



# Sulfonic Acid Functionalized SBA-3 Silica Mesoporous Magnetite Nanocomposite for Safranin O Dye Removal

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## Abstract

At the present study, sulfonic acid functionalized SBA-3 silica mesoporous magnetite nanocomposite ( $\text{Fe}_3\text{O}_4@ \text{SiO}_2@ \text{SBA-3-SO}_3\text{H}$ ) was synthesized and its adsorption ability for removing Safranin O dye from aqueous samples was investigated. X-ray diffraction analysis (XRD), vibrating sample magnetometer (VSM), energy dispersive X-ray spectroscopy analysis (EDX), field emission scanning electron microscopy (FESEM) and Fourier transform infrared spectroscopy (FT-IR) were used to characterize the adsorbent. The FESEM images confirmed the synthesis of nanocomposites with good morphology and size below 30 nm. The experimental variables affecting the removal efficiency were optimized by Taguchi orthogonal array experimental design method ( $L_{16}$  array). At the optimal conditions (pH = 6, ionic strength =  $0.005 \text{ mol L}^{-1}$ , sample volume = 25 mL, adsorbent weight = 0.12 g and contact time = 15 min) the efficiency for Safranin O removal was obtained as higher than 91%. The pseudo-first-order, pseudo-second-order, intra particle and Elovich kinetic models were investigated, and the kinetic data followed the pseudo-second-order kinetic model ( $R^2 = 0.9999$ ). Also, the study of three isotherm models (Langmuir, Freundlich and Temkin) showed that Freundlich isotherm was suitable for describing Safranin O adsorption ( $R^2 = 0.9941$ ,  $n = 1.428$ ). The reusability experiments showed high removal efficiency of Safranin O after 9 cycles of usage. Finally, the results of Safranin O removal from the aqueous real samples showed the applicability of this nanocomposite for Safranin O removal applications.

**Keywords** Nanocomposite · Taguchi · Removal · Safranin O · Magnetite · Mesopore · SBA

## 1 Introduction

Contamination of water by dyes that are consumed in many industries is an important environmental problem because it threatens health of humans and aquatic organisms [1, 2]. It has been reported that 10,000 different dyes are produced annually for different industrial activities [3]. Many of these dyes are toxic and dangerous for aquatic life organisms. Also, release of dye compounds

into the water system is hazardous for human and can cause mutagenic effects, allergic dermatitis, skin irritation, cancer, and mutation [4, 5]. For removing dyes from aqueous solutions, physical and chemical methods such as flocculation, electro-flotation, precipitation, electro-kinetic coagulation, ion exchange, membrane filtration, electro-dialysis, photocatalytic degradation, oxidation, irradiation, and ozonation have been used [6–8]. Safranin O (3,7-dimethyl-10-phenylphenazin-10-ium-2,8-diamine chloride) as an oldest synthetic dye is reddish brown powder and water-soluble [9]. It is widely used in flavoring and coloring candies and cookies as food dye as well as for dyeing tannin, cotton, bast fibers, wool, silk, leather and paper [10, 11]. Safranin O has a lot of harm for human health such as irritation to mouth, throat, tongue, lips and pain in stomach even causes diarrhea, vomiting and nausea [12, 13]. Moreover, it leads to eye irritation that even cause damage the cornea and conjunctiva [14, 15]. The various methods

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were used for removing this dye from wastewater like coagulation, flocculation, reverse osmosis, and adsorption onto several adsorbent materials [16, 17]. Up to now, different types of adsorbent materials have been successfully investigated for the removal of various dyes [18–28]. In this study,  $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{SBA-3-SO}_3\text{H}$  nanocomposite was synthesized and used as an adsorbent to remove Safranin O from aqueous samples. After characterization of the synthesized nanocomposite, kinetic and isotherm models were studied to clarify the adsorption process. Also, Taguchi experimental design was examined to determine the optimum conditions of the experiment.

## 2 Experimental

### 2.1 Materials and Instruments

All of chemicals used including ferric chloride hexahydrate ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ), ferrous chloride tetrahydrate ( $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ), ammonia solution (28%, w/w), hydrochloric acid (37%, w/w), cetyl trimethyl ammonium bromide (CTAB), ethanol, sodium chloride, tetraethyl orthosilicate (TEOS), mercaptopropyl trimethoxysilane (MPTS) and Safranin O were purchased with high purity from Merck (Darmstadt, Germany) and Sigma-Aldrich (ST. Louise, Missouri, USA). FT-IR spectra of samples were determined using Shimadzu FT-IR spectrophotometer (model 470, Japan) by using KBr pellets. An Agilent UV-Vis spectrophotometer (Carry 60, USA) was used for spectrophotometric measurements. The XRD analysis of the synthesized nanocomposite was studied by Phillips X-ray diffractometer (pw-1840) with  $\text{Cu-K}\alpha$  radiation source ( $\lambda = 1.54056^\circ$ ). The morphologies of the as-synthesized particles were analyzed by FESEM (MIRA3, TE-SCAN Co., Czechoslovakia). VSM instrument (LBKFB model- Meghnatis Daghigh, Kavir Co.,) was used to investigate the magnetic property of the synthesized nanocomposite. Energy dispersive X-ray spectroscopy analysis (EDX) was carried out using a FESEM (Sigma VP, ZEISS company, Germany) equipped to EDS detector and was used to confirm the elemental composition of the synthesized nanocomposites. A digital Bante pH meter (model 930, China) was used to adjust the pH values of the solutions. Digital ultrasound (DSA100-SK2 code, DIY brand, China) and oven (Memert, Germany) were utilized. For magnetic separations, a strong super magnet ( $1 \times 3 \times 5$  cm) with 1.4 Tesla magnetic field was applied.

### 2.2 Synthesis of Magnetite Nanoparticles ( $\text{Fe}_3\text{O}_4$ )

The co-precipitation method was applied for the synthesis of magnetite nanoparticles (MNPs). Briefly, 10.4 g of

$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , 4.0 g of  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  and 1.7 mL of HCl 37% (w/w) were dissolved in distilled water and the solution was adjusted to the mark of a 50 mL volumetric flask. Afterward, the solution was transferred into a separatory funnel and degassed for 20 min using nitrogen gas.

Then, 250 mL of  $1.5 \text{ mol L}^{-1}$  ammonia solution was transferred into a three necked flask containing a magnet. This solution was heated to  $80^\circ\text{C}$  in the oil bath. Thereafter, the mixture of iron chlorides was added dropwise to a solution of ammonia in a degassed environment during 60 min. When the first drop entered, the nucleation process was started and black nanoparticles of  $\text{Fe}_3\text{O}_4$  sediment was formed. After the reaction was completed, the MNPs were washed with double distilled water four times and were separated from the reaction environment with a strong super magnet (1.4 T). The synthesized MNPs were located in  $0.1 \text{ mol L}^{-1}$  NaOH solution during 24 hours due to prevent the accumulation of MNPs. Eventually, MNPs washed with distilled water and were dried at  $120^\circ\text{C}$  for 120 min in the oven [29].

### 2.3 Surface Modification of the MNPs with Silica Coating ( $\text{Fe}_3\text{O}_4@\text{SiO}_2$ )

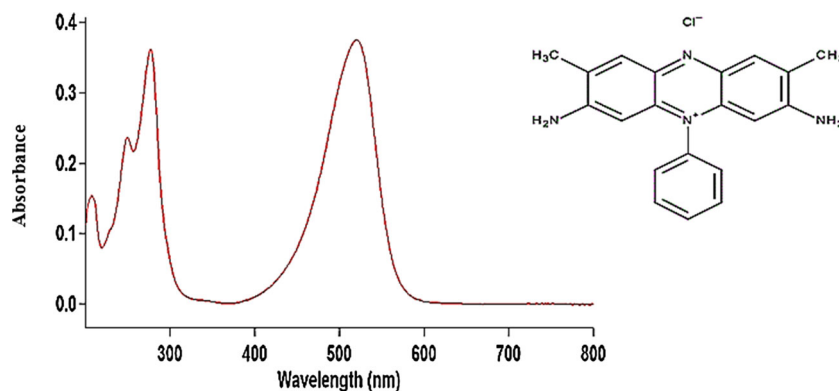
The surface of produced MNPs was modified with silica coating for increasing their stability against oxidation and other side reactions. For silica coating the following steps were applied:

200 mL of the suspension of MNPs (2.4 g of MNPs in 600 mL ethanol 96%) was added to a 1 L volumetric flask and was put in an ultrasonic bath for 10 min at  $80^\circ\text{C}$ . Afterwards, 25 mL of ammonia solution (28% w/w) was added to the suspension (solution A).

On the other hands, 100 mL of pure ethanol and 10.8 mL of TEOS were mixed (solution B). The solution B was added to a solution A during 2 h using a separatory funnel. After that, the mixture was stirred strongly for 7 h under the same conditions. Then, the mixture was separated by magnet and washed three times with 1:1 mixture of distilled water/ethanol. The produced brown sediment was dried at  $100^\circ\text{C}$  for 5 h [30, 31].

### 2.4 Synthesis of Santa Barbara Amorphous Mesoporous Magnetite Nanoparticles ( $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{SBA-3}$ )

Synthesis of Santa Barbara Amorphous (SBA-3) mesoporous structure on the surface of  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  nanoparticles was carried out according to our previous study [29]. First, 4.1 g of CTAB surfactant was dissolved into distilled water (35 mL) in a beaker and was stirred for 10 min at  $35^\circ\text{C}$ . Then, 2.5 mL of concentrated HCl was added to the

**Fig. 1** Absorption spectra of Safranin O dye

mixture and was stirred for 1 h. Afterward, 1.5 g of prepared magnetite nanoparticles with silica coating ( $\text{Fe}_3\text{O}_4@\text{SiO}_2$ ) was added to the mixture and stirred for 20 min. In the next step, 4 mL of TEOS was added to the mixture and stirred for 0.5 h in the same conditions. The mixture was washed several times with distilled water to remove HCl from the environment. In the end, the obtained precipitate was washed with distilled water and was separated by the magnet. This product dried in an oven at 100 °C for 12 h. The dried precipitate was transferred into a jelly balloon and added to 100 mL of ethanol. The dried precipitate was poured into a volumetric flask and 100 mL of ethanol was added to it and refluxed for 6 h. After time period of reflux, the content of the container was washed with double distilled water (5 times), separated with the magnet and dried in an oven at 90 °C. Then, the nanoparticles were placed in the furnace for 5 h to calcify at 550 °C. The color of the final product was orange [32].

### 2.5 Synthesis of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{SBA-3}$ Functionalized with Sulfonic Acid Group ( $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{SBA-3-SO}_3\text{H}$ )

For this purpose, 1 g of synthesized  $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{SBA-3}$  nanoparticles and 1.25 mL of MPTS were added to 30 mL of toluene and the mixture was stirred. Then, the mixture was refluxed for 24 h at 130 °C. The mixture was washed with distilled water and separated by a magnet. Eventually,

it dried in the oven at 90 °C. 2 mL of hydrogen peroxide and 20 mL of methanol were added to nanoparticles and the mixture was stirred at 25 °C for 24 h. Finally, the nanoparticles were washed with double distilled water, separated by a magnet and dried in an oven at 90 °C for 2 h [31].

### 2.6 Preparation of Safranin O Solutions

In this study, magnetic nanoparticles ( $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{SBA-3-SO}_3\text{H}$ ) were used to remove Safranin O dye from aqueous samples. For this purpose, 1000 mg  $\text{L}^{-1}$  of Safranin O was prepared in distilled water and by diluting it, the desired concentrations were prepared. Initially, to determine the dependence of UV-Vis absorption behavior of Safranin O on the pH of the solution, solutions containing 10 mg  $\text{L}^{-1}$  of Safranin O were prepared in the pH range of 2 to 10. As shown in Fig. 1, maximum absorption wavelength of the Safranin O was obtained as 517 nm.

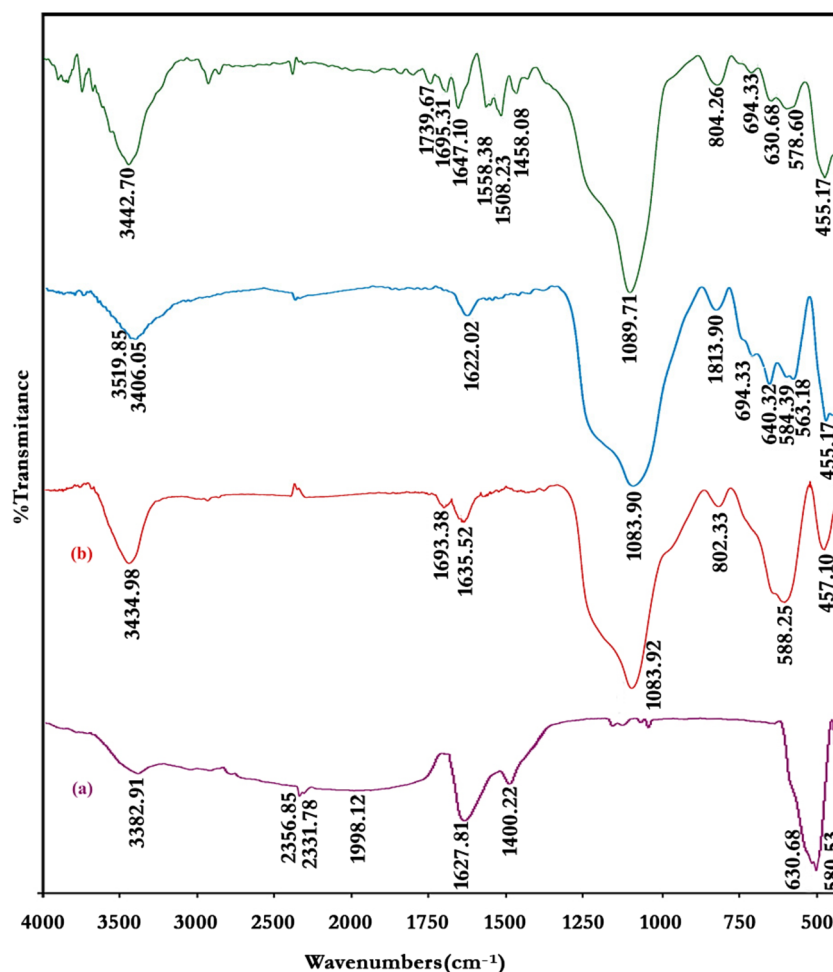
### 2.7 Experimental Design Method to Remove Safranin O

In this study, five experimental variables affecting the extraction efficiency including adsorbent weight, adsorbent contact time with solution (stirring time), ionic strength, pH, and volume of dye solution were investigated in four levels using Taguchi experimental design (Table 1). 16 experiments were carried out to determine the optimum conditions for the test. Briefly, for each removal experiment, the certain amount of dye solution was poured into the beaker and after pH adjustment, its initial UV-Vis absorption was measured using the spectrophotometer. Then, adsorbent was added to the beaker and the mixture was stirred for a specific time. After completion of removal period, the beaker was placed on a magnetic stirrer, the MNPs were separated and the absorption of residual solution was

**Table 1** Factors and levels of Taguchi experimental design

Parameter	Level 1	Level 2	Level 3	Level 4
pH	3	4	5	6
Ionic strength ( $\text{mol L}^{-1}$ )	0	0.005	0.01	0.05
Contact time (min)	5	10	15	30
Volume of solution (mL)	25	50	75	100
Weight of adsorbent (g)	0.01	0.05	0.08	0.12

**Fig. 2** FT-IR spectra of  
**a** Fe<sub>3</sub>O<sub>4</sub>, **b** Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>,  
**c** Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@SBA-3  
**d** Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@SBA-3/SO<sub>3</sub>H



measured spectrophotometry. The dye removal efficiency was calculated according to Eq. 1.

$$\% \text{ Removal} = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

Where,  $C_0$  and  $C_t$  are the initial and equilibrium concentrations of Safranin O dye after adsorption process, respectively.

## 3 Results and Discussion

### 3.1 Characterization of the Synthesized Nanocomposites

Figure 2 shows the FT-IR spectrum of Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@SBA-3 and Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@SBA-3/SO<sub>3</sub>H. Fig. 2a displays FT-IR spectra of Fe<sub>3</sub>O<sub>4</sub> MNPs. The absorption band in the region of 500–600 cm<sup>-1</sup> is related to the Fe-O vibrating bands. This absorption band is observed in all spectra and because of its coating with the silica layer, its intensity is reduced in the spectra of (b) to (d).

Part (b) shows the FT-IR spectrum of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> MNPs. The observed peaks in 1083 and 699 cm<sup>-1</sup> are related to asymmetric and symmetric vibrations of Si-O-Si which is shown in (b) to (d). The absorption band at 1820 cm<sup>-1</sup> is related to the stretching vibrations of S-OH. Width peak at 3000 to 3500 cm<sup>-1</sup> is related to adsorbed water molecules. Part (c) represents the spectrum of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@SBA-3 and it shows that the intensity of the peaks in this spectrum is reduced. Also, the spectrum of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@SBA-3/SO<sub>3</sub>H is shown in part (d). The peaks of symmetric and asymmetric stretching vibrations of O=S=O and the S-O from the SO<sub>3</sub>H group are observed in 1200–1250, 980–1100 and 628 cm<sup>-1</sup>, respectively. O=S=O peaks indicate overlap with the Si-O-Si peak.

Figure 3a shows the XRD spectrum of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@SBA-3. In (a), the two peaks are in  $2\theta$  equal to 1° and 0.84° in the range of 0–2. This represents the hexagonal structure of the cavities for the magnetic combination of the SBA-3. In (b), appeared peaks in  $2\theta$  are equal to 35.66°, 43.35°, 57.3° and 62.96° related to Fe<sub>3</sub>O<sub>4</sub> nanoparticles that displays the XRD pattern of the reference for the Fe<sub>3</sub>O<sub>4</sub> standards (19-629 JCPDS).

**Fig. 3** The XRD spectra of  $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{SBA-3}$  **a** Low angles **b** High angles

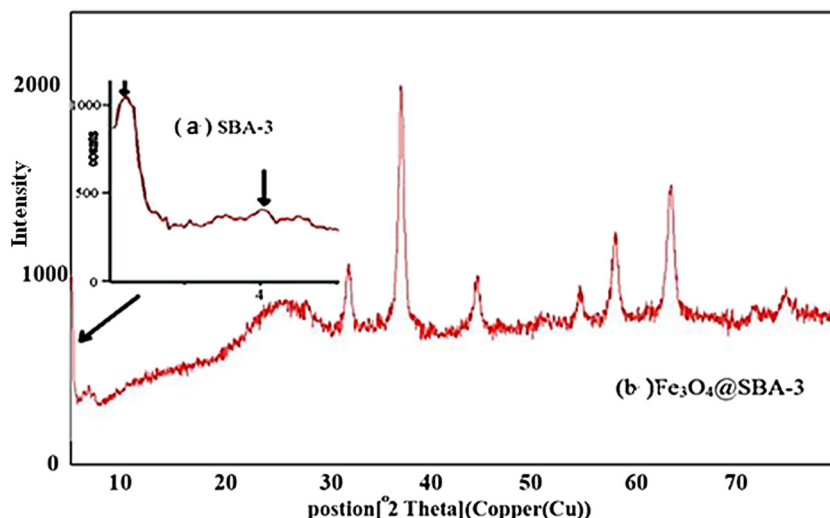


Figure 4 shows the EDX image for the identification of  $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{SBA-3}$  nanocomposite. The spectrum confirms the presence of Fe (32.50%), O (38.13%) and Si (29.37%) elements in the nanocomposite structure that shows the presence of 44.8% wt of  $\text{Fe}_3\text{O}_4$  in the structure of synthesized nanocomposite.

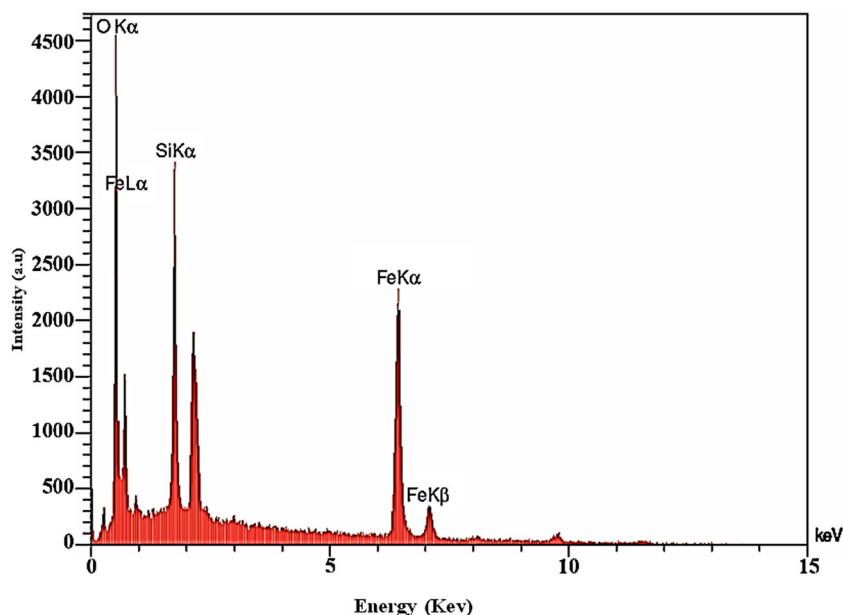
Figure 5 indicates the FESEM image of the synthesized  $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{SBA-3}$  nanocomposite. This figure shows that the particle size is less than 30 nm.

The vibrating scanning magnetometry intensity (VSM) of  $\text{Fe}_3\text{O}_4$ ,  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  and  $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{SBA-3}$  magnetic nanoparticles are demonstrated in Fig. 6. The magnitude of their magnetic properties are obtained as 55, 40, and

30 emg /u, respectively. Reducing the magnetic properties of the mesoporous coated magnetite relative to bare magnetite nanoparticles are due to the coating of  $\text{Fe}_3\text{O}_4$  magnetic particles with non-magnetic SBA-3 and  $\text{SiO}_2$  shell. In addition, the magnetic property of  $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{SBA-3}$  is lower than that of  $\text{Fe}_3\text{O}_4@\text{SiO}_2$ , because magnetic property gets less by adding the SBA-3 layer to  $\text{Fe}_3\text{O}_4@\text{SiO}_2$ . The experiments showed that the samples are easily separated from the water solution by the magnet within short time.

The surface area and pore size of the  $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{SBA-3}$  nanoparticles were measured in our previous study by nitrogen adsorption–desorption isotherms (at 77 K) and BET method as  $627.87 \text{ m}^2\text{g}^{-1}$  and 2.44 nm, respectively [29].

**Fig. 4** The EDX spectrum of  $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{SBA-3}/\text{SO}_3\text{H}$



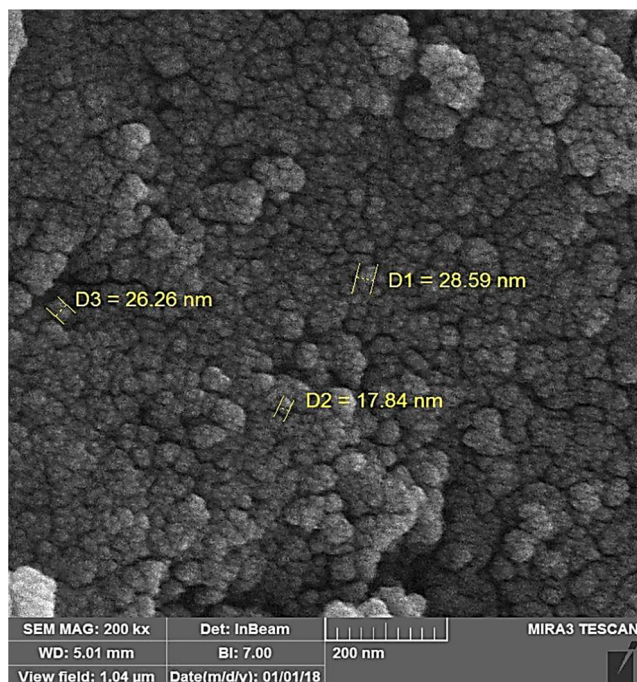


Fig. 5 FESEM image of  $\text{Fe}_3\text{O}_4@SiO_2@SBA-3$  nanocomposite

### 3.2 Effect of Solution pH on the Efficiency of Safranin O Removal

In preliminary studies, alkaline and acidic pHs were investigated in the pH range of 3–10 using HCl ( $1 \text{ mol L}^{-1}$ )

and NaOH ( $1 \text{ mol L}^{-1}$ ) solutions. The preliminary experiments showed the better removal efficiency of Safranin O under pHs lower than 6. Therefore, pHs between 3 to 6 were investigated in optimization step. As shown in Fig. 7a, the highest dye adsorption was obtained at pH = 6. Therefore, this pH was chosen as the optimum value for other experiments.

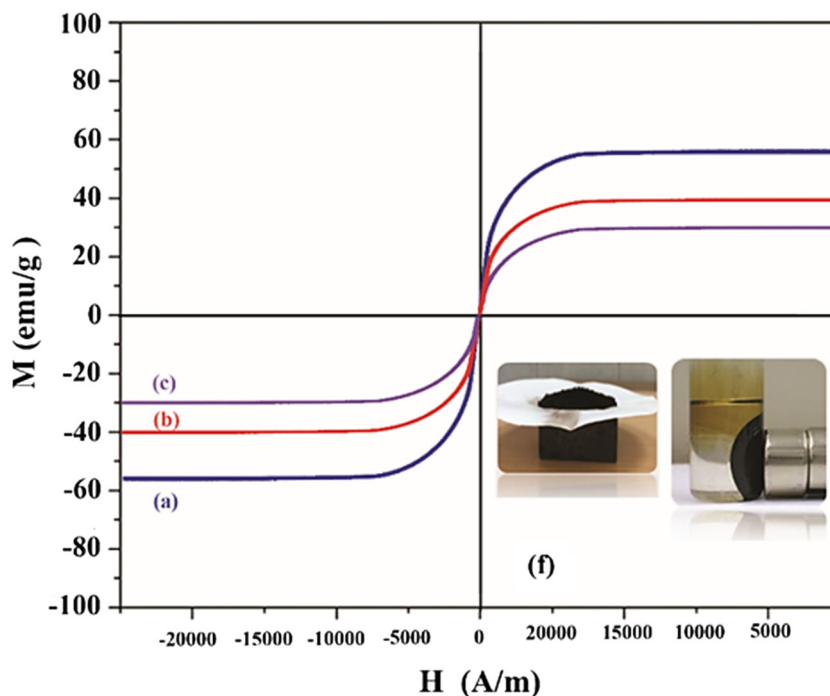
### 3.3 Effect of Ionic Strength on the Efficiency of Safranin O Removal

The effect of ionic strength on the dye removal was investigated by adding different concentrations of NaCl to solution. Initially, with the increase of ionic strength, amount of dye removal increased due to the salting out effect. Furthermore, by more increasing in ionic strength, the amount of dye removal has gradually decreased due to the competition between  $\text{Na}^+$  and Safranin O dye for adsorption sites. According to the results in Fig. 7b, the salt concentration of  $0.005 \text{ mol L}^{-1}$  was obtained as the optimum amount of salt for ion strength adjustment.

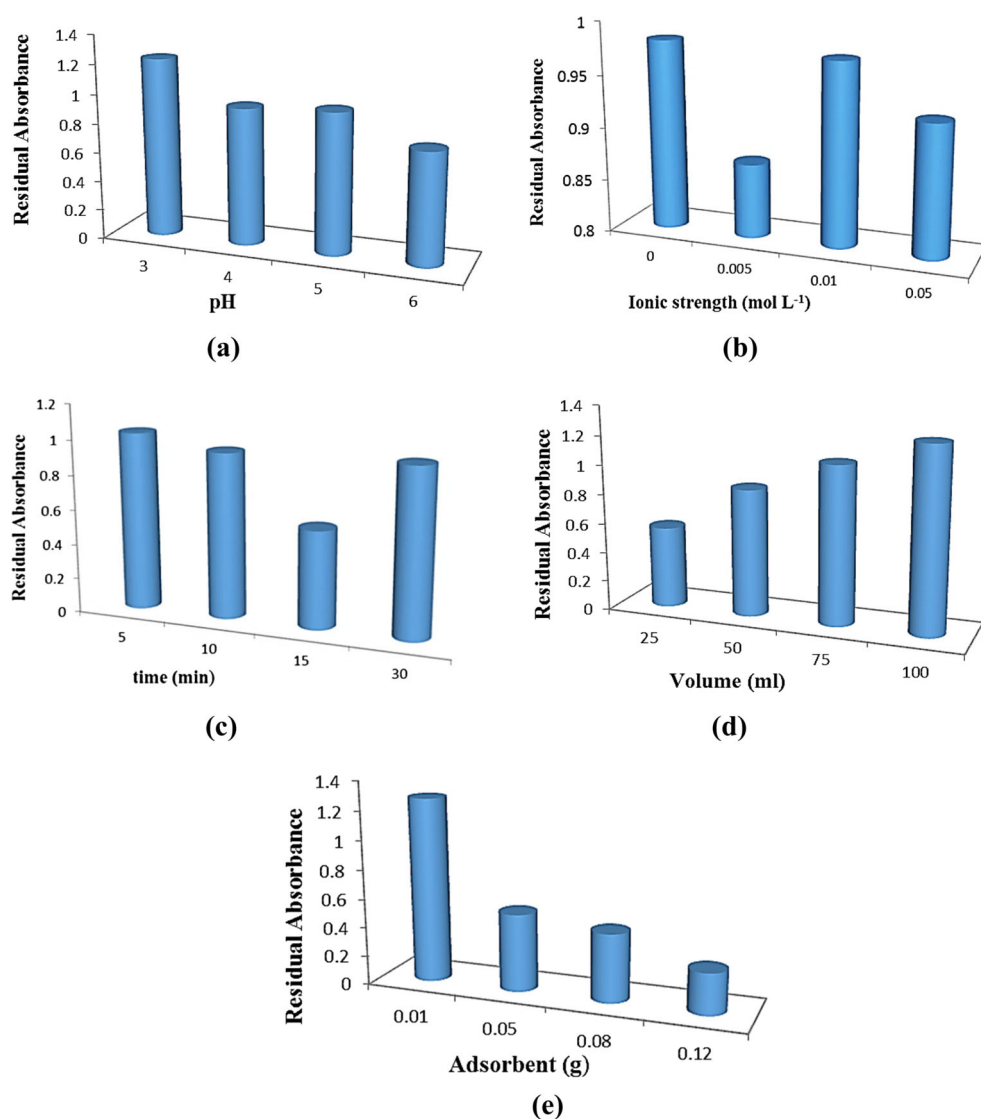
### 3.4 The Effect of Contact Time on the Efficiency of Safranin O Removal

To investigate the effect of contact time between the adsorbent and solution, contact times of 5, 10, 15 and 30 min were studied. As shown in Fig. 7c, the adsorption process was rapid and finally, the system reached to equilibrium

Fig. 6 Results of the VSM curve for identification of **a**  $\text{Fe}_3\text{O}_4$ , **b**  $\text{Fe}_3\text{O}_4@SiO_2$ , **c**  $\text{Fe}_3\text{O}_4@SiO_2@SBA-3$



**Fig. 7** **a** Effect of pH, **b** effect of ionic strength, **c** effect of contact time, **d** effect of volume of sample and **e** effect of weight of adsorbent on the efficiency of removal Safranin O



after 15 min. This time is less than similar investigations on Safranin O dye adsorption [33].

### 3.5 The Effect of Volume of Sample on the Efficiency of Safranin O Removal

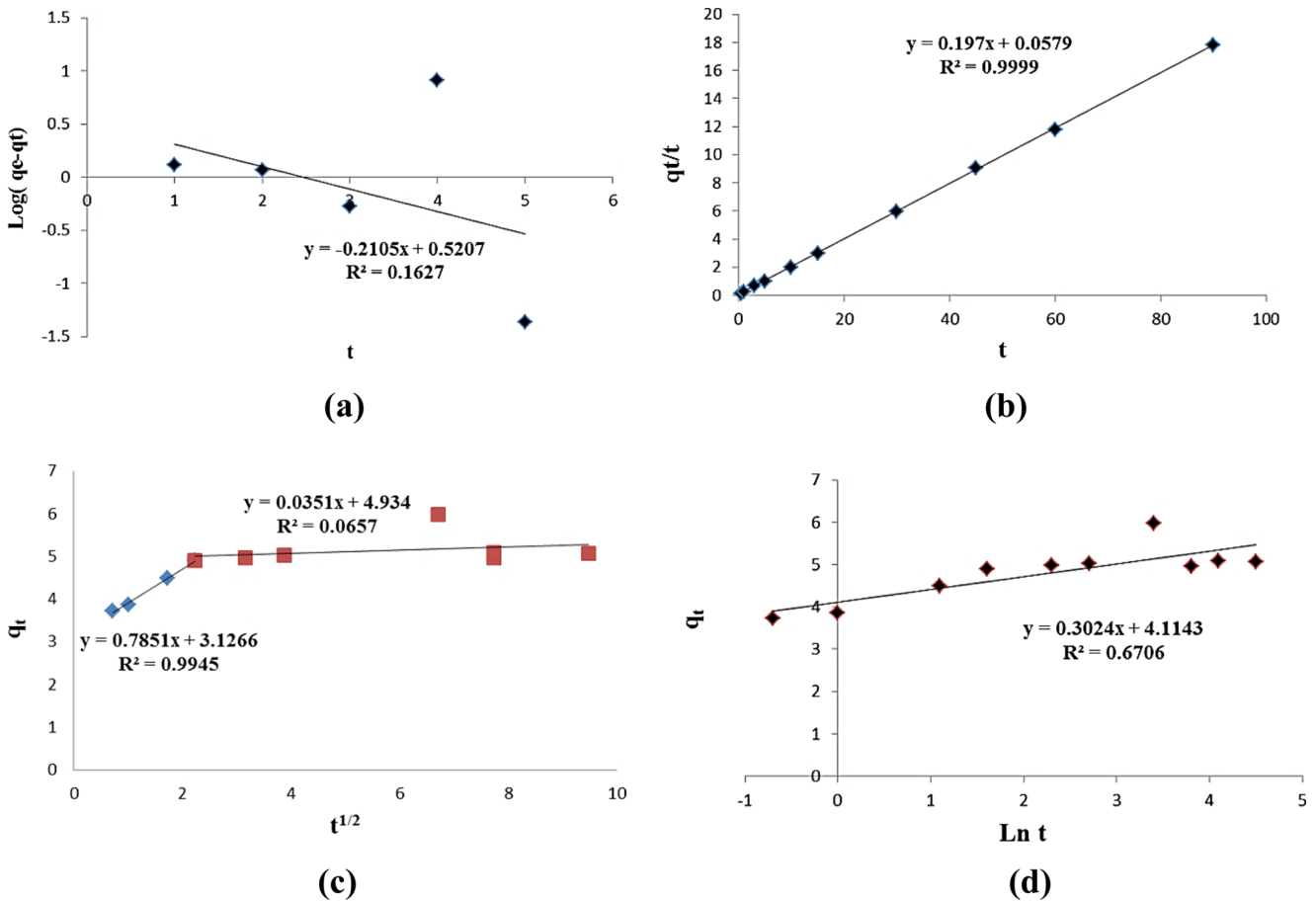
Figure 7d displays that with increasing of sample volume from 25 to 100 mL, the percentage of dye removal decreased. Therefore, the volume of 25 mL was selected as optimal volume. Afterwards, the amount of dye removal was reduced by increasing the volume of the solution. With increasing volume at constant concentration, the amount of dye increases. At higher volumes of sample, more mass of Safranin O is present in the sample and at a constant weight of adsorbent, the adsorption sites of adsorbent is not enough for complete removal.

### 3.6 The Effect of Adsorbent Weight on the Efficiency of Dye Removal

According to the results of the experiments in Fig. 7e, the dye removal is increased by increasing the amount of adsorbent. Hence, 0.12 g of adsorbent (4.8 g L<sup>-1</sup>) was considered as the optimum adsorbent weight for dye removal.

### 3.7 Approval Test in Optimal Conditions for Removing Safranin O

To investigate the accuracy of the optimum values obtained by Taguchi orthogonal array for removing Safranin O dye, five experiments were carried out under the optimum conditions (initial Safranin O concentration = 25 mg L<sup>-1</sup>, ionic strength = 0.005 mol L<sup>-1</sup>, pH 6, adsorbent weight



**Fig. 8** **a** pseudo-first-order kinetic, **b** pseudo-second-order kinetic, **c** Intra-particle diffusion and **d** Elovich models for removal Safranin O

=0.12 g, contact time = 15 min and sample volume = 25 mL). The results showed that under optimum conditions, the removal efficiency is higher than 94.5% ( $S_D = 0.436$  for five removal replicates in optimum conditions) with relative standard deviation percent (RSD %) of 0.462 that indicates the process of Safranin O removal by the proposed adsorbent is repeatable.

**3.8 Investigating of Kinetic Models**

To examine the rate of the adsorption process and rate controlling step, kinetic models are used. Pseudo first order, pseudo second order, Elovich and intra-particle diffusion are the

most kinetic models [34]. In the present study, these kinetic models were used for studying adsorption kinetic behavior of Safranin O on  $Fe_3O_4@SiO_2@SBA-3/SO_3H$  adsorbent. Using Eq. 2 related to the pseudo- first -order, the values of  $q_e$ ,  $q_t$ , and  $K_1$  were calculated, which  $q_e$  and  $q_t$  are the amount of dye adsorbed ( $mg\ g^{-1}$ ) at equilibrium time and at the time  $t$ , respectively. The curve corresponding to first order kinetic model is shown in Fig. 8a. The correlation coefficient of this model is undesirable ( $R^2 = 0.1627$ ). So, the empirical data does not follow the pseudo first order kinetic model.

$$\log (q_e - q_t) = \log q_e - \frac{k_1 \cdot t}{2.303} \tag{2}$$

**Table 2** The obtained parameters of kinetic models for removal of  $25\ mg\ L^{-1}$  of Safranin O

Kinetic model	Pseudo first order			Pseudo second order			Intraparticle diffusion			Elovich		
	$q_e$	$K_1$	$R^2$	$q_e$	$K_2$	$R^2$	K	C	$R^2$	$\alpha$	$\beta$	$R^2$
Concentration ( $25\ mg\ L^{-1}$ )	5.980	-0.210	0.1627	5.076	0.670	0.9999	0.143	4.177	0.485	156227.660	3.309	0.6702



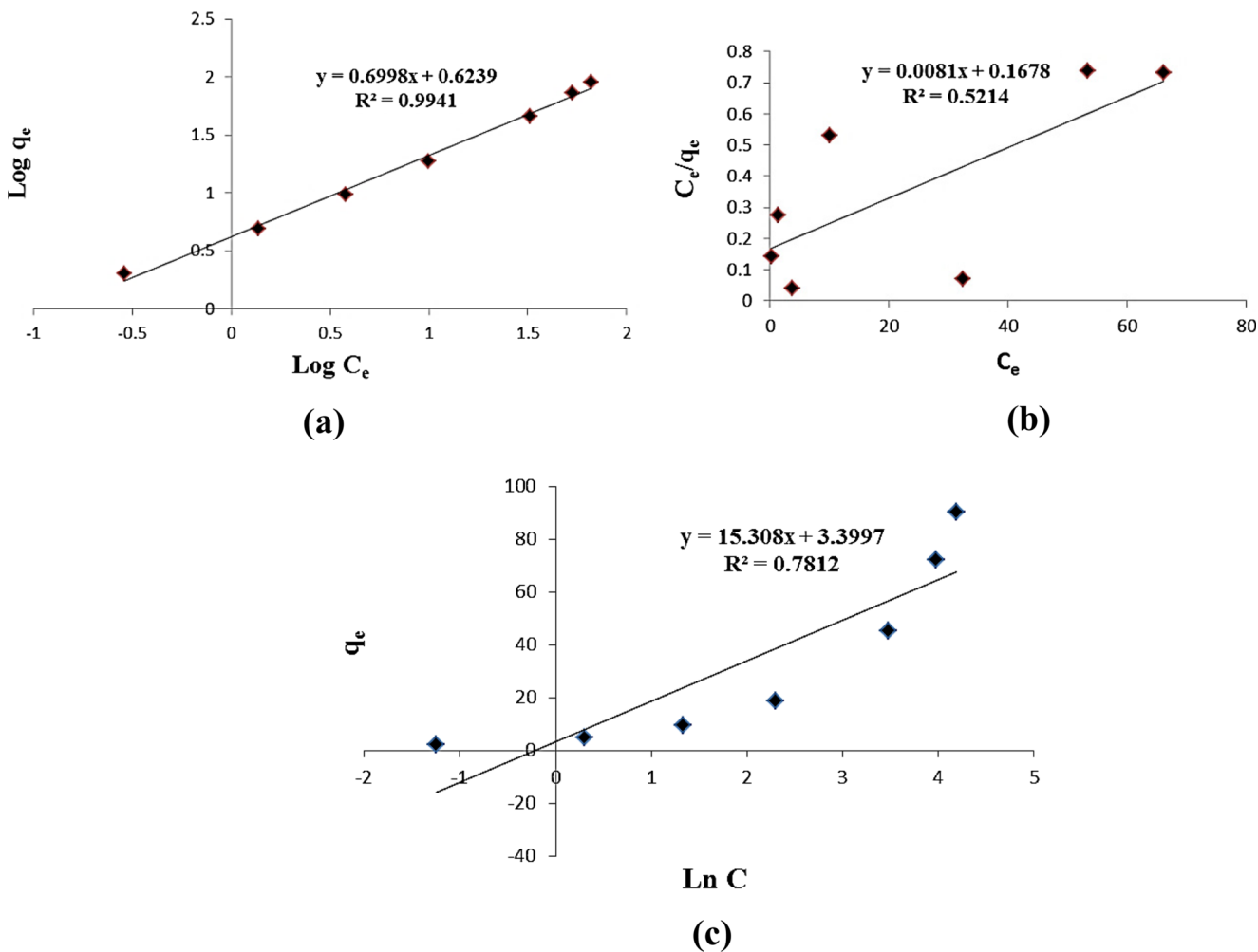


Fig. 9 a Freundlich, b Langmuir and c Temkin isotherms to remove Safranin O

On the other hand, the pseudo second order kinetic equation is shown as follows (3):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right) \cdot t \tag{3}$$

Where  $k_2$  is the equilibrium rate constant ( $g\ mg^{-1}\ min^{-1}$ ). As shown in Fig. 8b, the correlation coefficient of this model was obtained as  $R^2 = 0.9999$ . Therefore, this model is suitable for the interpretation of empirical data. It shows that adsorption of dye on the synthesized adsorbent is chemical. Also, intra-particle diffusion model

was investigated, which equation related to it is given as:

$$q_t = k_{diff} t^{1/2} + C \tag{4}$$

Where  $K_{diff}$  is the intra-particle diffusion rate constant ( $mg\ g^{-1}\ h^{1/2}$ ) and  $C$  ( $mg\ g^{-1}$ ) is the thickness of the boundary layer. The obtained result of this model is shown in Fig. 8c. The model shows that intra-particle diffusion is not the only stage for determining speed [35].

The other studied kinetic model is Elovich that its equation is shown in Eq. 5.

$$q_t = 1/\beta \cdot \ln(\alpha \cdot \beta) + 1/\beta \cdot \ln(t) \tag{5}$$

Table 3 The obtained parameters of isotherm models for removal of Safranin O

Langmuir			Freundlich			Temkin		
$q_m$	$K_1$	$R^2$	$K_f$	$n$	$R^2$	$K_t$	$K_1$	$R^2$
123.45	0.048	0.5214	4.206	1.428	0.9941	1.248	15.308	0.7812

**Table 4** Results of adsorbent efficacy on the removal of Safranin O in real samples

Sample <sup>a</sup>	Sample absorption before adding dye	Absorption of dye solution	Sample absorption after dye removal	Recovery (%)
Water of dye industry	0.004	1.482	0.194	91.653
Water of Pasikhan river	0.007	1.393	0.153	93.262
Tap water	0.001	1.427	0.091	98.211

<sup>a</sup>Samples were collected from Rasht city, Guilan Province, Iran

Where  $\alpha$  is the initial sorption rate ( $\text{mg g}^{-1} \text{min}^{-1}$ ) and  $\beta$  is the extent of surface coverage and activation energy of chemical adsorption ( $\text{g mg}^{-1}$ ). According to Fig. 8d and its correlation coefficient, it can be concluded that its sorption data does not follow the Elovich kinetic model (Table 2).

### 3.9 Study of the Adsorption of Safranin O Isotherms

The obtained results in adsorption of Safranin O using Langmuir, Freundlich and Tamkin isotherms were studied in concentration range of 10–500  $\text{mg L}^{-1}$  of Safranin O dye. Langmuir equation is shown in Eq. 6.

$$\frac{c_e}{q_e} = \frac{1}{k_1 q_m} + \frac{c_e}{q_m} \quad (6)$$

Where  $c_e$  and  $q_e$  are the equilibrium concentration of the Safranin O solution ( $\text{mg L}^{-1}$ ) and the amount of adsorbed dye per gram of adsorbent ( $\text{mg g}^{-1}$ ), respectively.  $K_1$  displays the energy of correlation ( $\text{L mg}^{-1}$ ) and  $q_m$  is the maximum adsorption capacity ( $\text{mg g}^{-1}$ ).

The Freundlich isotherm is obtained from the following equation:

$$\text{Log } q_e = \text{log}(k_f) + \frac{1}{n} \text{log}(C_e) \quad (7)$$

Where  $q_e$  is the amount of adsorbed Safranin O in equilibrium condition ( $\text{mg g}^{-1}$ ),  $k_f$ ,  $n$  and  $C_e$  are capacity of adsorption, intensity of adsorption and equilibrium concentration, respectively.

Temkin isotherm can be presented by the Eq. 8:

$$q_e = k_1 \text{Ln}(k_2) + k_1 \text{Ln}(C_e) \quad (8)$$

Where  $k_1$  ( $\text{L g}^{-1}$ ) and  $k_2$  ( $\text{Kj mol}^{-1}$ ) are constants of the isotherm, respectively.

The Freundlich isotherm with  $R^2 = 0.9941$  shows the best interpretation of the results. It can be concluded that the adsorption process is multi-layered. The results are presented in Fig. 9 and Table 3.

### 3.10 Investigating the Reusability of Adsorbent for Safranin O Removal

The adsorbent recycling is an important case that reduces the removal cost and waste production. For recycling

the  $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{SBA-3}/\text{SO}_3\text{H}$  adsorbent, 0.1 M HCl solution was used to desorb Safranin O dye from the surface of nanocomposite. After washing the synthesized adsorbents, the adsorbent was used for 10 repetitious adsorption process at optimum conditions. The results show that adsorbent keep its ability after nine removal process with removal efficiency higher than 90%.

### 3.11 Safranin O Adsorption from Real Samples

To investigate the ability of synthesized nanoparticles to remove Safranin O, water samples from a dye industry, Pasikhan river and tap water were collected from Rasht city (Guilan Province, Iran) and used for investigating the dye removal efficiency via spiking Safranin O to their matrix. The results of Safranin O removal from each spiked sample are summarized in Table 4.

## 4 Conclusion

In this study,  $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{SBA-3}/\text{SO}_3\text{H}$  MNCs were synthesized and their ability for removal of Safranin O cationic dye was investigated. The results showed the proposed adsorbent is an efficient adsorbent for removing this dye. The kinetic results suggested that the pseudo-second-order kinetic model is the best kinetic model for interpretation of results respect to three others. Also, the results showed that Langmuir isotherm is a suitable model for experimental data. Based on the results of this study, it can be concluded that the  $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{SBA-3}/\text{SO}_3\text{H}$  is a potential adsorbent for removal of Safranin O dye from the aqueous solutions.

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