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Highly facile removal of Acid Red 88 from aqueous samples by using synthesized iron oxide magnetic nanoparticles and 1-butyl-3-methylimidazolium tetrachloroferrate magnetic ionic liquid

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ABSTRACT

In this study, the application of synthesized Fe_3O_4 magnetic nanoparticles and 1-butyl-3-methylimidazolium tetrachloroferrate (bmim [$FeCl_4$]), as a magnetic ionic liquid, for removal of Acid Red 88 (AR88) from aqueous solution was investigated. At first, Fe_3O_4 magnetic nanoparticles (MNPs) were synthesized via a chemical co-precipitation method with drop-wise addition of sodium hydroxide to an ideal mole ratio mixture of Fe^{2+} and Fe^{3+} solutions (Fe^{2+}/Fe^{3+}), about 0.5, as well as under argon gas protection. X-ray diffraction and transmission electron microscopy were used to characterize the synthesized nanoparticles. The effect of important experimental parameters on the removal of Acid Red 88 such as pH of solution, contact time, temperature, ionic liquid and sorbent dosages was investigated. Also, Langmuir and Freundlich isotherm models were used for evaluation of the equilibrium adsorption. Acid dye adsorption equilibrium data were fitted well to the Langmuir isotherm and the maximum monolayer capacity q_{max} was calculated from it as 909.1 mg g^{-1}. Thermodynamic studies indicated that the adsorption process was exothermic and spontaneous, and the adsorption mechanism was physisorption. On the other hand, a rapid sorption dynamics and quantitative removal of dye (≈95%) were observed under optimal conditions: 50 mL of 50 ppm dye solution at pH 3, 5 mg of ionic liquid, 10 mg of magnetic nanoparticles (MNPs), 2 min contact time at 10°C. Finally, this method was used for the removal of AR88 from real water samples of Chalus River. The obtained results indicated that Fe_3O_4 MNP and magnetic ionic liquid (bmim [$FeCl_4$]) could be used as an efficient sorbent material for very simple and fast removal of acid dyes from aqueous solutions.

Keywords: Removal of acid dye; Magnetic nanoparticles Fe_3O_4; Magnetic ionic liquid; Acid Red 88

1. Introduction

Dyes are a kind of pollutants which can be recognized so easily in the natural environment. These substances are widely used in various industries such as plastic, paper, textile, cosmetics, carpet, leather, pharmaceutical and food to color their products. By introducing dye-containing wastewaters into natural streams and rivers, many serious environmental problems such as threatening the water supply and quality are concluded. This is mainly because of their high toxicity, non-degradability and possible accumulation in the environmental medium through the food chain [1–3]. On the other hand, even the presence of very small amounts of synthetic dyes in natural water makes serious damages such as reduction of light penetration through the water surface and so preventing photosynthesis of the aqueous flora. Also many of them possess toxic effects on human beings, microorganisms and fish species, besides their carcinogenic, mutagenic and teratogenic characteristics. Therefore, it is environmentally important to remove them from aquatic wastewater [4].

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Many physical and chemical treatment methods, such as flocculation, electrofloatation, electrokinetic coagulation, ion exchange, membrane filtration, chemical oxidation, photocatalytic degradation and precipitation, have been examined to remove dyes from aqueous solutions [5,6]. However, these processes are expensive and cannot effectively be used in treating of various dye-bearing wastewaters [7]. Oxidation and adsorption technologies are the most available [8]. But adsorption method has been found to be superior to other techniques for the removal of odor, colors, oils and organic pollutants from process or waste effluents treatment because of its low cost and simplicity of design as well as ease of its operation [9]. Various adsorbents such as activated carbon [5], chitosan [10], cotton [11], orange peel [2], palm fruit [12] and shale oil ash [13] have been investigated for dye removal from aqueous solutions. Among them, activated carbon (granular or powder) has been extensively used as an adsorbent to eliminate dyes from wastewaters. It is likely due to its high level of effectiveness and adsorption capacity, simplicity, microporous structure and large surface area [5]. The main drawback of activated carbon is its high cost both to the manufacturing and treatment. On the other hand, it is also ineffective against dispersing and vat dye [14]. Thus many researchers have focused their efforts on developing novel alternative adsorbents with large adsorptive capacity and low price. Thus, nanometer-sized materials have attracted essential interest in the scientific community because of their special properties such as large surface area, high available fraction of active sites and small diffusion resistance for chemical species [15]. The application of various nanoparticles in the treatment of environmental pollutants [16–18] and specifically dye removal [19–21] have been published in literatures. Also, we introduced the synthesis and application of NiO nanoparticles for the removal of azo dyes [22,23].

At present, magnetic separations have obtained great attention by researchers in many areas to remove and concentrate the desired components from complex matrices. Thus, magnetic iron oxide nanoparticles have been extensively studied, as a new sorbent, for the isolation, pre-concentration, capture and detection of chemical compounds such as metals [24–26], dyes [27–29], herbicides [30] and biological species [31]. MNPs are nearly produced by one of some wet chemical methods: high-temperature thermal decomposition and reduction, microemulsion and co-precipitation methods. Among these routes, co-precipitation is a reliable, facile and suitable method to synthesize iron oxides from aqueous Fe(II)/Fe(III) salt solutions in the presence of an alkaline solution with a high yield and a relatively narrow size distribution [32,33]. On the other hand, nanoparticles such as Fe_3O_4 are super paramagnetic at room temperature and can be easily attracted to the external magnetic field but in the absence of an external magnet they are easily dispersed in solution without attractive magnetic forces including aggregation. This property has made them convenient for pollutant removal and also no centrifugation or filtrations are needed. However, the MNPs suffer from two main drawbacks [31]. First, large magnetic field gradients are needed, dependent upon the magnetic properties of the particles. Second, since the MNPs have a large ratio of surface area to volume, in order to reduce the agglomeration of NPs, the MNP surface should be modified by physical and/or chemical adsorption of the desired molecules, depending on the specific applications. Recently, ionic liquid (IL) coated MNPs have been successfully used as adsorbent for the removal of target from real samples. The adsorption ability of MNPs could be improved by surface modification of the MNPs with ionic liquid [34]. 1-butyl-3-methylimidazolium tetrachloroferrate (bmim [$FeCl_4$]) as ionic liquid possesses interesting physical–chemical properties such as: low vapor pressure and viscosity as well as low toxicity. So, these properties have made it a good candidate to modify the MNP surface [34,35].

In this study, MNPs @IL were used for the removal of Acid Red 88 (AR88), an anionic dye, from aqueous solutions by a simple and facile adsorption process. Acid Red 88 was selected due to its extensive application in variety of fields such as dyeing textile fabrics, silk, wool, leather and nylon. Also, its degradation byproducts have carcinogenic effects [36–38]. The effect of various important parameters was investigated and optimum conditions for maximum removal were determined. Also, the thermodynamic parameters were studied and isotherm models were used to evaluate the equilibrium adsorption process.

2. Materials and methods

2.1. Chemicals and reagents

Ferric chloride ($FeCl_3$ $6H_2O$), ferrous chloride ($FeCl_2$ $4H_2O$), sodium hydroxide, ethanol, acetone, sodium chloride and hydrochloric acid were all of analytical grade from Merck Chemical Company. Azo dye Acid Red 88 ($C_{20}H_{13}N_2NaO_4S$, molar mass 400.38) was obtained from Sigma-Aldrich Corporation, St. Louis, MO, USA, and was used as received. The chemical structure of AR88 is shown in Fig. 1. 1-butyl-3-methylimidazolium tetrachloroferrate (bmim $FeCl_4$) has been purchased from IoLiTec Ionic Liquids Technologies GmbH, Germany. The purity of the purchased ionic liquid was 99.5%. The chemical structure of the ionic liquid is presented in Fig. 2.

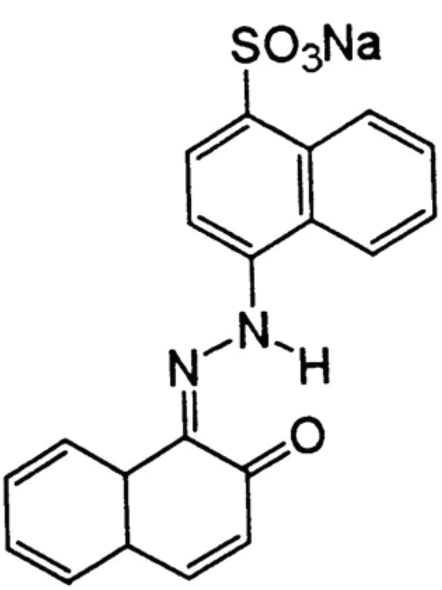

Fig. 1. Chemical structure of Acid Red 88.

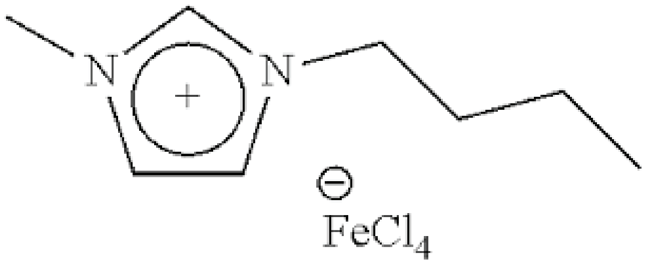

Fig. 2. Chemical structure of ionic liquid (1-butyl-3-methylimidazolium tetrachloroferrate).

2.2. Apparatus

The dye concentrations were measured by a double beam UV/Vis spectrophotometer (Shimadzu, Model UV 1601, Japan) at a wavelength of 512 nm. The X-ray diffraction (XRD) patterns of the solid products were obtained using a PW-1840 X-ray diffractometer from Philips Company with Cu-Kα radiation (λ = 1.54056 Å). Transmission electron microscopy (TEM) was carried out by using a Zeiss-EM10C operated at a 100 kV accelerating voltage. The pH values were measured with a Consort C860 multiparameter analyzer.

2.3. Synthesis of Fe_3O_4 nanoparticles

The chemical co-precipitation method was used in the preparation of the Fe_3O_4 NPs [39]. First, for preparing a stock solution, 10.4 g of $FeCl_3{\cdot}6H_2O$, with 4.0 g of $FeCl_2{\cdot}4H_2O$ and 1.7 mL of HCl (12 mol L^{-1}) were dissolved in 50 mL of deionized water in a beaker. Then it was degassed by using argon gas for 20 min before use. Simultaneously, 200 mL of 1.5 mol L^{-1} NaOH solution was added drop-wise with a dropping funnel and heated up to 80°C in a reactor for 30 min under argon gas protection and vigorously stirring (1,000 rpm) with a glassware stirrer. During the whole process, the solution temperature was maintained at 80°C and argon gas was used to prevent the intrusion of oxygen. The precipitated Fe_3O_4 NPs were separated from the suspension medium by using a magnetic field, and then washed three times with 50 mL of deionized water and three times with pure ethanol. Finally, Fe_3O_4 nanoparticles were dried at 50°C under vacuum for 4 h.

2.4. Dye adsorption procedure

Adsorption of Acid Red 88 by Fe_3O_4 NPs has been studied in batch experiments. A known amount of nanosorbent (10 mg) was mixed with 50 mL of 50 mg L^{-1} aqueous dye solution at pH 3.0 in 10°C. Then, 0.5 mL of ionic liquid solution containing 5 mg of ionic liquid was added into the sample solution. The solution was sonicated for 2 min to facilitate the adsorption of dye onto the nanoparticles. Subsequently, an Nd-Fe-B strong magnet was held next to the bottom of the vial, and Fe_3O_4 NPs were isolated from the solution. The amount of dye adsorbed was estimated by determination of dye concentration remaining in solution after adsorption process. The dye concentrations were investigated by a UV–Vis spectrophotometer. The percentage of dye removal was calculated by the following equation (Eq. (1)):

$$R(\%) = \frac{(C_0 - C_e)}{C_0} \times 100 \qquad (1)$$

where R is the removal efficiency of dye, C_0 is the initial concentration of dye (mg L^{-1}) and C_e is the concentration of dye remaining in the solution (mg L^{-1}).

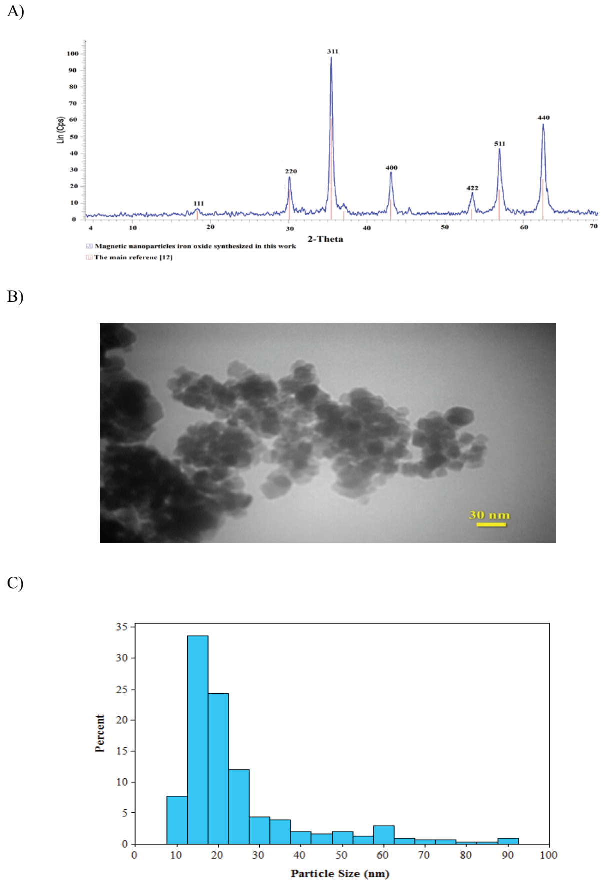

Fig. 3. (A) XRD pattern of synthesized Fe_3O_4 NPs. (B) TEM image of synthesized Fe_3O_4 NPs. (C) Size distribution of synthesized Fe_3O_4 nanoparticles.

3. Results and discussion

3.1. Characterization of the MNPs

XRD measurement was carried out to investigate the materials phase structure (Fig. 3(A)). The Joint Committee on Powder Diffraction Standards (JCPDS) reference pattern of magnetite (No. 19-629) was appended for comparison. As shown in Fig. 3(A), all the significant diffraction peaks of the Fe_3O_4 sample matched well with the data from the JCPDS card (19–629) for Fe_3O_4 at 2θ = 30.0°, 35.3°, 42.9°, 53.4°, 56.9° and 62.5° which is assigned to (220), (311), (400), (422), (511) and (440) of the crystal planes of Fe_3O_4. The single formula, given by Debye Scherrer, Eq. (2), can be used to calculate the crystalline size from the available RD data:

$$D = \frac{K\lambda}{\beta\cos(\theta)} \qquad (2)$$

where λ is the incident X-ray wavelength (0.154056 nm), θ is the Bragg diffraction angle, β (FWHM) is the radian-based full width at half-maximum and *K* is the grain shape factor (0.94) [40]. The average size of the Fe_3O_4 nanoparticles using Debye Scherrer was calculated to be about 21 nm, as shown in Fig. 3(B). To analyze quantitatively the size distribution of MNPs, the particle size distribution was obtained from size histograms [41]. The size distribution histogram for 300 particles shows statistically an average particle size of 24.57 nm with size distribution standard deviation of 15.47 nm (Fig. 3(C)). As can be seen in Fig. 3(C), more than 80% of the MNPs possess the size distribution in the range of 10–30 nm.

3.2. Adsorption experiments

The efficiency of Fe_3O_4 NPs and IL, as a sorbent, has been determined for removal of AR88 from aqueous solutions. So, some important and affecting experimental parameters were investigated in order to find their optimum values, as discussed below.

3.2.1. Effect of dye solution pH

Solution pH is an important parameter that influences the degree of ionization of the species and the surface charge of the sorbent [42,43]. The effect of pH on the adsorption of AR88 onto Fe_3O_4 NPs was studied in the range of 2.0–11.0 at a fixed dye concentration of 50 mg L^{-1}. The experiments were performed in a batch technique and each solution was sonicated for 2 min. The results of these experiments are shown in Fig. 4.

As seen in Fig. 6, the percentage of dye removal increased as the pH of aqueous dye solution was increased from 2 up to 3, but it was decreased when increasing the pH from 4 up to 11. Therefore, the optimum pH at 3 was selected for removal of AR88 from the aqueous solution. It may be due to dissolving of Fe_3O_4 NPs at lower pH values as reported in literatures [44]. Acid Red 88 is an anionic mono azo dye that has sulfonic acid group ($R–SO_3Na$) (Fig. 1). In aqueous solution, Acid Red 88 dissociates therefore or then the sodium ions Na^+ and the sulfonate anions $R—SO_3^-$ are formed. It should be highlighted that the dye molecules are in their anionic forms even at higher acidic solutions, because the pK_a of the sulfonic acid groups attached to the dye molecules are known to be very low ($pK_a < 1$) [45]. The surface charge of bared Fe_3O_4 NPs is neutral at the pH ≈ 7.0 (pH_{pzc}) [46]. At pH values below the pH_{pzc}, surface of Fe_3O_4 NPs are positively charged, and hence the higher adsorption of dyes at lower pH can be due to the electrostatic attractions between negatively charged anions of dye and the positively charged nanoparticles. By increasing the pH value from 4 up to 7, the positive charge density on the surface of the Fe_3O_4 NP is decreased. As a result, the physical adsorption of dye molecules on the surface of MNP is reduced; therefore, the percentage of dye removal is decreased. In addition, when solution pH is higher than pH_{pzc}, the Fe_3O_4 NP surface is more negatively charged, which does not favor the adsorption of the dye anions due to the electrostatic repulsion. Similar results have been reported for the adsorption of AR88 from aqueous solutions [47,48].

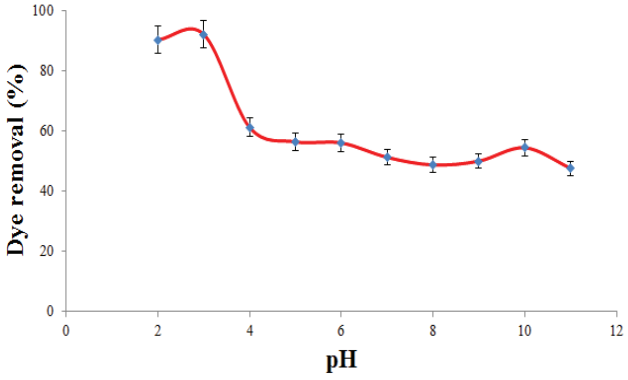

Fig. 4. Effect of initial pH of dye solution on removal of Acid Red 88. Experimental conditions: 10 mg of Fe_3O_4 NPs, 5 mg of ionic liquid, 50 mL of 50 mg L^{-1} of dye solution, 2 min contact time at 10°C.

3.2.2. Effect of nanoparticle dosage

The effect of Fe_3O_4 dosage on the removal of AR88 was investigated by using a batch technique: addition of 1–50 mg of the magnetic sorbent into vials containing 50 mL of 50 ppm of dye solution. The resulting suspension was sonicated for 10 min. Then, the Fe_3O_4 NPs were magnetically separated from the solution and it was investigated by UV–Vis spectrophotometer to determine the residual dye concentration. The efficiency of dye removal as a function of nanosorbent dosage is shown in Fig. 5.

The obtained results showed that by increasing the sorbent amounts from 1 up to 5 mg, the efficiency of dye removal was increased and remained nearly constant at higher sorbent dosages. This is mainly due to the greater number of adsorption sites made available for dye molecules at greater Fe_3O_4 dosages [49]. Although the optimum amount of Fe_3O_4 NPs, which can remove AR88 from aqueous solution, was found to be 5 mg, 10 mg of MNPs were used in other experiments, as optimum amount of the sorbent.

3.2.3. Effect of ionic liquid amount

The amount of ionic liquid is an important parameter which has significantly affected on the dye removal efficiency [50]. The effect of ionic liquid amounts on the removal

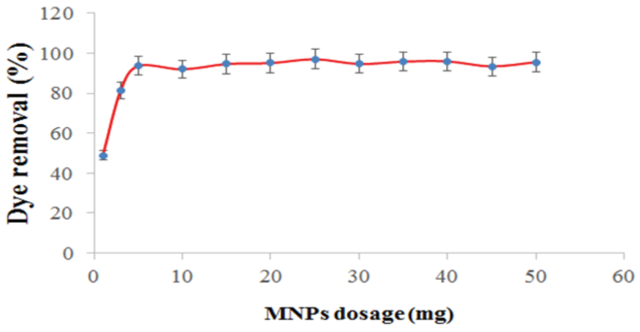

Fig. 5. Effect of initial dosage of Fe_3O_4 nanoparticles on removal of Acid Red 88. Experimental conditions: 50 mL of 50 ppm dye solution at pH 3, 5 mg of ionic liquid, 2 min contact time at 10°C.

efficiency of dye was considered in the range of 0–10 mg, the results are shown in Fig. 6. As seen in Fig. 6, in the absence of ionic liquid, the dye molecules were hardly adsorbed onto the surface of Fe_3O_4 NPs (~40%). In contrast, the sorption amount of dye molecules was increased remarkably (~94%) by the addition of ionic liquid [51]. The phenomenon can be explained by the formation of hydrophobic ion pairs between negatively charged dye anions and the positively charged ionic liquid (Figs. 1 and 2) by the electrostatic interactions. On the other hand, since phenyl ring on AR88 can interact with the magnetic IL, the electronic π–π interaction between phenyl groups of dye and IL is possible and may significantly lead to higher percentage of dye removal in the presence of bmim [$FeCl_4$] [50]. Also, as reported previously [37,38], 1-butyl-3-methylimidazolium tetrachloroferrate (bmim [$FeCl_4$]) is a magnetic ionic liquid and can be attracted to a magnet by magnetic fields. Then, its presence with MNPs can enhance the removal process of the analyte. Therefore, the bulky hydrophobic ion pairs of AR88 anion and IL cation can be adsorbed on the positively charged MNP at pH 3 via their negative heads and electrostatic interactions. Since the ionic liquid possesses magnetic property [37,38], which causes its better attraction onto the magnet in the separation process, AR88 can be quantitatively removed from aqueous solution (~94%). As shown in Fig. 6, the efficiency of dye removal was increased by increasing the amount of IL up to 5 mg and remained nearly constant at higher values of IL. So, 5 mg of ionic liquid was selected as the optimum amount of IL in order to achieve the highest possible removal efficiency during the next studies.

3.2.4. Effect of contact time

To study effect of contact time (sonication time) on the removal efficiency of AR88, the contact times were varied in the range of 1–10 min. Fig. 7 shows the removal efficiency of AR88 as a function of sonication time. The results indicate that the adsorption process for AR88 started immediately upon addition of ionic liquid and Fe_3O_4 NPs. The dye removal efficiency of about 92% was achieved in 1 min and rapidly increased from 92% to 95% after 2 min. It was observed that after 2 min, the removal efficiencies of the AR88 had no significant variations. Thus, the optimum contact time of 2 min was selected for further studies. The rapid adsorption, at the initial contact time, is due to the availability of fresh positively charged surfaces of magnetic adsorbent which led to a fast electrostatic adsorption of the ionic dye molecules from the solution [52]. The presence of ionic liquid in aqueous solution makes some increase in both electrostatic and hydrophobic interactions between Fe_3O_4 NPs and dye molecules which consequently increases both rate of dye adsorption process and dye removal efficiency [53].

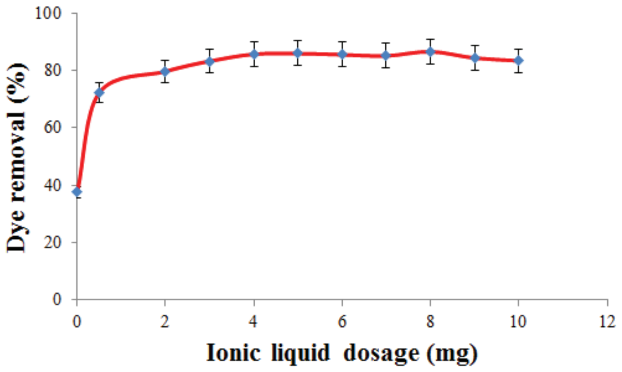

Fig. 6. Effect of ionic liquid dosage on removal efficiency of Acid Red 88. Experimental conditions: 50 mL of 50 ppm dye solution at pH 3, 5 mg of magnetic NP, 2 min contact time at 10°C.

3.2.5. Effect of solution temperature

To investigate the effect of temperature on the adsorption process of AR88 onto Fe_3O_4 NPs, removal efficiency of a 50 mg L^{-1} dye solution under optimal conditions (i.e., contact time: 2 min, pH: 3.0 and sorbent dosage: 10 mg) was monitored in the temperature range of 283–333 K (Fig. 8). The results indicate that the solution temperature has strongly affected on the adsorption efficiency of AR88. The adsorption efficiency of AR88 was about 95% at 283 K, but it decreased to 62.6% at 333 K. The results show that the adsorption process possesses the exothermic nature. This result is similar to that obtained by another researcher [48].

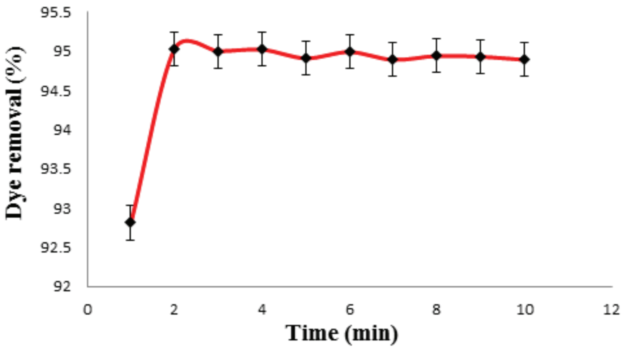

Fig. 7. Effects of contact time on removal of Acid Red 88. Experimental conditions: 50 mL of 50 ppm dye solution at pH 3, 5 mg of ionic liquid, 5 mg of magnetic NP, at 10°C.

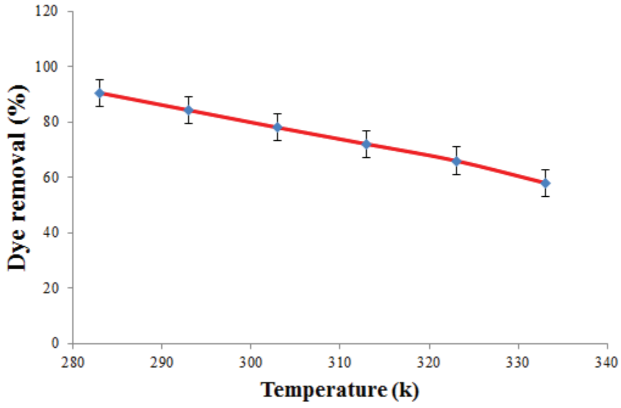

Fig. 8. Effect of solution temperature on the removal of the Acid Red 88. Experimental conditions: 50 mL of 50 ppm dye solution at pH 3, 5 mg of ionic liquid, 5 mg of magnetic NP, 2 min contact time.

The photograph of dye removal in optimum conditions is shown in Fig. S1. It is seen in Fig. S1 that the adsorption of dye on the MNP surface in the presence of magnetic IL can be performed very easily, fast and quantitatively.

3.2.6. Study of thermodynamic parameters and dye removal nature

According to Van't Hoff equation, the slope and intercept of the plot $\ln(q_e/C_e)$ vs. $1/T$ determine the changes of enthalpy (ΔH) and entropy (ΔS), respectively (Eq. (3)):

$$\ln\left(\frac{q_e}{C_e}\right)=\frac{\Delta \mathrm{S}}{\mathrm{R}}-\frac{\Delta \mathrm{H}}{\mathrm{RT}} \tag{3}$$

where R is the universal gas constant (8.314 J mol^{-1} K) and T is the absolute temperature (K) as well as $q_e = (c_0-c_e)V/m$, where C_0 and C_e are the initial and remaining dye concentrations in mg/L after 2 min, respectively, V is the volume of dye solution in L and m is the weight of magnetic sorbent in g.

Thermodynamic parameters of AR88 adsorption onto the nanosorbent are shown in Table 1. The feasibility and the spontaneity of the adsorption process can be confirmed by the negative free energy of the adsorption processes (ΔG) at all temperatures. The decrease of ΔG values by reducing the temperature shows that more feasible sorption of AR88 on the magnetic sorbent can be taken place at lower temperatures. The exothermic nature of the process could be judged from the negative value of ΔH. The negative value of ΔS indicates that the dye molecules have got higher order by being adsorbed onto the surface of Fe_3O_4 NPs. It is notable when ΔG values are between from –20 to 0 and from –80 to –400 kJ mol^{-1}, the adsorption process is corresponding to spontaneous physical and chemical process, respectively [54–56]. As it is seen in Table 1, since the obtained ΔG values are in the first range mentioned above, the adsorption mechanism is dominated by physisorption. Besides ΔG value, physical adsorption process can also be supported by the fact of $\Delta H < 40$ kJ mol^{-1} [54–56].

3.2.7. Effect of dye concentration

To investigate the effect of dye concentration on its removal process, different initial concentrations of AR88 (C_0) from 20 up to 300 mg L^{-1} were studied under the optimal experimental conditions. The results are shown in Fig. 9. As seen in Fig. 9, when the dye concentration range was between 20 and 50 mg L^{-1}, its removal was nearly quantitative (~94%) and independent of the initial concentration of dye [27]. But at higher concentrations (more than 150 mg L^{-1}), the efficiency of dye removal was reduced. This is mainly due to the saturation of MNP surface [27]. On the other hand, the results show that the presence of both magnetic ionic liquid and Fe_3O_4 NP have high capacity for the adsorption of AR88 from aqueous solutions.

3.3. Adsorption isotherms

The adsorption isotherm of a specific adsorbent represents its adsorptive characteristics which are very important for designing the adsorption processes [57]. To obtain the dye adsorption isotherms onto the Fe_3O_4 NP surface, 50 mL of various concentrations of dye (50–210 mg L^{-1}) at pH 3 were used in optimal experimental conditions. 5 and 10 mg of ionic liquid and Fe_3O_4 NP, respectively, were added to each dye solution. After 2 min sonication of experimental solution, the dye residual was determined in aqueous solution. So, q_e was calculated as described before. Several isotherm models are developed to evaluate the equilibrium adsorption; however, Langmuir and Freundlich are the most common ones [23]. Langmuir isotherm theory is based on the assumption of monolayer adsorption of analyte on a homogeneous surface. The linear form of the Langmuir model is expressed as (Eq. (4)):

$$\frac{C_e}{q_e}=\frac{1}{bq_{\max}}+\frac{C_e}{q_{\max}} \tag{4}$$

where $q_{\max}$ (mg g^{-1}) is the maximum monolayer adsorption capacity and b (L mg^{-1}) is a constant related to energy of adsorption. The values of $q_{\max}$ and b were calculated from the slope and intercept of the linear plot C_e/q_e vs. C_e, respectively.

The Freundlich isotherm is derived by assuming a heterogeneous surface with a non-uniform distribution of heat of adsorption over the surface. The linearized form of the Freundlich equation (Eq. (5)) is expressed as follows: [23]

$$\log q_e=\log K_F+\frac{1}{n}\log C_e \tag{5}$$

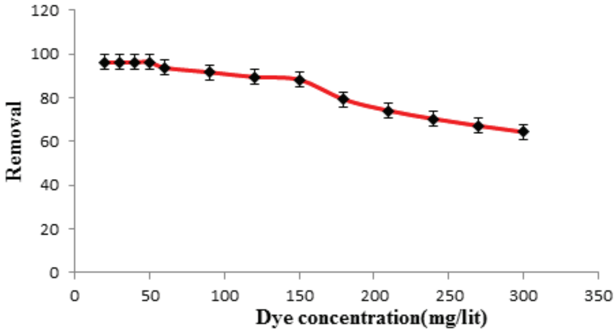

Fig. 9. Effect of initial dye concentration on removal of Acid Red 88. Experimental conditions: 50 mL of different concentration of dye solution at pH 3, 5 mg of ionic liquid, 5 mg of magnetic NP, 2 min contact time at 10°C.

Table 1
Thermodynamic parameters for dye adsorption onto MNPs

ΔS (J mol^{-1} K^{-1})	ΔH (kJ mol^{-1})	ΔG (kJ mol^{-1})					
		283 K	293 K	303 K	313 K	323 K	333 K
–62.84	–27.03	–9.24	–8.61	–7.99	–7.36	–6.73	–6.10

where K_F is the Freundlich constant and $1/n$ is the heterogeneity factor. K_F is the capacity of the adsorbent for the adsorbate and n is the reaction order while $1/n$ is a function of the strength of adsorption. The values of n and K_F were calculated from the slope and intercept of the linear plot $\log q_e$ vs. $\log C_e$, respectively. Table 2 indicates the values of Langmuir and Freundlich constants, and the correlation coefficients, R^2, obtained from the linear regressions. The results show that Langmuir model fitted better ($R^2 = 0.9993$) than the Freundlich model ($R^2 = 0.9903$), which indicate the suitability of Langmuir isotherm model for describing adsorption of AR88 onto Fe_3O_4 NPs [48]. The constant $1/n$ (0.3615) indicates favorable physical adsorption because of the obtained $1/n$ value ($0 < 1/n < 1$). The term $1/n$ also expresses an affinity between the adsorbate and the adsorbents [58]. The $\log K_F$ value was 2.275 and exhibited an adsorption capacity of Fe_3O_4 for the AR88 [59,60].

3.4. Desorption and reusability studies

The primary objective of regeneration is to recover valuable components present in the adsorbed phase [29]. Desorption of the AR88 from the Fe_3O_4 NPs was studied by using different eluting solutions such as: sodium chloride (1.0 mol L^{-1}), NaOH (1.0 mol L^{-1}), pure acetone, and different mixture of sodium chloride (1.0 mol L^{-1}) and acetone, with volume ratios of 1:1, 2:1 and 1:2, respectively. The desorbing ability of pure acetone was found to be higher than that of the other eluting solutions. In this study, more than 95% of dye could be desorbed and recovered in a short time of 1 min and in a single step elution by using 2 mL of pure acetone, when 50 mL of 50 ppm dye had been already adsorbed onto the Fe_3O_4 NPs in the presence of magnetic ionic liquid.

The reusability of the adsorbents in several successive separation processes was tested and the results showed that after five sorption–desorption cycles, the efficiency of magnetic nanosorbent for the AR88 removal was not significantly reduced but in the sixth run, 9% decrease in its performance was observed. It may be due to oxidation, losing and/or dissolving of some amounts of the adsorbent during the successive steps [29]. Therefore, a specific amount of Fe_3O_4 NPs could be used during five repeated cycles to remove AR88 from aqueous solutions.

Table 2
Adsorption isotherm parameters of Acid Red 88 onto Fe_3O_4 NPs

Freundlich model			Langmuir model		
R^2	$\log K_F$	n	R^2	q_m (mg g^{-1})	K_L (L mg^{-1})
0.9993	2.275	2.77	0.9993	909.1	0.116

3.5. Real sample analysis and comparison study

Under optimum conditions, removal of AR88 was studied from the natural river water. River water was collected from Chalus River (Mazandaran province, Iran). A significant amount of standard AR88 solution (50 mg L^{-1}) was spiked into the river samples and analyzed by UV–Vis spectrophotometer (standard addition). Then AR88 was removed from river samples under optimal conditions: 50 mL of 50 ppm dye solution at pH 3, 10 mg of MNP, 5 mg of ionic liquid (bmim [$FeCl_4$]), 2 min contact time at 10°C. No Acid Red 88 was detected in the river water sample. For evaluating accuracy of the method, relative recoveries were determined by spiking Acid Red 88 to the analyzed samples at concentration level of 50 mg L^{-1}. The results showed that the average percentage of dye removal from river samples was about 92.7% ± 2.05% ($n = 5$). So the complexity of dye medium had no significant effects on its removal with using Fe_3O_4 NPs and bmim [$FeCl_4$] ionic liquid under optimal conditions.

Also, this study was compared with other researches in removal of AR88. The results are shown in Table 3. As seen in Table 3, the sorbent efficiency of MNP and IL for AR88 removal in this work is much better than that of other reported methods, except for untreated clay [36] and Kaolin modified with a long chain IL [50]. Also the removal rate is much faster in comparison with other reported researches. In comparison with IL modified Kaolin, it should be noted that 909 mg/g of $q_{\max}$ was obtained in 200 ppm of AR88 solution, while it was reported that the percentage of dye removal from 50 ppm of AR88 solution was about 40% after 14 min [50]. But 909.1 mg/g of $q_{\max}$ and 95% of dye removal were achieved from 50 ppm of dye solution in this work. However, the results show that the combination of Fe_3O_4 MNPs and bmim [$FeCl_4$] magnetic IL has been a good candidate as a suitable adsorbent for removal of AR88 from aqueous solutions.

Table 3
Comparison of the present study with other studied methods for the removal % of Acid Red 88 from aqueous solutions

Adsorbent	$q_{\max}$ (mg/g) and/or removal %	Removal time	Reference
Magnetic $ZnFe_2O_4$	111.1	340 min	[48]
Kaolin modified with 1-hexyl, 3-decahexyl imidazolium	909.09	<5 min	[50]
Azolla rongpong	78.74	7 h	[60]
Azolla microphylla	54.89	12 h	[61]
Anion exchange membrane	42.01	140 min	[38]
Untreated clay	1133.10	15 min	[36]
Calcinated alunite	832.81	10 min	[62]
Fe_3O_4 magnetic NP with 1-butyl-3-methylimidazolium tetrachloroferrate IL	909.1	2 min	This study

4. Conclusion

The proposed method offers a simple and inexpensive method for removal of acid dye from aqueous solutions. In this study, we have combined the extraction ability of ILs with the advantages of MNPs for AR88 dye removal from aqueous solution. The effective operational parameters such as contact time, ionic liquid amount, nanoparticle dosage, pH and temperature were optimized and under optimal conditions nearly 95% of AR88 was removed from aqueous solution. The equilibrium data fitted well with the Langmuir model. The thermodynamic study indicated that the adsorption of AR88 onto Fe_3O_4 NPs was spontaneous and possessed an exothermic process. The advantages of this removal method are large surface-to-volume ratio, easy separation and low time-consuming due to magnetically-assisted separation of the adsorbent. Magnetic nanosorbent also could be reused for five successive removal cycles. Its reusability for five removal cycles has made it as an economic method to remove AR88 from aqueous solutions. The proposed method can be a guideline for the removal of other acid dyes from aqueous solutions.

In the present work, Acid Red 88 was selected as the analyte to investigate the applicability of the method for removal of Acid Red 88 from water samples. Major interactions which expected for the extractions were the driving forces included: (1) hydrophobic interactions, (2) hydrogen bonds, (3) electronic π-π interaction between phenyl groups of dye and IL and (3) electrostatic interaction between negatively charged dye anions and the positively charged ionic liquid. So, many compounds, which possess the ability to interact with the IL, may be extracted with this strategy. Also, the removal efficiency was diminished due to the disruption of electrostatic affinity between sorbent and the anionic dyes in the presence of salt ions in the water samples.

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Supplementary material

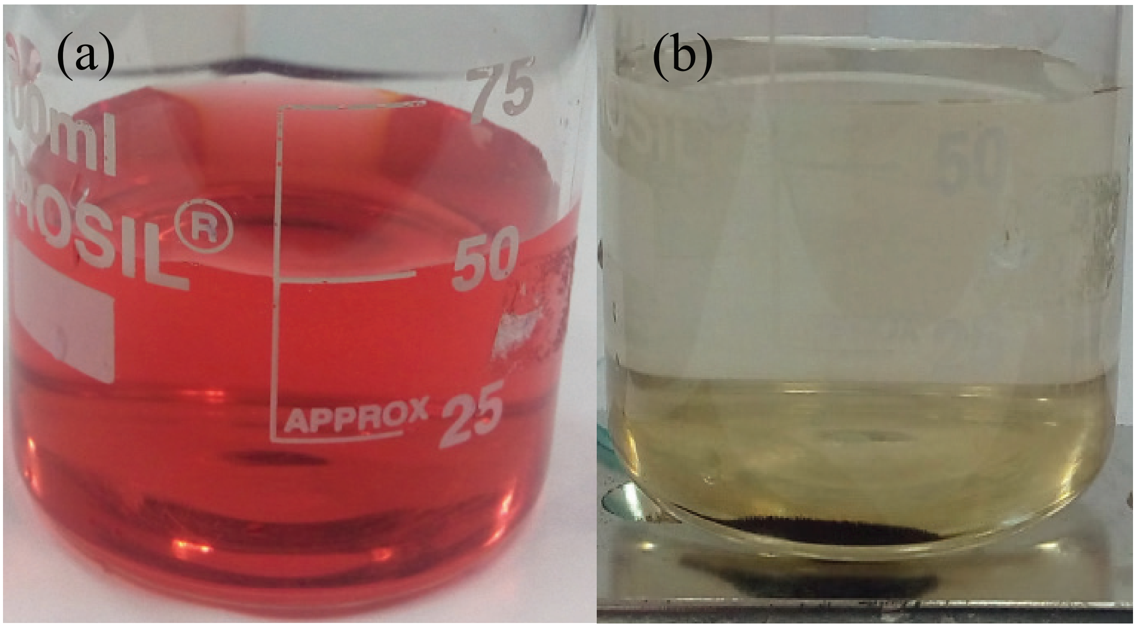

Fig. S1. Photograph of dye solution (a) before and (b) after the dye removal process in optimum conditions: 50 mL of 50 ppm dye solution at pH 3, 5 mg of ionic liquid, 5 mg of magnetic NP, 2 min contact time at 10°C.