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## ORIGINAL ARTICLE

# Removal of copper, nickel and zinc by sodium dodecyl sulphate coated magnetite nanoparticles from water and wastewater samples

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## KEYWORDS

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**Abstract** In the present study, sodium dodecyl sulphate-coated Fe<sub>3</sub>O<sub>4</sub> nanoparticles (SDS-Fe<sub>3</sub>O<sub>4</sub> NPs) were applied to remove Cu(II), Ni(II) and Zn(II) ions from water and wastewater samples. The effects of pH of solution, SDS, Fe<sub>3</sub>O<sub>4</sub> NPs and salt addition on removal efficiency of the metal ions were investigated and optimized. Salt addition has a negative effect on the removal efficiency of the metal ions, thus extraction follows the ion exchange mechanism. The results showed that the adsorption process onto the adsorbent is very fast under optimum conditions and nearly 1 min of contact time was found to be sufficient for completion of the metal ions' adsorption. Adsorption equilibrium of the metal ions reveals that data were fitted well to the Langmuir isotherm. Also, the maximum monolayer capacity,  $q_{max}$ , obtained from the Langmuir isotherm was 24.3, 41.2 and 59.2 mg g<sup>-1</sup> for Cu(II), Ni(II) and Zn(II), respectively. Desorption experiments by elution of the adsorbent with methanol show that the SDS-Fe<sub>3</sub>O<sub>4</sub> NPs could be reconditioned without significant loss of its initial properties even after three adsorption–desorption cycles. Finally, application of the SDS-Fe<sub>3</sub>O<sub>4</sub> NPs as efficient adsorbent material for removal of the metal ions from Iran Khodro's wastewater samples was investigated and satisfactory results were obtained.

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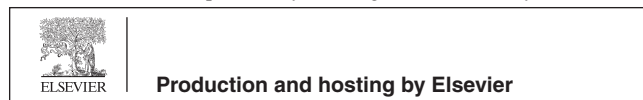
## 1. Introduction

Heavy metals released into the environment pose a significant threat to the ecosystem and public health because of their toxicity and persistence (Seiler et al., 1998). Therefore, heavy-metal contamination is still an important problem in both developing and developed countries throughout the world (Danazum and Bichi, 2010; Inglezakis et al., 2003; Momodu and Anyakora, 2010).

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Various methods have been developed for the removal of heavy-metal ions from wastewater which include chemical precipitation/coagulation, membrane technology, electrolytic reduction, ion exchange and adsorption. The advantages and disadvantages associated with each method are reviewed elsewhere (O'Connell et al., 2008). The adsorption process is one of the most common methods used for the removal of heavy-metal ions because of its simplicity, convenience, and high removal efficiency (Stafiej and Pyrzynska, 2007; Afkhami et al., 2007; Santos Yabe and de Oliveira, 2003; Cervera et al., 2003). The adsorption on activated carbon is attractive to many scientists due to the effectiveness of the removal of heavy-metal ions in trace quantities (Rao et al., 2009). However, the process has not been used extensively because of its high cost (Rao et al., 2009; Dias et al., 2007; El-Shafey et al., 2002). Therefore, the use of alternative low-cost materials as potential adsorbents for removal of heavy metals has been emphasized recently (Gupta et al., 2009). On the other hand, the development of heavy-metal adsorbents with high adsorption capacity, fast adsorption-desorption kinetics, and easy separation and regeneration is in great demand.

Recently, application of nanoparticles (NPs) for the removal of pollutants has come up as an interesting area of research (Faraji et al., 2010a). Compared to conventional adsorbents with micrometre size, nanomaterials offer a significantly higher surface area-to-volume ratio and a short diffusion route, resulting in high adsorbent capacity, rapid removal dynamics and high removal efficiencies (Klabunde, 2001). Moreover, magnetic nanoparticles (MNPs) can be easily separated under external magnetic fields (Faraji et al., 2010b-d; Ma'mani et al., 2010) and therefore, no sample centrifugation or filtration is needed after treatment.

In this study, MNPs have been synthesized using a co-precipitation method and after modification of them with sodium dodecyl sulphate (SDS), they were applied for the removal and recovery of copper, nickel and zinc from industrial wastewater due to high concentration of these metal ions in the real samples. The objectives of this study are: (1) to assess the performances of MNPs for the removal of the heavy-metal ions, (2) to achieve the possible regeneration of MNPs for reuse, and (3) to explore the mechanisms of metal adsorption onto MNPs.

## 2. Experimental section

### 2.1. Chemicals and reagents

All reagents were of analytical reagent grade and were used as supplied. Stock solutions ( $1000 \text{ mg L}^{-1}$ ) of Cu(II), Ni(II) and Zn(II) were prepared by direct dissolution of proper amounts of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{Ni}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  and  $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  salts from Merck (Darmstadt, Germany) in doubly distilled water. The standard solutions were diluted with doubly distilled water to prepare the mixed standard solutions. Ferric chloride ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ), ferrous chloride ( $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ), sodium hydroxide, sodium dodecyl sulphate (SDS), methanol, ethanol, sodium chloride and hydrochloric acid were obtained from Merck. The pH of the solutions was adjusted by dropwise addition of nitric acid ( $0.01 \text{ mol L}^{-1}$ ) and/or sodium hydroxide solutions ( $0.01 \text{ mol L}^{-1}$ ).

### 2.2. Apparatus

Concentrations of the heavy metals in all samples were determined using a Varian SpectrAA 200 (Springvale, Victoria, Australia) atomic absorption spectrometer (AAS). Hollow cathode lamps at respective wavelengths (resonance line) were used as radiation sources for each metal ion. An air-acetylene flame was used for determination of the metals ions. All instrumental settings were performed based on the procedure recommended by the manufacturer. Magnetic separation was fulfilled by a supermagnet with 1.2 Tesla magnetic field, N 35 model ( $5 \times 3 \times 2 \text{ cm}$ ) from Tehran Magnet (Tehran, Iran). A Heidolph mechanical-stirrer RZR 2102 control model (Kelheim, Germany) was applied for stirring of the metal ion solutions with a glassware stirrer. The pH values of solutions were determined and adjusted using a pH meter model WTW (Inolab, Germany) with a combined glass-calomel electrode.

### 2.3. Synthesis of $\text{Fe}_3\text{O}_4$ NPs

$\text{Fe}_3\text{O}_4$  NPs were prepared by the chemical co-precipitation method via a reactor designed in our previous work (Faraji et al., 2010b). 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 ( $12 \text{ mol L}^{-1}$ ) were dissolved in 50 mL of deionized water in order to prepare the stock solution of ferrous and ferric chloride in a beaker which was then degassed by nitrogen for 20 min. Simultaneously, 500 mL of  $1.5 \text{ mol L}^{-1}$  NaOH solution was degassed (for 15 min) and heated to  $80^\circ\text{C}$  in a reactor. Then, the stock solution was added dropwise using the dropping funnel during 30 min under nitrogen gas protection and vigorous stirring (1000 rpm) by a glassware stirrer. During the whole process, the solution temperature was maintained at  $80^\circ\text{C}$  and nitrogen gas was purged to remove the dissolved oxygen. After the completion of reaction, the obtained  $\text{Fe}_3\text{O}_4$  NPs precipitate was separated from the reaction medium by magnetic field, and then washed with 500 mL doubly distilled water four times. Finally, the obtained  $\text{Fe}_3\text{O}_4$  NPs were re-suspended in 500 mL of degassed deionized water. The synthesized  $\text{Fe}_3\text{O}_4$  NPs in this work as same as our previous work (Faraji et al., 2010b), were previously characterized by using IR, SEM, and XRD techniques (Faraji et al., 2010c).

### 2.4. Optimization of metal ion adsorption

Optimization studies were carried out according to the following procedure: (1) 20 mL aqueous solution of the metal ion ( $10 \text{ mg L}^{-1}$ ) was prepared in a 50 mL glass beaker by addition of the appropriate amount of the metal ion stock solutions; (2) 1 mL of the  $\text{Fe}_3\text{O}_4$  NPs suspension (containing 10 mg of  $\text{Fe}_3\text{O}_4$  NPs) was added to the metal ion solution; (3) pH of the solution was adjusted to the desired value and then SDS was added into the metal ion solution; (4) the mixed solution was stirred for a desired time; (5) after metal ion adsorption,  $\text{Fe}_3\text{O}_4$  NPs were magnetically separated from the sample solution; (6) the residual metal ion concentration in the supernatant clear solution was determined by AAS using a calibration curve. The following equation was applied to calculate the metal ion removal efficiency in the treatment experiments:

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

where  $C_0$  and  $C_e$  are the initial and residual concentrations of the metal ion in the solution ( $\text{mg L}^{-1}$ ), respectively.

The data for adsorption experiment were replicated three times and the average results were reported. Also, adsorption experiments were carried out individually for each metal ion.

### 2.5. Adsorption isotherms

Adsorption isotherms of metal ions on the SDS-coated  $\text{Fe}_3\text{O}_4$  NPs were obtained from batch experiments by adding 15 mg  $\text{Fe}_3\text{O}_4$  NPs and 25 mg SDS to a 50-mL beaker containing 20-mL of metal ions with initial concentrations ranging from 5 to 50  $\text{mg L}^{-1}$ . Suspensions were then mixed with a mechanical stirrer at  $25 \pm 2$  °C for 10 min. After reaching adsorption equilibrium, the SDS-coated  $\text{Fe}_3\text{O}_4$  NPs were magnetically separated from the aqueous solution and the residual concentrations of metal ions in the aliquot were determined by AAS. The equilibrium adsorbed concentration,  $q_e$  ( $\text{mg g}^{-1}$ ), was calculated according to the following equation:

$$q_e = \frac{(C_0 - C_e)V}{M} \quad (2)$$

where  $C_0$  and  $C_e$  ( $\text{mg L}^{-1}$ ) are the initial and equilibrium concentrations of metal ion in solution, respectively,  $V$  (L) is the total volume of solution, and  $M$  (g) is the adsorbent mass.

### 2.6. Preparation of wastewater samples

Wastewater samples were collected from the Iran Khodro Company's wastewater (Tehran, Iran) in clean glass bottles. No filtration or any further treatment was applied to any of the samples before performing removal experiments. Then, the proposed method under optimized conditions was applied to removal of the metal ions, without adjusting pH (pH of sample was  $\sim 7.0$ ). After treatment and before AAS analysis, the samples were filtered through a 0.45  $\mu\text{m}$  pore size membrane filter.

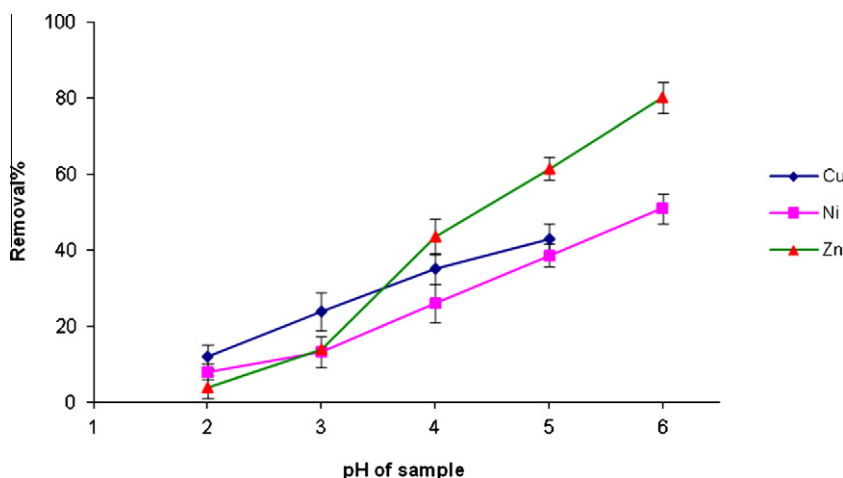
## 3. Results and discussion

### 3.1. Effect of sample's pH

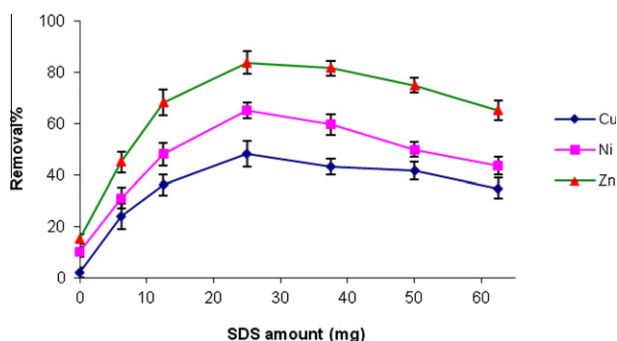
The pH is an important factor affecting the removal of metal ions from aqueous solutions. Dependence of metal sorption on pH is related to both the metal chemistry in the solution and the ionization state of functional groups of the adsorbent which affects the availability of binding sites (Heidari et al., 2009; Ngomsik et al., 2009).

In order to evaluate the influence of pH on adsorption of the metal ions, the experiments were carried out in the pH range of 2–5 for Cu(II) and 2–6 for Ni(II) and Zn(II). The pH ranges were chosen as mentioned ranges in order to avoid precipitation of metal ions in the form of metal hydroxides ( $K_{sp}$  values for  $\text{Cu}(\text{OH})_2$ ,  $\text{Ni}(\text{OH})_2$  and  $\text{Zn}(\text{OH})_2$  are  $2.20 \times 10^{-20}$ ,  $2.8 \times 10^{-16}$  and  $4.5 \times 10^{-17}$ , respectively (Wikipedia)). The effect of pH on removal efficiencies is shown in Fig. 1. It can be observed that the removal efficiency of Cu(II), Ni(II) and Zn(II) increased by increasing pH from 2 to 5 for Cu(II) and from 2 to 6 for Ni(II) and Zn(II). Removal of all metal ions increases with increasing the solution pH, and a maximum value was reached at an equilibrium pH of around 4.0 for Cu(II) and 6.0 for Ni(II) and Zn(II). Acidic conditions are not favorable because most functional groups of the components are protonated and leave few available ionized groups. Competition between protons and metal species could thus explain the weak adsorption efficiency in acidic media. Distribution of different forms of Cu(II) and Zn(II) as a function of pH indicates that the dominant species is Cu(II) at  $\text{pH} < 5$  and Zn(II) at  $\text{pH} < 6$  (Polat and Erdogan, 2007).

To achieve high extraction efficiency without metal hydroxide precipitation, pH of 4.0 for Cu(II) and pH of 6.0 for Ni(II) and Zn(II) were selected for subsequent experiments. Several researchers have investigated the effect of pH on adsorption of metal ions by using different kinds of adsorbents (Huang et al., 1997; Vázquez et al., 2009; Kandaha and Meunier, 2007; Cetin and Pehlivan, 2007; Villaescusa et al., 2004; Yavuz et al., 2003; White et al., 2009; Ngomsik et al., 2006). In all



**Figure 1** Effect of pH on removal efficiency. Sample volume = 20 mL; concentration of the metal ions = 10  $\text{mg L}^{-1}$ ; 10 mg  $\text{Fe}_3\text{O}_4$  NPs; 10 mg SDS; stirring time = 5 min.



**Figure 2** Effect of SDS amount on removal efficiency. Sample volume = 20 mL; sample's pH = 4.0 for Cu(II) and 6.0 for Ni(II) and Zn(II); concentration of the metal ions = 10 mg L<sup>-1</sup>; 10 mg Fe<sub>3</sub>O<sub>4</sub> NPs; 10 mg SDS; stirring time = 5 min.

cases, they have observed a maximum adsorption of metal ions between pH values 5 and 6.

### 3.2. Effect of SDS amount

Fig. 2 depicts the percentage of removed metal ions as a function of the amount of SDS added. In the absence of SDS, the metal ions are hardly adsorbed on the surface of Fe<sub>3</sub>O<sub>4</sub> NPs. In contrast, by increasing the SDS amount, removal of the metal ions increases remarkably. The increase in removal efficiency can be explained by the gradual formation of SDS aggregates on the surface of Fe<sub>3</sub>O<sub>4</sub> NPs and the metal ions are adsorbed gradually. These results can be proved by Lin et al. investigation for removal of Cu(II) and Zn(II) from aqueous solutions by sorption on the montmorillonite modified with SDS (Lin and Juang, 2002). Maximum removal was obtained when SDS amounts increased up to 25 mg ( $4.4 \times 10^{-3}$  mol L<sup>-1</sup>), whereas the removal efficiency decreased when the amount of added SDS is more than 25 mg. Under this circumstance, SDS molecules begin to form micelles in the bulk aqueous solution. Critical micellization concentration (CMC) of SDS is about  $8 \times 10^{-3}$  mol L<sup>-1</sup> (Marcolongo and Miranda, 2011). Furthermore, the micelles cause the metal ions to redistribute into the solution again, and they are not adsorbed on the adsorbent surface. On the other hand, SDS

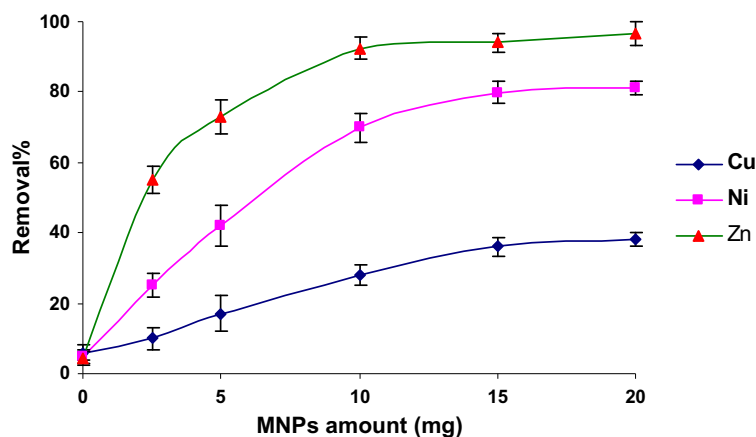
has been used to stabilize suspension of NPs. So, the increase of the metal ion sorption could be attributed to the reduction of aggregation of the NPs and therefore a higher surface area for sorption in comparison with "naked" MNPs. Given these findings, 25 mg SDS was added into the solution in the next studies.

### 3.3. Effect of adsorbent amount

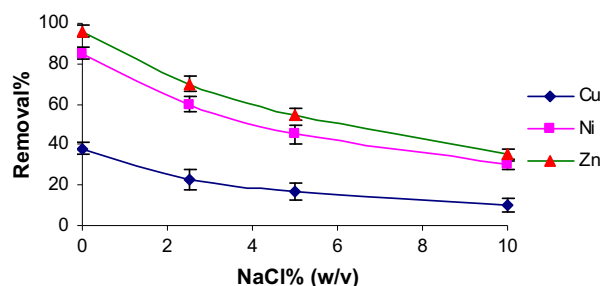
In comparison with the traditional sorbents (micro-sized sorbents), NPs offer a significantly higher surface area-to-volume ratio. Therefore, satisfactory results can be obtained with a fewer amounts of NPs. Generally, interaction of metal ions with SDS-coated Fe<sub>3</sub>O<sub>4</sub> NPs can be changed when amounts of Fe<sub>3</sub>O<sub>4</sub> NPs are changed individually. Hence, in order to study the effect of adsorbent amount, amounts of Fe<sub>3</sub>O<sub>4</sub> NPs and SDS were changed simultaneously to keep a constant interaction between Fe<sub>3</sub>O<sub>4</sub> NPs and SDS. Therefore, 0–20 mg of Fe<sub>3</sub>O<sub>4</sub> NPs was added to 20 mL of the sample solution by keeping a constant ratio of SDS to Fe<sub>3</sub>O<sub>4</sub> NPs amount as obtained in previous section (25 mg SDS for 10 mg Fe<sub>3</sub>O<sub>4</sub> NPs; SDS/Fe<sub>3</sub>O<sub>4</sub> NPs = 2.5). The obtained results (Fig. 3) showed that by increasing the adsorbent amounts from 0 to 15 mg (SDS from 0 to 37.5 mg), due to the raise in accessible sites, the removal efficiency increased remarkably and after that remained constant. So 15 mg of Fe<sub>3</sub>O<sub>4</sub> NPs and 37.5 mg of SDS were selected for all subsequent experiments.

### 3.4. Effect of salt addition

The effect of salt concentration on adsorption of the metal ions was investigated by the addition of NaCl in the range of 0–10% (w/v). The results are shown in Fig. 4. It can be seen that as the NaCl concentration increases, adsorption capacity of the Fe<sub>3</sub>O<sub>4</sub> NPs decreases significantly. The results can be justified by exchange reactions in solutions during adsorption as shown below (White et al., 2009):



**Figure 3** Effect of the adsorbent amount on removal efficiency. Sample volume = 20 mL; sample's pH = 4.0 for Cu(II) and 6.0 for Ni(II) and Zn(II); concentration of the metal ions = 10 mg L<sup>-1</sup>; 10 mg Fe<sub>3</sub>O<sub>4</sub> NPs; 25 mg SDS; stirring time = 5 min.



**Figure 4** Effect of salt addition on removal efficiency. Sample volume = 20 mL; sample's pH = 4.0 for Cu(II) and 6.0 for Ni(II) and Zn(II); concentration of the metal ions = 10 mg L<sup>-1</sup>; 15 mg Fe<sub>3</sub>O<sub>4</sub> NPs; 37.5 mg SDS; stirring time = 5 min.

Thus, according to the obtained results, the strategy of no salt addition was chosen for kinetic and isotherm studies. According to the obtained results, a probable removal mechanism of the metal ions was suggested as is shown schematically in Fig. 5 (for Zn(II) as example).

### 3.5. Kinetic study

Adsorption kinetics of the metal ions as percentage of metal ions removed *versus* time was studied under optimum conditions for an initial concentration of 10 mg L<sup>-1</sup>. The results showed that removal of all metal ions occurred at the first seconds of contact time, and no appreciable increase was observed in the contact time range of 0.5–60 min.

### 3.6. Isotherm study

Equilibrium data, generally known as adsorption isotherms, are basic requirements to provide insight into the adsorption mechanism, the surface properties, and the affinity of adsorbent; they have also been commonly used to evaluate the adsorption capacity of an adsorbate on an adsorbent (Ibrahim et al., 2010) and can be modeled using different simple adsorption models such as Langmuir and Freundlich isotherms. The Langmuir model assumes monolayer coverage of adsorbate over a homogeneous adsorbent surface, and the sorption of

**Table 1** Langmuir and Freundlich model parameters for the metal ions adsorption onto SDS-coated Fe<sub>3</sub>O<sub>4</sub> NPs.

Metal ion	Isotherm model					
	Langmuir			Freundlich		
	$q_{max}$ (mg g <sup>-1</sup> )	$K_L$ (L mg <sup>-1</sup> )	$R_L^2$	$n$	$K_F$ (L mg <sup>-1</sup> )	$R_F^2$
Copper	24.3	0.05	0.9900	1.8	2.25	0.9641
Nickel	41.2	0.21	0.9944	0.8	0.08	0.7392
Zinc	56.2	0.26	0.9919	2.4	15.40	0.9390

each molecule onto the surface has equal sorption activation energy. The linearized Langmuir equation can be expressed as:

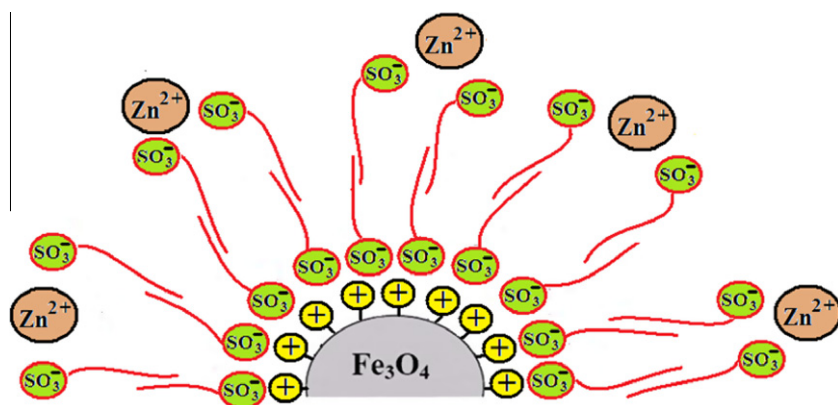
$$\frac{C_e}{q_e} = \frac{1}{K_L q_{max}} + \frac{1}{q_{max}} C_e \quad (5)$$

where  $q_{max}$  is the maximum amount of metal ion adsorbed per unit weight of Fe<sub>3</sub>O<sub>4</sub> NPs to form a complete monolayer on the surface (mg g<sup>-1</sup>),  $K_L$  is a constant related to affinity of the binding sites with the metal ions (L mg<sup>-1</sup>), and  $C_e$  (mg L<sup>-1</sup>) and  $q_e$  (mg g<sup>-1</sup>) are the equilibrium liquid phase and solid phase metal ion concentrations, respectively. The empirical Freundlich isotherm based upon sorption on heterogeneous surfaces was applied in linear form (Eq. (4)):

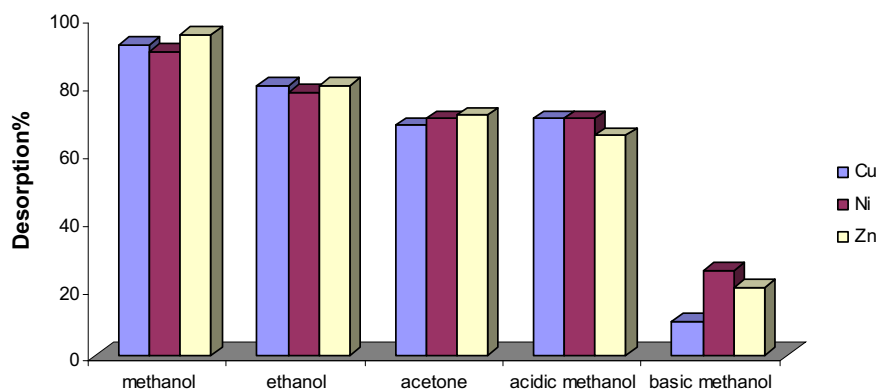
$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (6)$$

where  $K_F$  (mg<sup>1-(1/n)</sup> g<sup>-1</sup> L<sup>1/n</sup>) and  $1/n$  (dimensionless) are the Freundlich constants indicating the relative adsorption capacity and the intensity of adsorption, respectively.

Parameters related to each isotherm for the adsorption of the metal ions on the adsorbent were determined by using linear regression analysis, and square of the correlation coefficients ( $r^2$ ) were calculated (Table 1). The results showed that equilibrium data for all metal ions were well explained by the Langmuir isotherm model as compared to the Freundlich model. On the basis of the Langmuir analysis, maximum adsorption capacities were determined to be 24.3, 41.2 and 59.2 mg g<sup>-1</sup> for Cu(II), Ni(II) and Zn(II), respectively. This order can be justified by binding behavior of the metal ions to SDS at pH = 6. Huang and co-workers found that the order of association constant of SDS and metal ions is Cu(II)



**Figure 5** Schematic illustration of the probable adsorption mechanism of the metal ions on the surface of SDS-coated Fe<sub>3</sub>O<sub>4</sub> NPs (zinc as model).



**Figure 6** Comparison of desorption efficiency of the metal ions from surface of the SDS-coated Fe<sub>3</sub>O<sub>4</sub> NPs using different eluents. Sample volume = 20 mL; sample's pH = 4.0 for Cu(II) and 6.0 for Ni(II) and Zn(II); concentration of the metal ions = 10 mg L<sup>-1</sup>; 15 mg Fe<sub>3</sub>O<sub>4</sub> NPs; 37.5 mg SDS; stirring time = 5 min; eluent's volume = 2.0 mL.

**Table 2** Removal of the metal ions from different Iran Khodro's wastewater samples by applying the proposed method.

Sample	Analyte	Input (mg L <sup>-1</sup> )	SDS-coated Fe <sub>3</sub> O <sub>4</sub> NPs		Naked Fe <sub>3</sub> O <sub>4</sub> NPs	
			After treatment ± SD (mg L <sup>-1</sup> , n = 3)	Removal (%)	After treatment ± SD (mg L <sup>-1</sup> , n = 3)	Removal (%)
1	Copper	0.01 <sub>1</sub>	0.0097 ± 0.0003	12.0	0.0046 ± 0.0004	58.5
	Nickel	0.44 <sub>2</sub>	0.1834 ± 0.0158	58.5	0.1799 ± 0.0123	59.3
	Zinc	0.01 <sub>8</sub>	0.0052 ± 0.0004	71.0	0.0069 ± 0.0002	61.5
2	Copper	0.01 <sub>2</sub>	0.0108 ± 0.0021	10.3	0.0065 ± 0.0005	45.8
	Nickel	0.48 <sub>1</sub>	0.0904 ± 0.0060	81.2	0.0476 ± 0.0032	90.1
	Zinc	0.04 <sub>3</sub>	0.0108 ± 0.0007	75.0	0.0076 ± 0.0006	82.3
3	Copper	0.02 <sub>1</sub>	0.0178 ± 0.0009	15.0	0.0104 ± 0.0012	50.6
	Nickel	2.86 <sub>5</sub>	0.0544 ± 0.0032	98.1	0.4527 ± 0.0276	84.2
	Zinc	1.78 <sub>4</sub>	0.1909 ± 0.0198	89.3	0.0232 ± 0.0024	98.7

< Ni(II) < Zn(II) (O'Connell et al., 2008). These results demonstrated that the SDS-coated Fe<sub>3</sub>O<sub>4</sub> NPs exhibited interesting adsorption properties. Compared to some recent data in the literature (Table 2), the results also introduced the SDS-coated Fe<sub>3</sub>O<sub>4</sub> NPs to be an excellent adsorbent for removal of the metal ions.

### 3.7. Desorption and regeneration studies

Desorption of the metal ions from the SDS-coated-Fe<sub>3</sub>O<sub>4</sub> NPs was tested by using different kinds of organic solvents (methanol, acetone, ethanol, basic methanol and acidic methanol). The obtained results are illustrated in Fig. 6. Desorption ability of methanol was found to be higher than those of the other solvents. This can be explained by the suitable solubility of SDS in methanol.

To evaluate the reusability of the adsorbent, adsorption of the metal ions and regeneration of metal ion-loaded adsorbent

were performed in consecutive cycles. In each cycle, 200 µL of stock solution of metal ion (1000 mg L<sup>-1</sup>) was added to 20 mL of solution and then mixed with 15 mg Fe<sub>3</sub>O<sub>4</sub> and 25 mg SDS for 5 min. The SDS-coated Fe<sub>3</sub>O<sub>4</sub> NPs were separated magnetically and the supernatant was subjected to metal ions' measurements. The resultant SDS-coated Fe<sub>3</sub>O<sub>4</sub> NPs were mixed with 2 mL of methanol solution for 5 min. Prior to the next adsorption-desorption cycle, the regenerated Fe<sub>3</sub>O<sub>4</sub> NPs were washed thoroughly with double distilled water. The results indicated that Fe<sub>3</sub>O<sub>4</sub> NPs can be used at least in five consecutive cycles without a considerable reduction of removal efficiency.

### 3.8. Application of the proposed method to wastewater samples

Under optimum conditions, removal of the metal ions from the wastewater samples was studied. Standard deviations (SD) for analysis of the metal ions in wastewater samples using

**Table 3** Comparison of the proposed method with some of the methods reported in the literature for removal of the metal ions.

Metal ion	Adsorbent	$q_{max}$ ( $\text{mg g}^{-1}$ )	Removal (%)	Sample's pH	Removal time (min)	Ref.
Zn <sup>2+</sup> and Cu <sup>2+</sup>	Chestnut shell	2.4 and 5.5	70–85	5.5	5760	Vázquez et al. (2009)
Ni <sup>2+</sup>	As-produced and oxidized CNTs	18.083 and 49.261	<sup>a</sup>	6.0	20–50	Kandaha and Meunier (2007)
Ni <sup>2+</sup> and Zn <sup>2+</sup>	Fly ash	9.5 and 10.8	80 and 100	4.0–5.0	60	Cetin and Pehlivan (2007)
Cu <sup>2+</sup> and Ni <sup>2+</sup>	Grape stalk wastes	10.1 and 10.6	<sup>a</sup>	5.5–6.0	60	Villaescusa et al. (2007)
Ni <sup>2+</sup> and Cu <sup>2+</sup>	Kaolinite	1.669 and 10.787	<sup>a</sup>	<sup>a</sup>	120	Yavuz et al. (2003)
Cu <sup>2+</sup> , Ni <sup>2+</sup> and Zn <sup>2+</sup>	Poly-L-cysteine functionalized $\gamma\text{-Fe}_2\text{O}_3$	49.2, 32.8 and 24.1	> 50	7.0	2.5	White et al. (2003)
Ni <sup>2+</sup>	Magnetic alginate microcapsules	30.5	70	8.0	480	Ngomsik et al. (2006)
Cu <sup>2+</sup> , Ni <sup>2+</sup> and Zn <sup>2+</sup>	SDS-coated Fe <sub>3</sub> O <sub>4</sub> NPs	24.3, 41.2 and 59.2	35–95	< 6	1	This work

<sup>a</sup> Data not reported.

the proposed method based on three-replicate removal as well as determinations are provided in Table 2. It is demonstrated that satisfactory results can be obtained by applying the proposed method to a very complex matrix such as wastewater samples. Also, the results showed that by applying the proposed method to wastewater samples, turbidity of the samples increased. This can be attributed to the coacervation phenomenon due to the presence of cationic surfactants in the wastewater samples. Therefore, removal of metal ions from the wastewater samples was reconsidered in the absence of SDS. The obtained results (Table 2) indicate that by applying the new conditions, removal efficiency of the metal ions can be improved.

#### 4. Conclusions

The present study confirms the capability and effectiveness of the SDS-coated Fe<sub>3</sub>O<sub>4</sub> NPs adsorbent for removal of heavy metals from various water and wastewater samples. Based on obtained results, a probable mechanism for uptake of the metal ions can be electrostatic attraction and ion exchange. Adsorption of the metal ions on the adsorbent reached equilibrium very fast (< 1 min) and also adsorption data for the metal ions were fitted well by the Langmuir isotherm. Maximum adsorption capacity values of Cu(II), Ni(II) and Zn(II) ions from Langmuir equation were 24.3, 41.2 and 59.2  $\text{mg g}^{-1}$ , respectively. A comparison of maximum adsorption capacity ( $q_{max}$ ) of the SDS-coated Fe<sub>3</sub>O<sub>4</sub> NPs with those of other adsorbents used for removal of the metal ions was made. Data (Table 3) reveal its remarkable efficiency over other treated and untreated natural and synthetic adsorbents. Due to very high surface areas and short diffusion route of the SDS-coated Fe<sub>3</sub>O<sub>4</sub> NPs, high adsorption capacities can be obtained in a very short time (~1 min). Regeneration and re-adsorption studies demonstrated that the adsorbent could be recovered efficiently. Studies on batch adsorption using wastewater samples in order to remove the metal ions indicated that the adsorbent has a good potential to remove the heavy-metal ions from wastewater samples.

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