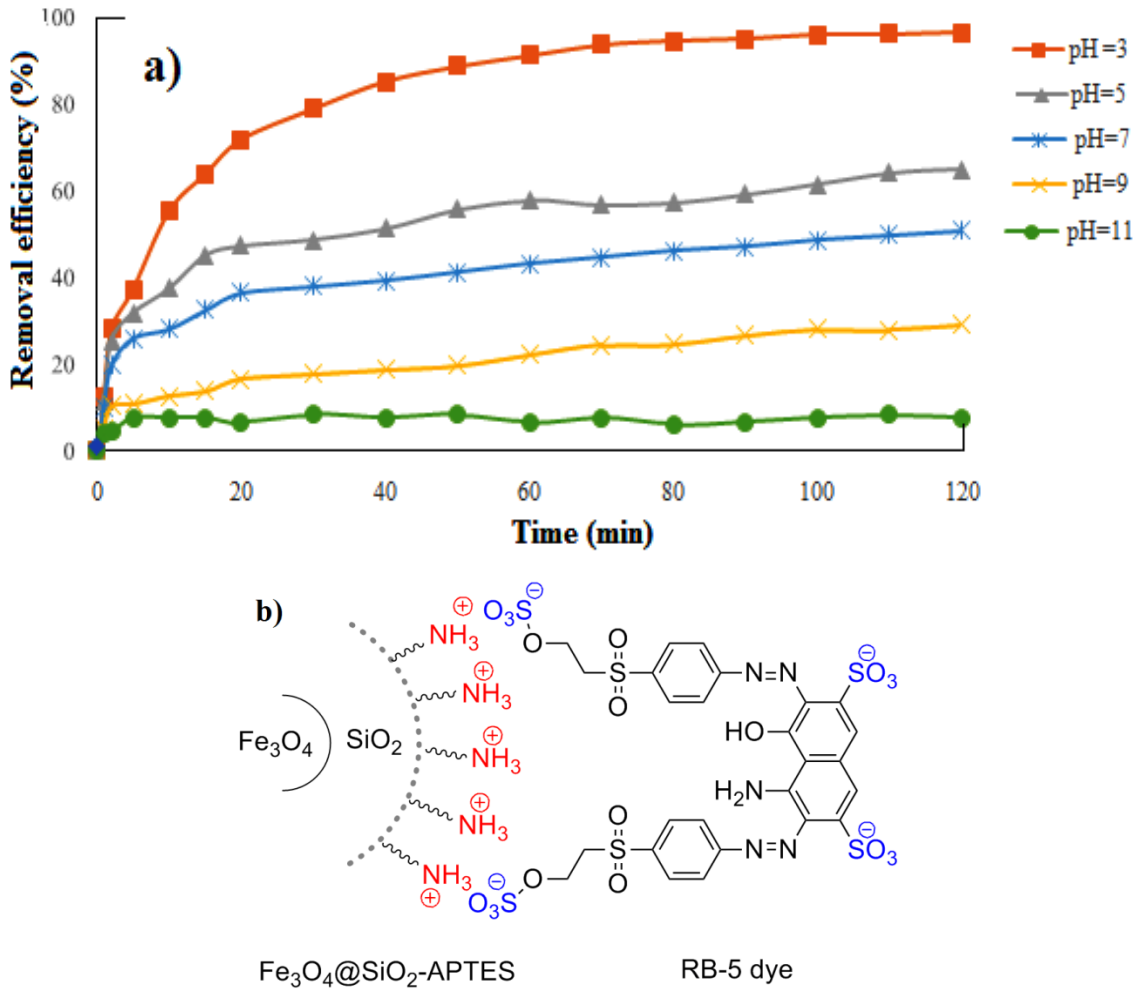


Fig. 4. (a) The effect of pH on the removal of RB-5 dye and (b) main interactions between Fe₃O₄@SiO₂-APTES NPs and RB-5 dye.

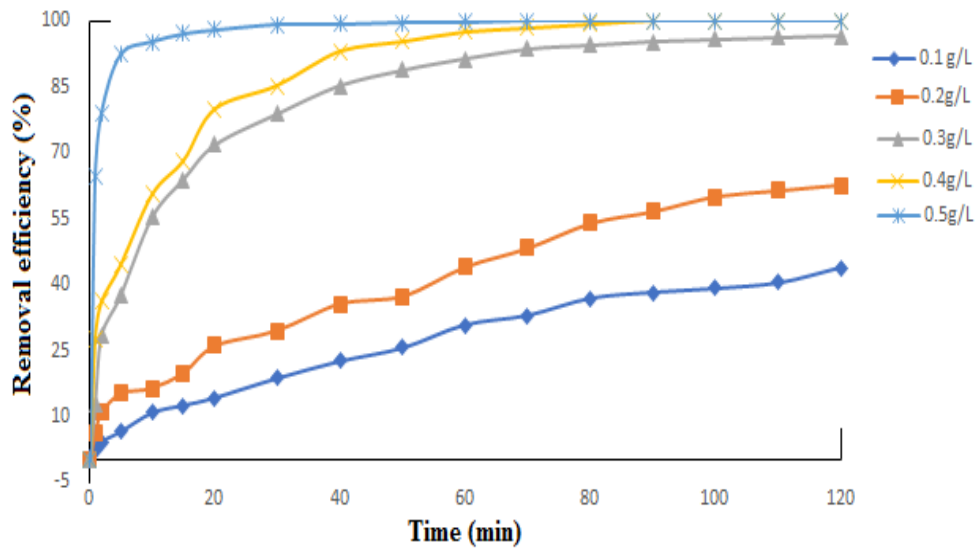


Fig. 5. The effect of adsorbent dosage on the removal of RB-5 dye.

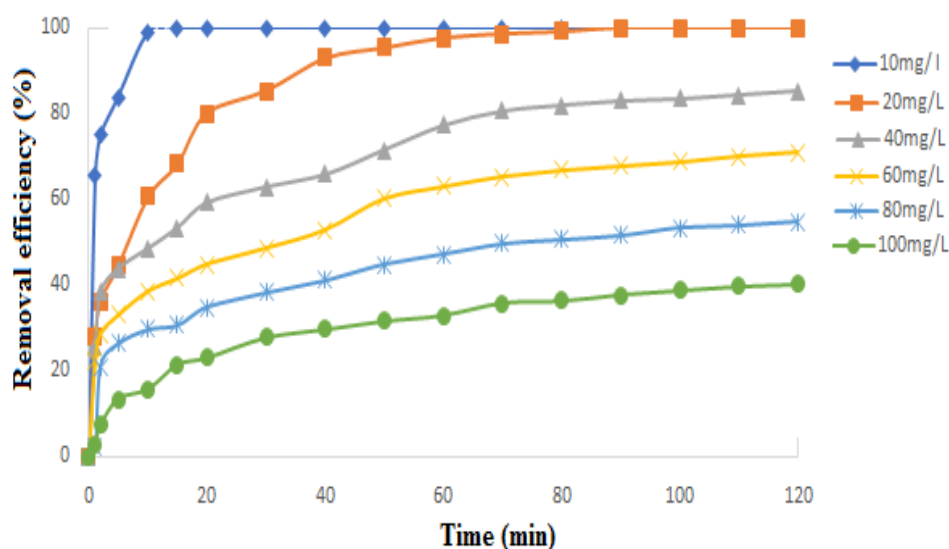


Fig. 6. The effect of initial RB-5 concentration.

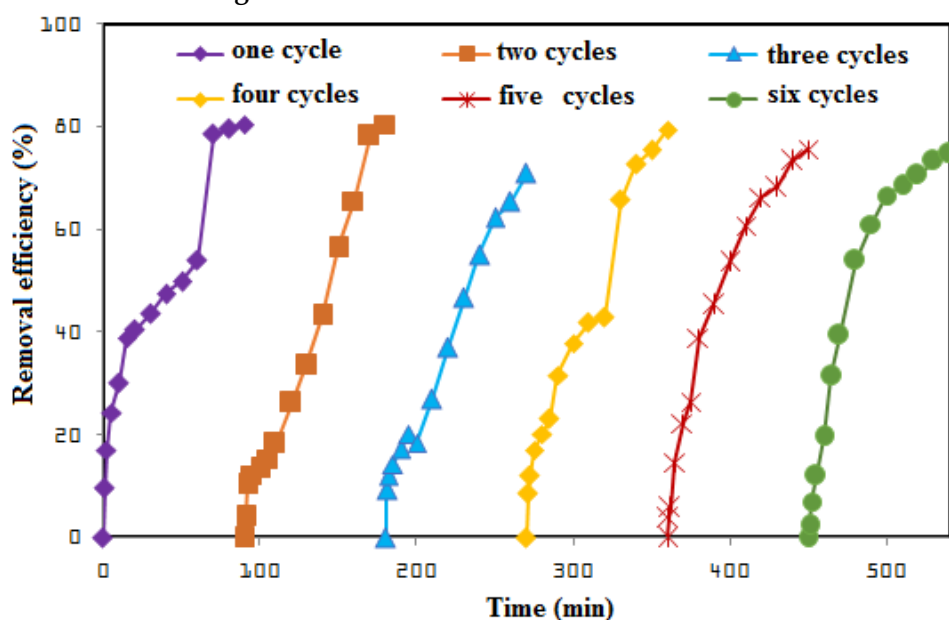


Fig. 7. The results of reusability test for the removal of RB-5 dye by $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-APTES}$ NPs (pH = 3, initial dye concentration = 20 mg L⁻¹, adsorbent dose = 0.4 g L⁻¹).

Kinetic and equilibrium studies

Adsorption kinetic experiments were performed at different RB-5 concentration 20, 40, 60 and 80 mg L⁻¹, at constant adsorbent dosage 0.4 g L⁻¹ and at pH = 3.

The kinetics and isotherms parameters are shown in Tables 3 and 4. The kinetic data for RB-5 adsorption showed the best fitting ($R^2 = 0.997$) with the pseudo-second order model. The values of correlation coefficient $R^2 = 0.995$, $R^2 = 0.987$ and $R^2 = 0.973$ at 20, 35 and 45 °C indicate that sorption of the RB-5 by

$\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-APTES}$ NPs follows the Langmuir isotherm. In these temperatures, interaction between the RB-5 and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-APTES}$ NPs is probably larger due to the presence of a higher number of potential adsorption sites. However, at high temperatures, the interaction between RB-5 and $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-APTES}$ NPs is weakened due to decrease in electrostatic and van der Waal interactions (Mohammadi Galangash *et al.* 2016). The Langmuir and Freundlich isotherm charts are displayed at 20 °C in Figs. 8 and 9.

Table 3. The kinetic parameters for removal of RB-5 dye by Fe₃O₄@SiO₂-APTES NPs.

Concentration mg L ⁻¹	Pseudo-first order				Pseudo-second-order		
	q _{e(exp)}	k ₁	q _{e(cal)}	R ²	k ₂	q _{e(cal)}	R ²
20	50	0.0215	51	0.0063	0.004007	52.63158	0.9947
40	85.101	0.0216	86.1	0.4818	0.001511	87.719	0.9855
60	106.32	0.0244	107.3	0.48	0.001336	109.89	0.979
80	109.4366	0.0032	108.8	0.4838	0.001047	114.9425	0.9748

Table 4. The isotherm parameters for the adsorption of RB-5 dye by Fe₃O₄@SiO₂-APTES NPs.

Temperature °C	Freundlich isotherm				Langmuir isotherm		
	K _F	N	R ²	q _m	K _L	R ²	R _L
20	35.07519	5.327651	0.8734	56.49718	1.041176	0.9957	0.045822
35	46.78429	2.85144	0.8848	116.2791	8.77551	0.9875	0.005665
45	43.05266	2.650411	0.9732	119.0476	6.774194	0.9734	0.007327

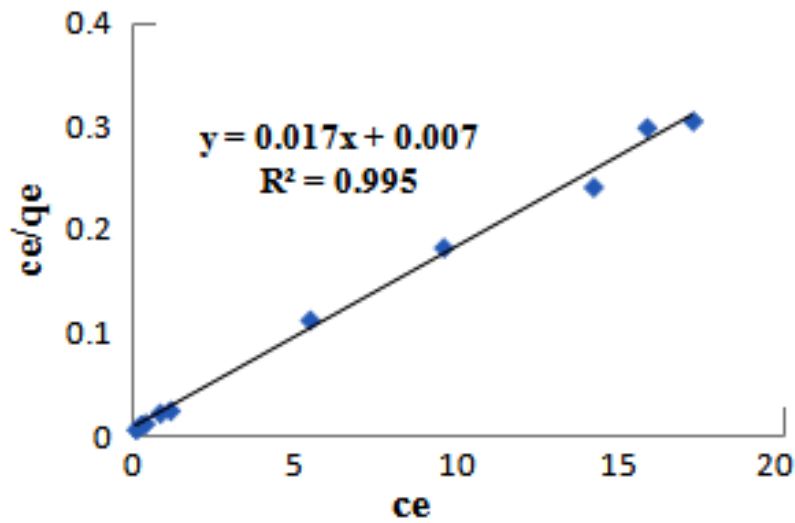


Fig. 8. Langmuir isotherm chart at 20 °C (pH = 3 and initial dye concentration = 20 mg L⁻¹).

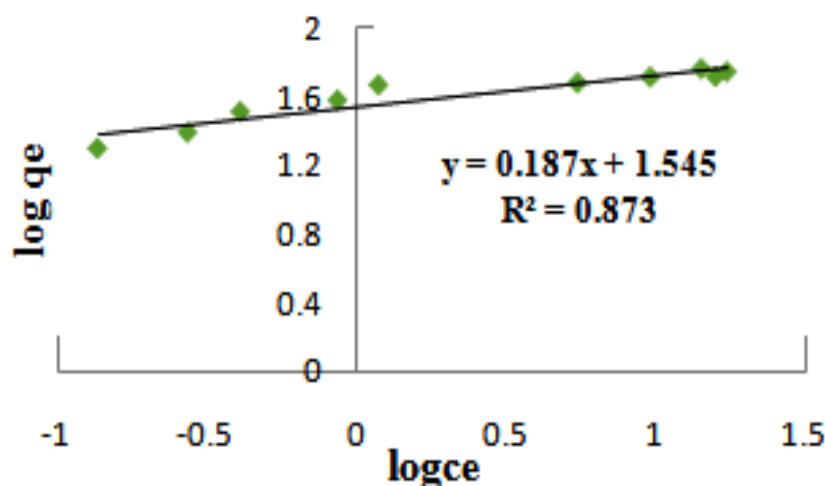


Fig. 9. Freundlich isotherm chart at 20 °C (pH = 3 and initial dye concentration = 20 mg L⁻¹).

DISCUSSION

In absorption studies, after synthesis and characterization of adsorbent, some parameters and models are evaluated to achieve the kind of adsorption process in the environment and the economic value of the prepared adsorbent. Kinetic evaluation is necessary to determine the rate and degree of dye removal efficiency (Soltani & Entezari 2013) and kinetic models are used to determine the absorption and penetration mechanisms (Salmani *et al.* 2011). As shown in Table 4, by increasing the initial concentration of RB-5 from 20 to 80 mg L⁻¹, the K_2 and R^2 ratios in the pseudo-second order kinetics were decreased from 0.004 to 0.001 g mg⁻¹ min⁻¹ and from 0.9947 to 0.9748, respectively. Also, q_e (mg g⁻¹) increased from 52.63 to 114.94 mg g⁻¹. These results show that the absorption process of RB-5 using Fe₃O₄@SiO₂-APTES NPs is more consistent with the Pseudo-second order model ($R^2 = 0.9999$). This model shows a chemical absorption (Wang *et al.* 2004).

The findings of Azizian (2004) and Xu *et al.* (2016) are consistent with the results of the present study.

The isothermal studies are carried out to explain the reaction between adsorbent and pollutant as well as the removal capacity (Alizadeh *et al.* 2012).

The Table 5 can be explained such that RB-5 absorption process is more compatible with Langmuir model ($R^2 = 0.9957$). The maximum

absorption capacity at 20 °C was 56.497 mg g⁻¹. Also, at this temperature, the amount of R_L factor was found 0.045 which is between 0 and 1 and this indicates the desirability of the absorption process (Farrokhi *et al.* 2014). The obtained results were consistent with those of Mohagheghian *et al.* (2015) and Mohammadi Galangash *et al.* (2016) on the removal of Azo dye by modified magnetic NPs.

The results also point out that the NPs have a homogeneous surface, and all of the absorbing sites are similar in surface and also the RB-5 absorption mechanism on Fe₃O₄@SiO₂-APTES NPs is monolayer and the adsorption sites in NPs surface have the same energy (Poursaberi & Hassanisadi 2013). The pH of the aqueous solution is an important effect on the surface charge of the adsorbents, the degree of ionization and speciation of the adsorbents. Therefore, in most water and wastewater treatment studies, this factor is always carefully considered. The results of this study, as shown in Fig. 4, illustrate that by increasing the pH, the absorption rate efficiency by the NPs has a decreasing trend, and these results are very consistent with those of Xu *et al.* (2016), Ballav *et al.* (2015) and Ballav *et al.* (2015).

The increased efficiency of the removal of RB-5 dye by Fe₃O₄@SiO₂-APTES NPs at acidic pH can be associated with an increase in positive H⁺ ion in the environment versus the

reduction of negative OH⁻ ions. Because RB-5 is an anionic dye, at low pH, and the adsorbent surface with positive charge, so a strong electrostatic interaction occurs between amine in the positively-charged groups on the adsorbent surface and negative RB-5 molecules. In other words, by decreasing the pH, the number of sites with positive charge on NPs increases, so these places tend to absorb dye due to electrostatic gravity (Geetha *et al.* 2014). Therefore, by increasing in pH, the removal efficiency of the RB-5 decreases, as shown schematically in Fig. 4b (Manimekalai *et al.* 2015). Subsequently, the adsorption of dye on Fe₃O₄@SiO₂-APTES NPs was investigated by changing the quantity of adsorbent on dye removal. The results of removal process showed that, by increasing the amount of adsorbent dosage from 0.1 to 0.4 g L⁻¹, the removal of dye performance had an aggregate trend. Apparently, by increasing the amount of active sites, the absorption process will be increased. But how long will this process last? Its response is shown in Fig. 5 that the removal rate of RB-5 at all doses was rapid in the first stages of contact time and then it was slowed down step by step. This kind of absorption process is consistent with results of Mohammadi Galangash *et al.* (2016). The rapid adsorption at the initial reaction time may be attributed to the easy availability of active sites for RB-5 molecules. As the active sites are occupied by RB-5, adsorption rates will be reduced due to less availability of active locates on the adsorbent surfaces (Xue *et al.* 2009). The concentration of the pollutant also plays an important role in the absorption process. By increasing the initial RB-5 concentration from 20 to 80 mg L⁻¹, the RB-5 removal efficiency was decreased. Similar observations were also reported for the removal of other dyes (Xue *et al.* 2009; Vimonses *et al.* 2009). These results can be explained with the fact that the adsorbent has a limited number of active sites, which would become saturated above a certain pollutant

concentration (Zhu *et al.* 2010). Therefore, we can determine, based on the optimum adsorbent dose rate, the maximum removable concentration of pollutant with proper efficiency for our operational planning (Fig. 6). As the amount of consumed NPs is considered in their economic assessment, the recycling potential and frequency of NPs recovery are other important factors that are very important for the economic justification of produced NPs (Mohammadi Galangash *et al.* 2016). According to Fig. 7, the reusability of adsorbent was examined and adsorption capacity of RB-5 by regenerated of Fe₃O₄@SiO₂-APTES NPs was maintained with proper efficiency up to six consecutive runs. Therefore, it can be recommended as a plausible adsorbent for treatment of the organic dyes. Regeneration of Fe₃O₄@SiO₂-APTES NPs by NaOH can be due to the weak electrostatic bond between the adsorbent and RB-5 dye in alkaline medium. As a result, the exchange of hydroxide ions and negative charge dye molecules will be occurred (Agarwal *et al.* 2016).

In fact, the RB-5 molecules on the surface of Fe₃O₄@SiO₂-APTES could be replaced with hydroxyl of the basic solution in adsorbent washing step. Under higher removal cycles, removal efficiency decrease may be due to oxidation, losing or dissolving some a mounts of the adsorbent through the following steps.

The adsorption capacity of Fe₃O₄@SiO₂-APTES for the removal of RB-5 has been compared with other adsorbents reported in literature and the values of q_{\max} have been listed in Table 5 (Kalkan *et al.* 2014; Mook *et al.* 2015; Samadi *et al.* 2015; Amin *et al.* 2015; Munagapati *et al.* 2018).

Therefore, noteworthy, the Fe₃O₄@SiO₂-APTES has important potential to remove RB-5 from aqueous solution.

Furthermore, the magnetic properties of Fe₃O₄@SiO₂-APTES make it as a more efficient adsorbent for the removal of contaminant from aqueous solution.

Table 5. Comparison of various adsorbents for RB-5 removal.

Adsorbents	q_m (mg g^{-1})	Adsorbent dosage (g L^{-1})	Concentration (mg L^{-1})	Best fit isotherm	Ref.
BPP ^a	49.2	0.60	300	Langmuir	Munagapati <i>et al.</i> 2018
Palm Shell ^b	25.1	3.0	40	Langmuir	Mook <i>et al.</i> 2015
LMSF ^c	322.58	1.0	5	Langmuir	Kalkan <i>et al.</i> 2014
MWCN ^d	36.2	0.50	50	Freundlich	Samadi <i>et al.</i> 2015
BC ^e	34.01	0.50	170	Freundlich	Amin <i>et al.</i> 2015
Fe ₃ O ₄ @SiO ₂ -APTES	56.497	0.40	20	Langmuir	This work

^a Banana Peel Powder^b Activated Carbon Derived from Biomass Waste^c Laccase-Modified Silica Fume^d Multi-Walled Carbon Nanotubes^e Bentonite Clay

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حذف رنگ راکتیو بلک ۵، از محلول‌های آبی با استفاده از نانو ذرات مغناطیسی آهن-سیلیکا آمین‌دار

بزرگ پناه خراط ز.^۱، محمدی گلنگش م.^{۱*}، قویدست ع.^۱، شیرزاد سبینی م.^۳

- ۱- گروه علوم و مهندسی محیط زیست، دانشکده منابع طبیعی، دانشگاه گیلان، صومعه‌سرا، گیلان، ایران و وابسته پژوهشی گروه مهندسی آب و محیط زیست، پژوهشکده حوضه آبی دریای خزر، دانشگاه گیلان
- ۲- گروه شیمی، دانشکده علوم، دانشگاه گیلان، رشت، ایران
- ۳- گروه مهندسی بهداشت محیط، دانشکده بهداشت، دانشگاه علوم پزشکی گیلان، رشت، ایران و مرکز تحقیقات بهداشت و محیط زیست، دانشگاه علوم پزشکی گیلان، رشت ایران

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چکیده

در این تحقیق، نانو ذرات مغناطیسی آهن-سیلیکا با پوشش آمین به روش تک ظرفی به طور موفقیت‌آمیزی برای حذف رنگ راکتیو بلک ۵ از محلول‌های آبی سنتز شدند. برای به دست آوردن شرایط بهینه، پارامترهایی از قبیل pH، غلظت اولیه رنگ و مقدار جاذب بر کارایی حذف بررسی شد. براساس نتایج آزمایش، راندمان حذف، با افزایش pH، غلظت رنگ و نیز با کاهش دوز جاذب، کاهش یافت. در واقع، ۱۰٪ رنگ راکتیو بلک ۵ با استفاده از ۰/۴ گرم بر لیتر از نانو ذرات آهن-سیلیکا آمین‌دار در pH=۳ و در مدت ۹۰ دقیقه، از محلول‌های آبی حذف شد. نتایج سینتیک نشان داد که بهترین مدل برای جذب رنگ، مدل شبه درجه دوم است و آنالیز حاصل از ایزوترم، تطبیق داده‌های تعادلی را با ایزوترم لانگمویر ثابت کرد که نشان‌دهنده جذب سطحی رنگ به صورت تک‌لایه‌ای بر روی سطح همگن نانوذرات است. همچنین نانو جاذب آهن-سیلیکا آمین‌دار به سهولت بازیابی شده و با وجود شش مرتبه بازیابی، از کارایی حذف مطلوبی برخوردار بودند.

*مؤلف مسئول