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Removal of erythrosine dye from aqueous solutions using magnetic chitosan with erythrosine as imprinted molecules

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ABSTRACT

A novel, chitosan coating on the surface of magnetite (Fe_3O_4) (erythrosine-imprinted magnetic chitosan (EIMC)) was successfully synthesized using erythrosine (ER) as a template for adsorption and the removal of ER from aqueous solutions. Characterization of the obtained EIMC was achieved by FTIR spectra, SEM micrographs, and TGA analysis. Batch adsorption experiments of EIMC and non-imprinted magnetic chitosan (NIMC) were performed to investigate the adsorption conditions. The results showed that the maximum adsorption capacity for EIMC and NIMC was observed at pH 6 and temperature 40°C. Equilibrium adsorption was achieved within 3 h. Adsorption process could be well described by Freundlich adsorption isotherms. Thermodynamic parameters namely ΔG°, ΔH°, and ΔS° of the ER adsorption process were calculated. The negative values of Gibbs free energy of adsorption (ΔG°) indicated the spontaneity of the adsorption of ER dye on the EIMC and NIMC. Desorption of ER from EIMC and NIMC could be done rapidly using 0.1 M NaOH solution and the beads could be used again to remove ER. Results show that imprinting technique increases the removal amount of ER dye from aqueous solutions.

Keywords: Chitosan; Erythrosine; Imprinting; Magnetite; Kinetic parameters

1. Introduction

Dyes and pigments represent one of the problematic groups, which are emitted into wastewaters from various industrial branches, mainly from the dye manufacturing, textile finishing, and also from food coloring, cosmetics, paper, and carpet industries [1,2]. The presence of these dyes in water, even at very low concentrations, is highly visible and undesirable. Many dyes are difficult to degrade due to their complex structures, and some of them are toxic, mutagenic, and carcinogenic [3]. Therefore, removing dyes from wastewater of industrial effluents before discharging them into the environment is extremely important. A lot of techniques, such as oxidation, biological treatment, or applying activated carbon, ion-exchange, and chitosan [4,5], have been developed to remove dyes. At present, the most common treatment for effective dyestuff removal is adsorption. Chitosan exhibits a higher adsorption capacity and faster adsorption rate of anionic dye pollutants than many conventional adsorbents due to the presence of large amounts of amino group ($–NH_2$) [6]. In acidic solution, the amino groups of chitosan are easily

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protonated and can bind anionic dye anions. Chitosan is efficient and easily regenerable relative to other adsorbent materials.

Coating chitosan with magnetic fluids is a new method to expand the function of the chitosan, and the method has been reported that it can improve the surface area for adsorption and reduce the required dosage for the adsorption of dyes [7–9]. They had succeeded the preparation of sorbents with high adsorption capacity for the removal of dyes, but without achieving any selectivity.

Molecular imprinting technology (MIT) is an emerging technology that has gained much attention in generating recognition sites by reversible immobilization of template molecules on cross-linked macromolecular polymer matrixes. Molecularly imprinted polymers (MIP) represent a new class of materials possessing high selectivity and good affinity for target molecule [10]. In comparison with the common absorbents, the MIT improves the absorbents' high reusability, selectivity, and lower consumption. However, the selective adsorbents were difficult to be separated from wastewater. Thus, MIT based on magnetic chitosan is a great potential adsorbent. In this work, erythrosine dye (ER)-imprinted magnetic chitosan nanoparticles based on MIT were first synthesized and applied in selective removal of ER from aqueous solution.

In this work, chitosan coating on the surface of magnetite (Fe_3O_4), which was using ER as imprinted molecules (erythrosine-imprinted magnetic chitosan (EIMC)) was successfully synthesized, and applied for removing ER from wastewater. Characterization of the obtained EIMC was achieved by FTIR spectra, SEM micrographs, and TGA analysis. Batch adsorption experiments were performed to investigate the adsorption conditions. In addition, Langmuir and Freundlich isotherm studies of results obtained from adsorption studies were investigated.

2. Materials and methods

2.1. Materials

Nickel sulfate hexahydrate and glacial acetic acid (analytical degree) were provided by Merck. Chitosan of commercial degree with 85% deacetylation was provided by Sigma. All other reagents used in this study were of analytical grade.

2.2. Preparation of magnetic chitosan

0.5 g of chitosan flake was dissolved in 30 mL of 1.5% acetic solution. 0.2 g of magnetic particles were added in the chitosan solution in a four-neck round-bottom flask. After ultrasonic dispersion, 3.0 mL of liquid paraffin and Span-80 were added in the solution. The solution's pH was adjusted to maintain a level of 8.0–9.0 by adding 25% (v/v) ammonium hydroxide solution during the reaction. After the above steps, 1.5 mL of pure glutaraldehyde was added into the reaction flask to mix with the solution and stirred at 60°C for 1.5 h. The precipitate was washed with petroleum ether, ethanol, and distilled water in turn until pH was about 7. The precipitate was then dried in a vacuum oven at 50°C. The obtained product was magnetic chitosan.

2.3. Preparation of molecularly imprinted and NIMC

The EIMC was prepared as follows: 50 mL of 0.5 mol/L ER solution was poured into a 250-mL three-neck flask. After that, 2 g of magnetic chitosan was added. The mixture was stirred for 2 h, and then 5 mL of epichlorohydrin solution was added to the above solution and mechanically stirred for another 1 h. At the end of this period, the resulted product was collected, washed with 0.1 mol/L NaOH, and dried in an oven at 60°C for 24 h. To prepare the desired adsorbent for ER solution separation from dilute aqueous solutions, the template ER molecules were leached out by stirring 1 g of EIMC particles in 200 mL of 0.1 M NaOH solution for 24 h at 200 rpm and 30°C. This step was repeated for three times to ensure the maximum extraction of imprinted molecule which would avoid its leaching in subsequent adsorption and extraction experiments. Non-imprinted magnetic chitosan (NIMC) was prepared by the same procedure in the absence of template ER molecules and treated in the same manner.

2.4. Characterization of EIMC

Fourier transform infrared (FTIR) analysis was accomplished on a Perkin Elmer spectrum BX scanning from 4,000 cm^{-1} to 400 cm^{-1} at room temperature. Samples were mixed with KBr and pressed to plates for measurements. The weight loss temperatures of the chitosan and EIMC were determined with a Mettler Toledo TGA analyzer (TGA/SDTA851e). The surface morphology of the particles was examined under scanning electron microscopy (SEM) (XL30-SFEG, FEI/Philips).

2.5. Adsorption studies

All batch experiments were performed on a thermostated shaker (THZ-98A) with a shaking of 150 rpm. All experiments were carried out three times.

The effect of agitation period was conducted at room temperature with 0.1 g of adsorbent. The influence of pH on ER removal was studied by adjusting ER solutions (100 mg/L) to different pH values (2.0, 3.0, 4.0, 5.0, 6.0, 7.0, and 8.0) using a pH meter (DELTA-320) and agitating 20 mL of ER solution with 0.1 g of adsorbent at 30℃ for 3 h. The effects of the temperature on dye removal were carried out in 20 mL of ER (100 mg/L, pH 6.0) with 0.1 g of adsorbent at different temperatures (30, 40, and 50℃) for 3 h. The effect of temperature on ER removal was carried out in 20 mL of ER solution (100 mg/L, pH 6.0) with 0.1 g of adsorbent for 3 h. Batch equilibrium adsorption experiments were carried out by agitating 20 mL of various concentrations of ER solution at pH 6.0 with 0.1 g of adsorbent at 40℃ until equilibrium was established. The samples were withdrawn from the shaker at predetermined time intervals and the dye solutions were separated from the adsorbent by magnetic separation. The absorbencies of samples were measured using a UV–vis spectrophotometer (Specord 200). Then, the concentrations of the samples were determined using linear regression equation ($A = 0.0039 + 0.009 \times C_e$, $R^2 = 0.9997$) obtained by plotting a calibration curve for ER over a range of concentrations. The amounts of ER adsorbed onto samples were calculated by subtracting the final solution concentration from the initial concentration of ER solution.

The amount of ER adsorbed per unit mass of EIMC and NIMC was calculated from the following equation:

$$q_e = \frac{(C_0 - C_e) \times V}{m} \tag{1}$$

where q_e is the amount (mg/g) of ER adsorbed by the EIMC, C_0 and C_e are the dye concentrations (mg/L) in the solution initially and after adsorption, respectively, V is the volume (L) of the solution, and m is the mass (g) of adsorbent used.

2.6. Selective determination

Selectivity of EIMC and NIMC for ER over other dyes solutions was evaluated. Adsorption capacity for all the dyes was determined under optimal conditions.

2.7. Desorption studies

In this study, several solvents/solutions (0.01, 0.1, and 0.5 M NaOH) were tried to regenerate the EIMC and NIMC. The amount of ER adsorbed per gram of sorbents was determined using linear regression equation ($A = 0.0039 + 0.009 \times C_e$, $R^2 = 0.9997$) obtained by plotting a calibration curve for ER over a range of concentrations.

The percentage of ER desorbed was calculated according to the following equations:

$$D = \frac{\text{Amount of ER desorbed}}{\text{Amount of ER adsorbed}} \times 100 \tag{2}$$

3. Results and discussion

3.1. Characterization of EIMC

As shown in Fig. 1, clear ER adsorption is seen on the EIMC surface. ER desorption is also performed succesfully. These graphs could show the quality of the ER adsorption and desorption process.

Infrared spectrums of chitosan and EIMC samples are shown in Fig. 2. Curve a in Fig. 2 shows the infrared spectrum of the chitosan. The major peaks for chitosan in Fig. 2(a) can be assigned as follows: the adsorption band around 3,420 cm^{-1} reveals the stretching vibration of N–H groups bonded with O–H groups in chitosan, and at 1,661 cm^{-1} confirms the N–H scissoring from the primary amino due to the free amino groups in the cross-linked chitosan. The band around 1,065 cm^{-1} is attributed to the combined effects of C–N stretching vibrations of primary amines and the C–O stretching vibrations from the primary alcohol of chitosan. The new peak of EIMC in Fig. 2(b) is displayed near 580 cm^{-1} (characteristic peak of Fe_3O_4), which demonstrates that a layer of chitosan was formed on the surface of magnetite particles.

Infrared spectra of the ER-adsorbed EIMC, ER removed EIMC, and ER are shown in Fig. 3. Curve a in Fig. 3 belongs to the infrared spectrum of the ER dye. Three major peaks around the 1,400, 1,500, and 1,600 cm^{-1} are assigned to ER dye. While these peaks are also seen in the infrared spectrum of the ER-adsorbed EIMC (Fig. 3(c)), they are not seen in the infrared spectrum of the ER-removed EIMC (Fig. 3(b)). The peaks near 580 cm in Fig. 3(b) and (c) belong to the ER-adsorbed and removed-EIMC particles.

TG curves of chitosan ad EIMC are presented in Fig. 4. The natural chitosan lost more weight at higher temperature than EIMC. The Fe_3O_4 coating process usually turns the polymerical matrices more resistant to degradation when compared to the former polymer [11].

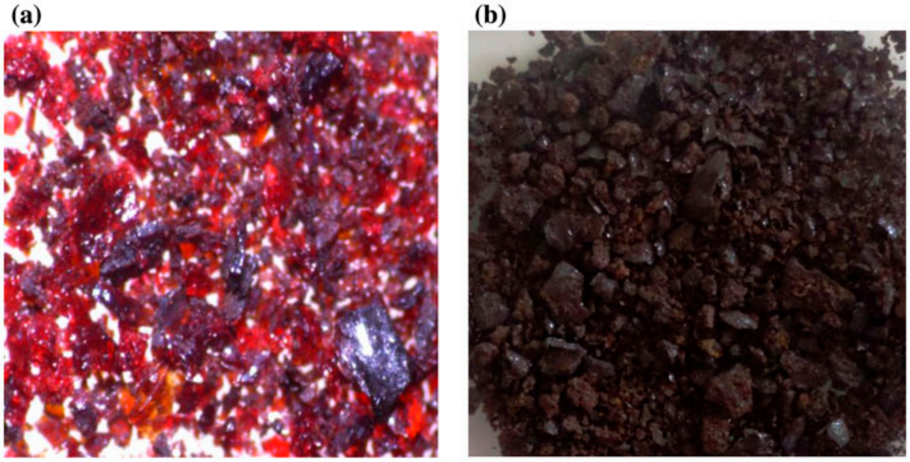

Fig. 1. Image of ER-adsorbed (a) and desorbed (b) EIMC particles.

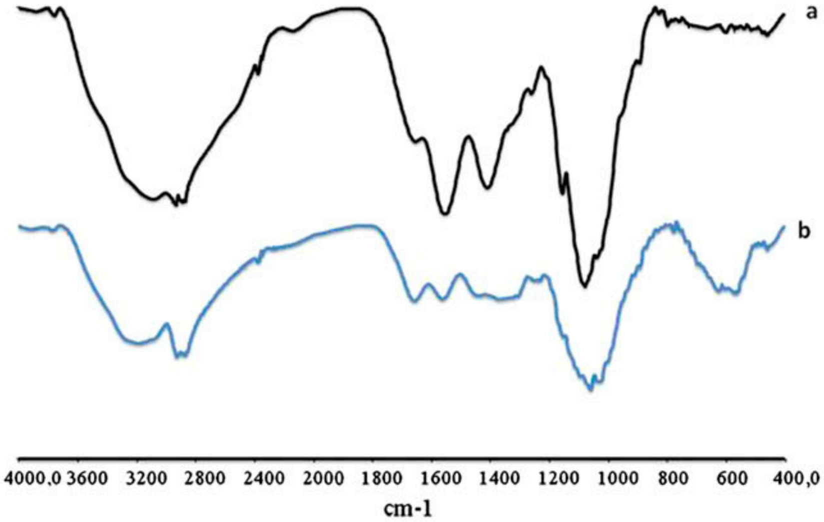

Fig. 2. FTIR spectrum of chitosan (a) and EIMC (b).

3.2. *Effect of agitation period*

Agitation period is the amount of time required for an adsorption process to become constant and reach the equilibrium. The adsorption capacity of EIMC and NIMC was determined by varying the contact time in the range of 20–180 min. It is shown in Fig. 5 that there was a rapid uptake within the first 60 min. The adsorption equilibrium for EIMC and NIMC was attained at 180 min. Therefore, 3 h of contact time was chosen as the optimum contact time for the EIMC and NIMC. The optimum contact time for adsorption of AR appeared to be 50 min. This could be attributed to the large surface area, the sufficient exposure of active sites, and the high surface reactivity of the EIMC. The sorption of ER was rapid during the initial stages of the sorption process, followed by a gradual process. In latter stages, however, the rate of ER adsorption became slower. The ER had to first encounter the boundary layer effect and then had to adsorb on the surface, and finally, they had to diffuse into the porous structure of the adsorbent which took a longer time.

3.3. *Effect of initial pH*

The removal of dye from aqueous solution was highly dependent on pH of the solution and in many cases, it altered the surface charge of the sorbent.

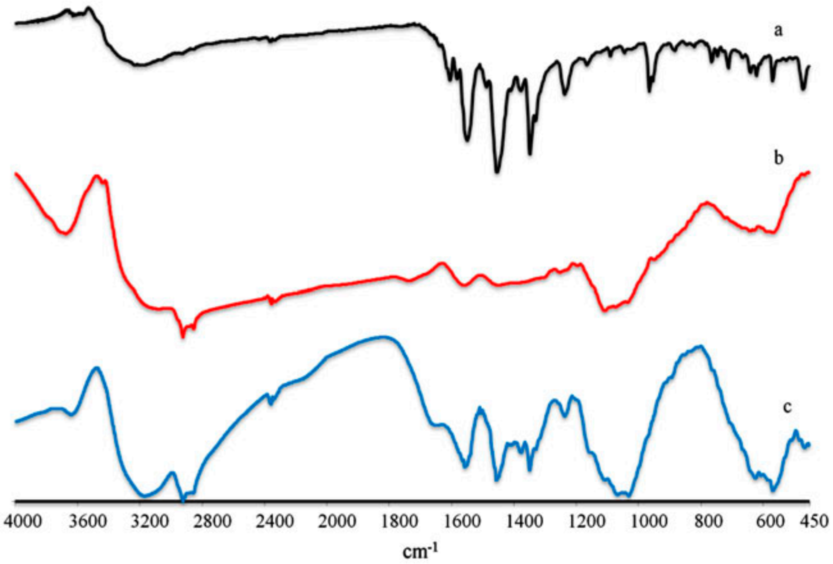

Fig. 3. FTIR spectrum of Er dye (a) ER-removed EIMC (b) and ER-adsorbed EIMC (c).

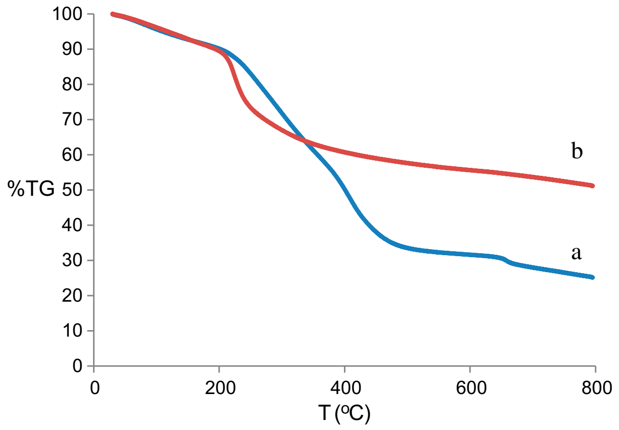

Fig. 4. TGA curves of (a) chitosan and (b) EIMC.

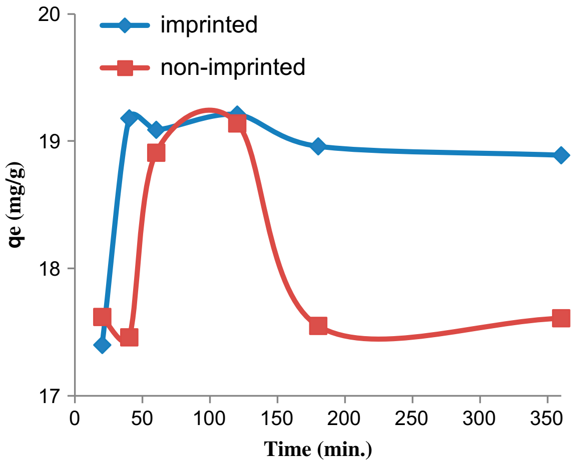

Fig. 5. Effect of contact time on the adsorption capacity of EIMC and NIMC.

Therefore, the sorption capacity of the EIMC and NIMC was performed at different pH levels in the range of 3.0–8.0. Fig. 6 shows the effect of pH on the sorption of ER on the prepared absorbents. The dye uptake was increased as the pH decreased. The maximum adsorption values for ER onto EIMC and NIMC were 17.45 and 10.21 mg/g at pH 6, respectively, from which the imprinting effect was greatly observed. The observed decrease in the uptake values at low pH (<pH 6) was attributed to the decrease in ER dissociation which led to a lower concentration of the anionic dye species available to interact with the EIMC's active sites. Above the optimum pH values, the EIMC displayed a sharp decrease in the uptake value as the pH increased. This behavior could be explained on the basis of the lower extent of protonation of amino groups at high pH.

3.4. Effect of temperature

To evaluate the thermodynamic parameters of ER removal on the EIMC and NIMC under study, the adsorption experiments were performed at four different temperatures (303, 313, and 323 K). Twenty five milliliters of the dye solution with a concentration of 1,000 mg/L was allowed to equilibrate with 0.1 g of bead. The equilibrium constant for the removal process,

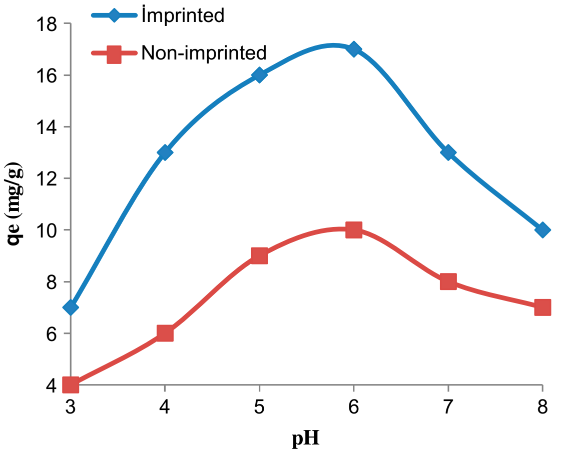

Fig. 6. Effect of pH on the adsorption capacity of EIMC and NIMC.

K_C, calculated with Eq. (3) [12] was evaluated at 298, 308, and 318 K for ER (Table 1):

$$K_C = \frac{X_e}{C_i - X_e} \tag{3}$$

where X_e is the concentration of solute adsorbed on the resin at equilibrium, mmol/L; C_i is the initial dye concentration, mmol/L. To calculate the free energy of the adsorption (ΔG°), the following Eq. (4) was employed:

$$\Delta G^\circ = -RT \ln K_C \tag{4}$$

The Eq. (5), allows to evaluate the standard enthalpy (ΔH°) and entropy (ΔS°) of the removal by plotting $\ln K_C$ vs. $1/T$.

$$\ln K_C = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{5}$$

where R (8.314 J/mol K) is the gas constant. The values of the slope $-\Delta H^\circ/R$ and the intercept $\Delta S^\circ/R$ from Fig. 7(a) and (b) give ΔH° and ΔS° for the removal of ER on the EIMC and NIMC. The values of the thermodynamic parameters (ΔG°, ΔH°, and ΔS°) are presented in Table 1. As presented in Table 1, the negative values of ΔG° under optimum conditions indicate the spontaneous nature of the removal. The negative ΔH° means a chemical exothermic process and support the chemisorption is the rate-determining step. The removal of ER on EIMC and NIMC is exothermic adsorption because of the negative entrophy change.

Table 1
Thermodynamic parameters for the adsorption of ER on EIMC and NIMC

	T (K)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (JmolK^{-1})
EICM	303	0.155		
	313	−5.541	−0.104	−320.58
	323	−6.570		
NICM	303	1.416		
	313	−3.131	−0.082	−259.01
	323	−3.847		

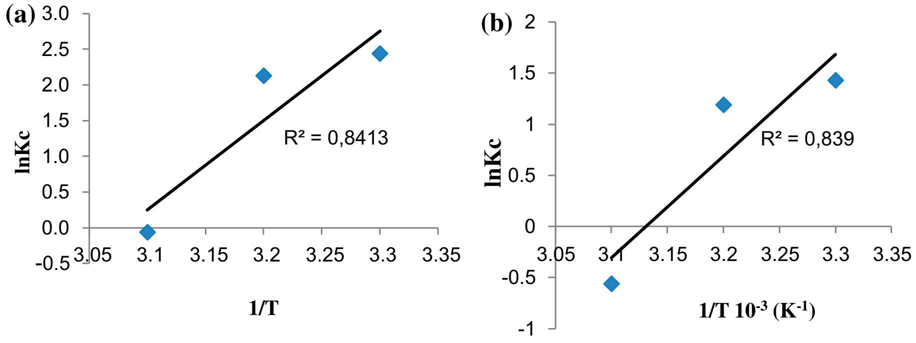

Fig. 7. Plot of $\ln K_C$ as a function of reciprocal of temperature ($1/T$) for the removal of ER by (a) EIMC and (b) NIMC.

3.5. Evaluation of adsorption isotherm models

The two most commonly used isotherms, namely Freundlich and Langmuir isotherms, have been adopted to describe the adsorption characteristics of EIMC and NIMC. The linearizations according to the Freundlich and Langmuir models of adsorption isotherms and isotherm were examined.

The linear form of Freundlich isotherm [13] is written as the following Eq. (6):

$$\log q_e = \log k_F + \frac{1}{n}\log C_e \tag{6}$$

where q_e is the amount of dye adsorbed per unit weight of the sorbent (mg/g), C_e is the equilibrium concentration of ER in solution (mg/L); k_F (mg/g), a measure of adsorption capacity, and $1/n$, the adsorption intensity were calculated from the slope and intercept of the plot $\log q_e$ vs. $\log C_e$ (shown in Fig. 8), and the values are listed in Table 2. The values of $1/n$ lying between 0 and 1 confirm the favorable conditions for adsorption. The R values for the modified sorbents are high, indicating the applicability of the Freundlich isotherm.

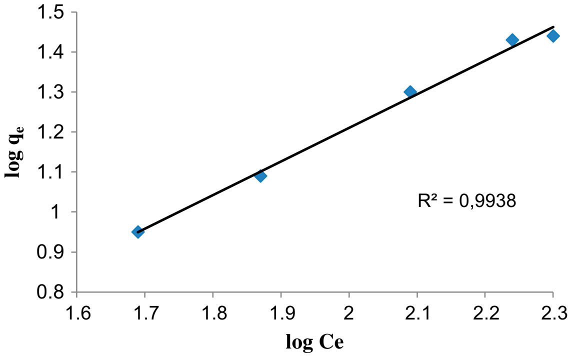

Fig. 8. Adsorption isotherm of ER on EIMC linearized according to the Freundlich equations.

Table 2
Freundlich and Langmuir isotherm constants of ER adsorption on EIMC and NIMC

Freundlich isotherm constants				
	$1/n$	n	k_F (mg/g)	R
MICM	0.8414	1.18	2.97	0.9968
NICM	0.6698	1.49	1.82	0.9644
Langmuir isotherm constants				
	Q° (mg/g)	b (L/mg)	R_L	R
MICM	116.27	0.0016	0.86	0.9144
NICM	39.06	0.0052	0.65	0.9059

Langmuir isotherm [14] model is expressed in the form of Eq. (7):

$$\frac{C_e}{q_e} = \frac{1}{Q^\circ b} + \frac{C_e}{Q^\circ} \tag{7}$$

where Q° is the amount of adsorbate at complete monolayer coverage (mg/g), which gives the maximum sorption capacity of sorbent, and b (L/mg) is the Langmuir isotherm constant that relates to the energy of adsorption calculated from the slope and intercept of the plot C_e/q_e vs. C_e (shown in Fig. 9), and the values are shown in Table 2.

The Langmuir and Freundlich adsorption constants and the corresponding correlation coefficients were gotten.The adsorption of ER on EIMC and NIMC was well fitted to the Freundlich isotherm model with the higher R^2 (0.99 for EIMC and 0.93 for NIMC). It indicated the adsorption-loading is spontaneous and heterogeneous with a high preference for dye molecules.

The essential characteristics of the Langmuir isotherm can be expressed in terms of the dimensionless constant separation factor or equilibrium parameter R_L [15].

$$R_L = \frac{1}{1 + bC_0} \tag{8}$$

where C_0 is the initial ER concentration for adsorption study which was determined as 100 mg/L. The R_L value was calculated and is listed in Table 2. The R_L value lying between 0 and 1 indicated that the conditions were favorable for adsorption.

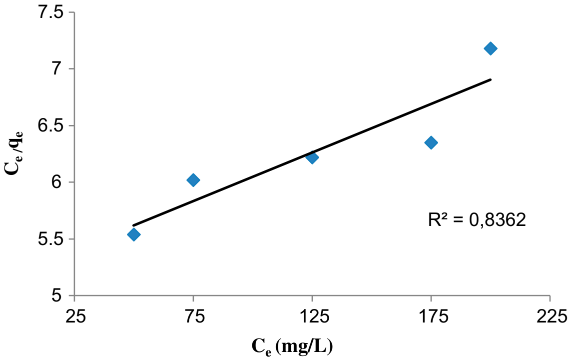

Fig. 9. Adsorption isotherm of ER on EIMC linearized according to the Langmuir equations.

Table 3
Selective determination

Dyes	Dye adsorption capacity (mg/g)	
	MICM	NICM
Erythrosine	46.05	20.39
Reactive Yellow	13.76	14.06
Kim Orange	18.48	18.76
Reactive Blue	8.29	13.90

3.6. Evaluation of selective adsorption

For the purpose of evaluating the selectivity of the adsorbent, the selective adsorption studies were carried out. The results are shown in Table 3. Based on the results shown in Table 3, it can be seen that the adsorption capacity of EIMC for ER was greater than the adsorption capacity of EIMC for other dyes. NIMC could easily adsorb other dyes as well as ER, it demonstrated that the specific recognition cavities for ER were created in EIMC unlike NIMC, which were developed by ER-imprinting. In the case of EIMC, the cavities created after the removal of the template were complementary to the imprinted ER in size, shape, and coordination geometries. It is evident that EIMC has a strong ability to selectively adsorb ER.

3.7. Desorption studies

Desorption studies will help to elucidate the nature of adsorption process and to recover the ER from EIMC and NIMC. Moreover, it also will help to regenerate the sorbents so that it can be used again to adsorb ER and develop the successful sorption process [16]. Desorption experiments were performed at 25˚C using 0.01, 0.01, and 0.5 M NaOH solutions. Percentage desorptions of ER from the sorbent are shown in Fig. 10. It can be seen from the results that 0.1 M NaOH solution exhibited the best desorption percentage.

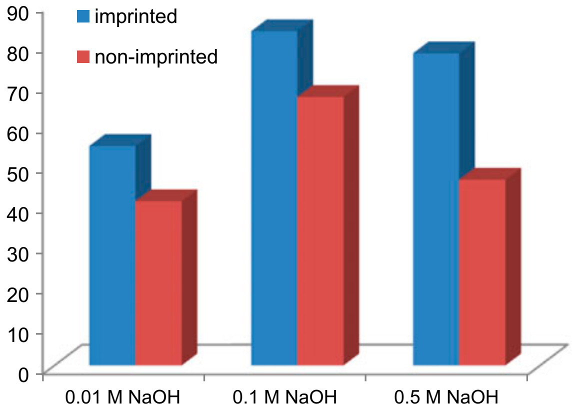

Fig. 10. ER desorption capacity of EIMC and NIMC in different concentrations of NaOH.

4. Conclusions

In the present investigation, the templated magnetic chitosan nanoparticles were prepared using the imprinting technique with the ER as a template and evaluated as sorbents for ER. The maximum adsorption capacity of EIMC and NIMC for ER was 46.05 and 20.39 mg/g under the optimal conditions, respectively. EIMC has a great selectivity for ER against the other dyes. Adsorption of ER onto EIMC and NIMC fitted the Freundlich adsorption isotherms. Furthermore, the templated nanoparticles could be regenerated through the desorption of ER in 0.1 M NaOH solution and could be reused to adsorb ER. EIMC can be easily separated from aqueous solution by external magnetic field.

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