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# Amino Functionalized Silica Coated Fe<sub>3</sub>O<sub>4</sub> Magnetic Nanoparticles as a Novel Adsorbent for Removal of Pb<sup>2+</sup> and Cd<sup>2+</sup>

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**ABSTRACT:** The present study synthesizes a novel adsorbent by coating Fe<sub>3</sub>O<sub>4</sub> magnetic nanoparticles with amino functionalized mesoporous silica. The FTIR spectrums indicate that silica has been successfully coated on the surface of Fe<sub>3</sub>O<sub>4</sub> and 3-aminopropyl tri methoxysilane compound have been grafted to the surface of silica-coated Fe<sub>3</sub>O<sub>4</sub>. The XRD analysis shows the presence of magnetite phase with cubic spinel as a highly crystalline structure, before and after silica coating. The study also investigates the potentials of amino functionalized silica-coated Fe<sub>3</sub>O<sub>4</sub> magnetic nanoparticles for extraction of Pb<sup>2+</sup> and Cd<sup>2+</sup> cations from aqueous solutions, where it has used flame atomic absorption spectrometry to determine ion concentration in both recovery and sample solutions. The optimum conditions of removal of Pb<sup>2+</sup> and Cd<sup>2+</sup> ions turn out to be pH= 4-8 with a stirring time of 20 minutes. The minimum amount of 3M nitric acid to strip ions from functionalized magnetic nanoparticles is 10 mL. The experimental data show the adsorption isotherms have been well described by Langmuir isotherm model, with the maximum capacity of the adsorbent being 1000.0 (± 1.4) µg, 454.5 (± 1.6) µg of Pb<sup>2+</sup>, and Cd<sup>2+</sup> per each mg of functionalized magnetic nanoparticles, respectively. Finally, the proposed adsorbent is successfully applied to remove Pb<sup>2+</sup> and Cd<sup>2+</sup> ions in wastewater samples.

Keywords: Fe<sub>3</sub>O<sub>4</sub> nanoparticles, silica coated, Amino functionalized, Pb<sup>2+</sup>, Cd<sup>2+</sup>.

## **INTRODUCTION**<sup>\*</sup>

Application of an adsorbent for the purpose of removing toxic heavy ions from wastewater has been a continuous aim of researches dealing with the issue of environmental pollution control (Mahmoud et al., 2010a,b; Ciftci et al., 2010; Chakravarty et al., 2010). Some of such polluting materials like clay, alumina, and silicates have displayed several problems

including low mechanical and thermal stability or weak chemical affinity to the pollutants. metals. In face such of nanostructure materials show some important physicochemical properties to render them particularly attractive as separation media for purification. There are examples of the use of nanoporous or mesoporous materials for adsorption applications like the removal and preconcentration of metal ions (Lee & Yi,

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2001; Lam et al., 2007; Hajiaghababaei et al., 2012), organics (Lim & Stein, 1999), dyes (Ho et al., 2003; Habibi et al., 2017), radio nuclides (Ju et al., 2000), and anionic complexes (Fryxell et al., 1999; Lee et al., 2003) and different mesoporous materials have been developed through grafting a variety of functional groups on the surface of mesopore channels (Rajabi et al., 2017; Barczak, 2019).

Recent years have witnessed a growing rate of interest and research in magnetic adsorbents (Kanani et al., 2018; Vojoudi et al., 2017b), which due to magnetism are quite favorable. These adsorbents can be separated from aqueous samples rapidly by means of a magnet. The Fe<sub>3</sub>O<sub>4</sub> nanoparticles are a good choice for magnetic adsorption thanks to their low costs, simplicity of design, easy operation, and biocompatibility. However. there are several inevitable problems, such as the aggregation, oxidization, and instability at pH<4, which significantly reduce their superparamagnetism; therefore, it is important to design a suitable coating in order to protect magnetic nanoparticles. Silica is one of the most ideal materials for the protection of Fe<sub>3</sub>O<sub>4</sub> particles due to its chemical stability, biocompatibility, and easy surface modification with a wide range of organosilane Magnetic groups. silica nanoparticles have been synthesized with many techniques, such as layer-by-layer selfassembly, Stöber process, ferrite plating, sonochemical aerosol pyrolysis. and deposition. In this way, amino-functionalized Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> magnetic core shell to get synthesized for  $Pb^{2+}$ ,  $Cu^{2+}$ , and  $Cd^{2+}$  removal (Wang et al., 2010). It must mentioned that the silica, used in this study, was not mesoporous. Contiguity of magnetic nanoparticles and functionalized mesoporous silica materials provides active sites for adsorption and the simple as well as rapid separation process (Vojoudi et al., 2018; Tang et al., 2013). Tang et al. prepared amino-functionalized  $Fe_3O_4@$ mesoporous  $SiO_2$  microspheres for  $Pb^{2+}$  and  $Cd^{2+}$ removal. There, functionalization was done in ethanol/DI water under ultra-sonication.

On the other hand, heavy metals pose significant threats to the ecosystem, with lead and cadmium being of greater concern. Lead compounds are used in six categories, namely batteries, petroleum additives, alloys, pigments, cables, and ammunitions, with drinking water, food, air and soil establishing the major instances of exposure to lead ions, which in high quantities, can meddle with the synthesis of hemoglobin, affect the kidneys, gastrointestinal tract, joints, and reproductive system, and cause acute or chronic damages to the nervous system (HSDB, 1996).

The most significant use of cadmium is in nickel/cadmium batteries, pigments, PVC stabilizers, alloys, electronic compounds, phosphate fertilizers, and refined petroleum products. Long-term exposure to this metal could bring about obstructive lung-related maladies like lung cancer. Cadmium also causes bone defects (osteomalacia, osteoporosis) in humans and animals (HSDB, 1996).

The current study synthesized and used  $Fe_3O_4$  magnetic nanoparticles, coated with amino functionalized silica (Figure 1) for the purpose of removing  $Pb^{2+}$  and  $Cd^{2+}$  ions from aqueous solutions.

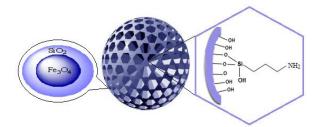


Fig. 1. Structure of amino functionalized silica coated Fe<sub>3</sub>O<sub>4</sub> magnetic nanoparticles

# MATERIALS AND METHODS

Fourier transform infrared (FT-IR) spectra were acquired in the range of 400 to 4000 cm<sup>-1</sup> via a RAYLEIGH WQF-510A FT-IR spectrophotometer and by means of KBr pellet technique. X-ray diffraction (XRD) analysis helped determining the crystalline structures of the products, using an X'Pert Pro MPD diffractometer, equipped with a Cu K<sub>a</sub> radiation source ( $\lambda$ = 1.5418 Å) at 40 kV and 40 mA. A UP 400S Hielscher ultrasonication probe was used to disperse the species at an operating voltage of 450 V. What is more, 1.4 T strong magnet (5 cm×5 cm×4 cm) was applied for magnetic material separation. Atomic absorption analyses were run on a PG-990 flame atomic absorption spectrometer, using hollow cathode lamps as well as an air/acetylene burner at a slit width of 0.4 nm with the lamp current equal to 5.0 mA. Lead and cadmium were measured at the wavelengths of 273.3 nm and 164.1 nm, respectively. Deuterium lamp background correction was also used. In case of other cations, the corresponding recommended conditions were employed.

98% FeCl<sub>2</sub>.4H<sub>2</sub>O, The 98% FeCl<sub>3</sub>.6H<sub>2</sub>O, absolute 99% ethanol. glycerol, 25% aqueous solution of ammonium, and all solvents and analytical grade nitrate salts of sodium, manganese, magnesium, cobalt, silver, nickel, zinc, cadmium, lead, chromium, and copper were prepared from Merck. Tetraethyl orthosilicate (TEOS, 98%) and 3aminopropyl trimethoxysilane (APTES, 97%), purchased from Sigma-Aldrich. Doubly-distilled deionized water was used throughout the research. It involved preparing 1000 mg/L solutions of all metal ions by dissolving appropriate amounts of the corresponding nitrate salts in DDIW. These were used as stock solutions for preparation of the rest of the solutions through dilution.

The  $Fe_3O_4$  magnetic nanoparticles (MNPs) were prepared as described in

other researches (e.g., Banaei et al., 2017) minor alterations. The typical with procedure involved dissolving 4.30 and 11.68 g of FeCl<sub>2</sub>.4H<sub>2</sub>O and FeCl<sub>3</sub>.6H<sub>2</sub>O in 200 mL deionized water in nitric atmosphere under vigorous stirring at 85 °C. Afterwards, the solution received 25 mL of 25% aqueous ammonia, which immediately changed its color from orange to black and the produced MNPs got separated, being washed with deionized water thrice and with 100 mL NaCl solution 0.02 mol/L once. Finally, it got dispersed in deionized water for further use.

The Silica-coated  $Fe_3O_4$ magnetic nanoparticles (SCMNPs) were prepared likewise our previous work (Vojoudi et al., 2017a). The method included transferring 25 mL of a suspension of the magnetite nanoparticles (MNPs) into an Erlenmeyer flask. Then, the MNPs got separated from the supernatant, using a magnet and then dispersed in 80 mL of a 10% v/v aqueous solution of tetraethoxysilane (TEOS). Afterwards, as much as 60 mL of glycerol was added and the mixture's pH was decreased, using glacial acetic acid to 4.6. This mixture was stirred at 90 °C for 2 hours under a nitric atmosphere, with the product getting separated and washed several times with not only 500 mL deionized water but 500 mL ethanol, also. The final product was dispersed in deionized water for further use. In order to modify SCMNPs and prepare amino functionalized silica-coated Fe<sub>3</sub>O<sub>4</sub> magnetic nanoparticles (SCMNPs-N), one gram of the prepared silica-coated MNPs got dispersed in 200 mL of water-free toluene, followed by addition of 25 mL 3aminopropyl trimethoxysilane (APTES) in toluene (10% V/V) to the reaction vessel, later refluxed for 24 h under a dry N<sub>2</sub> atmosphere. The resulting solid particles got separated, using a magnet; they also were repeatedly washed with ethanol and vacuum dried.

The extraction procedure, using the SCMNPs-N, involved addition of desirable amounts (e.g. 20 mg) of the adsorbent to 25 mL of the sample solution, containing 3 mg/L Pb<sup>2+</sup> and Cd<sup>2+</sup> ions and stirring for at least 20 min. Then, the resulting mixture was filtrated by filter paper and the ions got stripped via washing with 10 mL of a 3.0 mol/L solution of nitric acid and analyzed through flame atomic absorption spectroscopy. In order to adsorb the isotherm, some solutions with different concentrations were agitated in the range of 50-1500 mg/L of ions until achieving equilibrium.

### **RESULTS AND DISCUSSION**

The FTIR spectra, obtained for the MNPs, SCMNPs, and SCMNPs-N (Figure 2), offered meaningful information about the bonding sites of the samples. For pure Fe<sub>3</sub>O<sub>4</sub>, the strong broad signals at around 576 and 455 cm<sup>-1</sup>, reflected the stretching vibrations of Fe–O bonds. The band, observed at 3462 cm<sup>-1</sup>, in some cases originated from the O–H group, while the ones observed at 803 and 1091cm<sup>-1</sup>, reflected the stretching of Si–OH and Si–O–Si, being observed in the spectra of the silica-coated Fe<sub>3</sub>O<sub>4</sub>, indicating that SiO<sub>2</sub> had been successfully coated on the surface

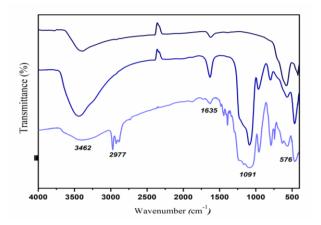


Fig. 2. FT-IR spectra of MNPs, SCMNPs, and SCMNP-N

of Fe<sub>3</sub>O<sub>4</sub>. Comparison of IR spectra of the SCMNPs, showed that the SCMNP-N contained the characteristic bands at 2854 and 2977 cm<sup>-1</sup>, typical of the C-H stretch of methylene of the alkyl chain, and confirmed that organosilane compound had been successfully grafted to the SCMNPs surface (Vojoudi et al., 2017b).

The crystallinity of the modified and unmodified nanoparticles were studied by X-rav diffraction analysis with their results, presented in Figure 3. The respective diffraction peaks at  $2\theta = 30.3^{\circ}$ ,  $35.7^{\circ}$ ,  $43.2^{\circ}$ ,  $53.3^{\circ}$ ,  $57.1^{\circ}$ , and  $62.5^{\circ}$ corresponded to (220), (311), (400), (422), (511), and (440) planes, respectively, agreeing well with the magnetite database (JCPDS No. 19-0629) and indicating that the magnetite  $(Fe_3O_4)$  phase had a cubic spinel as a highly crystalline structure. Further, the pattern included a broad reflection at  $20 - 30^\circ$ , due to the coating of the amorphous  $SiO_2$  (Vojoudi et al., 2018).

Extraction of the target species with SCMNPs-N adsorbents was evaluated at different pH values within the range of 2.0 to 8.0. The changes in the solution pH were caused by one mol/L solutions of nitric acid or sodium hydroxide, with the results demonstrated in Figure 4.

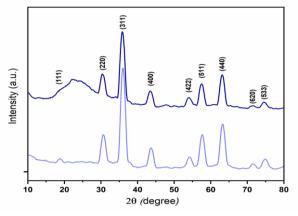


Fig. 3. X-ray diffraction patterns of MNPs and SCMNPs-N

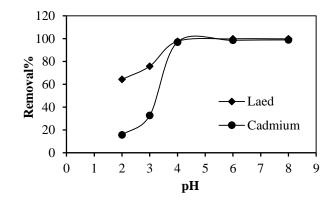


Fig. 4. Effect of pH on the removal efficiency of Pb<sup>2+</sup> and Cd<sup>2+</sup> ions by SCMNPs-N (initial ion concentration: 3 mg/L Pb<sup>2+</sup> and Cd<sup>2+</sup>, volume of solution: 25 mL, adsorbent amount: 20 mg)

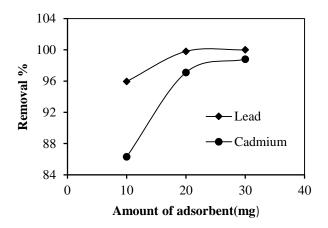


Fig. 5. Effect of adsorbent amount on the removal percentage of Pb<sup>2+</sup> and Cd<sup>2+</sup> ions (initial ion concentration: 3 mg/L Pb<sup>2+</sup> and Cd<sup>2+</sup>, volume of solution: 25 mL, pH≅ 5)

As can be seen.  $Pb^{2+}$  and  $Cd^{2+}$  can be extracted quantitatively by the SCMNPs-N in the pH range of 4-8. This could be explained by the fact that depending on pH, surface groups of adsorbent (N and OH) may change their charges. At low pH condition, most of the binding sites on SCMNPs-N are protonated and the surface of adsorbent is surrounded by hydronium ions, thus inhibiting the binding of Pb<sup>2+</sup> and  $Cd^{2+}$  ions. As the pH of ions solution rise, the surface groups will be deprotonated, resulting in an increase of negativelycharged sites which favour the sorption of Pb<sup>2+</sup> and Cd<sup>2+</sup> cations due to electrostatic attraction. Therefore, the optimum pH for the removal of  $Pb^{2+}$  and  $Cd^{2+}$  ions is between 4-8.

To determine the best amount of

adsorbent required for maximum removal of  $Pb^{2+}$  and  $Cd^{2+}$  ions, some experiments were conducted in 25 mL of  $Pb^{2+}$ , and  $Cd^{2+}$  solution, using different amounts of the SCMNPs-N from 10-30 mg.

As can be seen from Figure 5, the ions' removal efficiency was initially increased by raising the amount of the adsorbent, due to availability of higher adsorption sites. Then, the percentage removal reached almost a constant value. In the light of the results, the rest of the experiments were performed, using 20 mg of SCMNPs-N.

The effect of time on the extraction efficiency was studied, using a series of solutions that contained 75  $\mu$ g of Pb<sup>2+</sup> and Cd<sup>2+</sup> ions, with the results presented in Figure 6. The overall adsorption process took place in three phases, namely, the

initial fast uptake, the slow uptake, and the equilibrium. The initial stage occurred due to the existence of considerable gradients between concentration the surface of the adsorbent and the bulk solution as a result of the large number of available vacant sites. Consequently, the adsorption rate was high at this stage. As time passed. both the gradient and the number of adsorption sites reduced due to the accumulation of target species on the adsorbent. gradually decreasing the adsorption rate until the final equilibrium state was reached. Based on the results, the best results were achieved after stirring the reaction mixture for 20 min or more, hence chosen as the optimal extraction time.

In order to investigate  $Pb^{2+}$  and  $Cd^{2+}$  ions removal from water samples with diverse metal ions, as much as 25 mL aliquots of aqueous solutions, containing 75  $\mu$ g of Pb<sup>2+</sup>,  $Cd^{2+}$ , and different amounts of other cations, were subjected to the extraction experiments under optimal conditions, with the obtained results given in Table 1. Obviously, the target species were completely removed by the SCMNPs-N under these conditions, at up to rather high amounts of the third component without significant any interference effect observed.

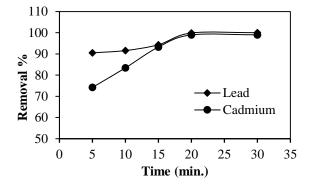


Fig. 6. Effect of contact time on removal of Pb<sup>2+</sup> and Cd<sup>2+</sup> ions (initial ion concentration: 3 mg/L Pb<sup>2+</sup> and Cd<sup>2+</sup>, volume of solution: 25 mL, adsorbent amount: 20 mg, pH≅ 5)

Table 1. Removal of Pb<sup>2+</sup> and Cd<sup>2+</sup> ions from triple mixtures<sup>a</sup> (initial concentration: 3 mg/L Pb<sup>2+</sup> and Cd<sup>2+</sup>, volume of solution: 25 mL, adsorbent amount: 20 mg, pH≅ 5, contact time: 20 min)

Divers ions	Amount taken(µg)	%Removal of Pb <sup>2+</sup>	%Removal of Cd <sup>2+</sup>
Na <sup>2+</sup>	2500	$100.0(1.0)^{b}$	
$Na^{2+}$	250		98.4 (0.7)
$Mg^{2+} \\ Mg^{2+} \\ Cr^{3+} \\ Cr^{3+} \\ Co^{2+} \\ Co^{2+} \\ Ag^{+} \\ Ag^{+} \\ Ag^{+} \\ Ni^{2+} \\ Ni^{2+} \\$	2500	99.5(0.9)	
$Mg^{2+}$	250		95.0 (1.1)
$Cr^{3+}$	2500	100.0 (0.8)	
$Cr^{3+}$	150		96.0 (0.6)
$\mathrm{Co}^{2+}$	2500	99.9 (0.9)	
$\mathrm{Co}^{2+}$	250		95.8 (0.7)
$Ag^+$	2500	99.3 (1.0)	
$Ag^+$	250		98.7 (1.0)
Ni <sup>2+</sup>	2500	100.0 (1.2)	
$Ni^{2+}$	250		97.1 (0.9)
$Zn^{2+}$	2500	97.2 (1.3)	
$Zn^{2+}$	150		99.5 (1.0)
$Cu^{2+}$	2500	100.0 (0.7)	
$Cu^{2+}$	150		98.7 (1.0)
$Mn^{2+}$	2500	99.9 (0.9)	
$Mn^{2+}$	250		95.0 (0.7)

<sup>a</sup> Initial samples contained 75µg lead and cadmium ions in 25 ml water.

<sup>b</sup>Values in parentheses are RSDs based on three replicate analysis.

In order to optimize the use of SCMNPs-N, it is important to establish the most appropriate adsorption isotherm. Freundlich, Langmuir and Temkin isotherm models were evaluated in these studies. The Freundlich model was derived under the assumption that one is dealing with a heterogeneous surface with a nonuniform distribution of adsorption heat, while the Langmuir model was build based on the assumption that the sorption process takes place at specific homogeneous sites within the make-up of the adsorbent.

The linearized form of the Langmuir is (Langmuir, 1918):

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m}$$

where  $q_m$  is the maximum adsorption capacity corresponding to complete monolayer coverage and b is the equilibrium constant (L/mg).

The Freundlich model can take the following linearized form (Freundlich, 1906):

$$\log q_e = \log K_f + \frac{1}{n_f} \log C_e$$

where  $K_f$  is roughly an indicator of the adsorption capacity and  $1/n_f$  is the adsorption intensity. The slope  $1/n_f$ , ranging between 0 and 1, is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero.

The Temkin isotherm is usually used for heterogeneous surface energy systems (non-uniform distribution of sorption heat) (Temkin & Pyzhev, 1940). This model can take the following linearized form:

$$q_e = BLn k_t + BLnC_e$$

where B = RT/b is a constant related to sorption heat (J/mol) and obtained from the Temkin plot (qe versus lnCe); b, Temkin isotherm constant; R, universal gas constant (8.314 J/mol. K); T, the temperature (K); and K<sub>t</sub>, Temkin isotherm equilibrium binding constant (L/g).

Table 2 shows the obtained isotherm values. The parameters, related to each isotherm for the adsorption of the metal ions on the SCMNPs-N, were determined by means of linear regression analysis, and the square of the correlation coefficients  $(\mathbf{R}^2)$  was calculated. The results of equilibrium data for both target species fitted into the Langmuir isotherm model with correlation coefficients  $(R^2)$  in the range of 0.9996 and 0.9976 for Pb<sup>+2</sup> and Cd<sup>+2</sup>, respectively, as compared to the Freundlich and Temkin model. Pb<sup>2+</sup> and  $\mathrm{Cd}^{2+}$ ions formed a homogeneous monolayer on the surface of adsorbent. On the basis of the Langmuir analysis, maximum adsorption capacities were determined to be 1000 and 454.5 µg of  $Pb^{+2}$  and  $Cd^{+2}$  ions per each mg of adsorbent, respectively.

Isotherm	Parameters	$Pb^{2+}$ $Cd^{2+}$
Langmuir	$q_m(mg/g)$	1000 454.5
		0.14 0.06
	b(L/mg) R <sup>2</sup>	0.9996 0.9976
Freundlich	n	4.06 3.37
	$K_{f}(mg/g)$	243.05 80.04
	$\frac{K_{f}(mg/g)}{R^{2}}$	0.7960 0.9080
Temkin	В	119.74 59.63
	$K_{T}(L/g)$	9.69 3.93
	$\frac{K_{T}(L/g)}{R^{2}}$	0.9508 0.8855

Table 2. Values of isotherm parameters for sorption of Pb<sup>2+</sup> and Cd<sup>2+</sup> ions

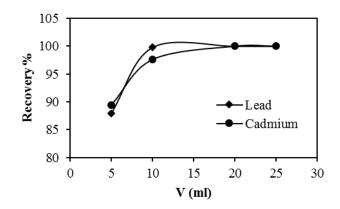


Fig. 7. Effect of volume of stripping acid on the recovery percentage of Pb<sup>2+</sup> and Cd<sup>2+</sup> ions (initial concentration: 3 mg/L Pb<sup>2+</sup> and Cd<sup>2+</sup>, volume of solution: 25 mL, adsorbent amount: 20 mg, pH≅ 5, contact time: 20 min)

The reusability of adsorbent is of great importance as a cost effective process in water treatment. Various experiments have been performed to specify proper volumes of nitric acid for recovering adsorbed  $Pb^{2+}$ and  $Cd^{2+}$  ions from SCMNPs-N, by means of different volumes of the acid. Based on the observations, illustrated in Figure 7, ten mL of the 3.0 mol/L nitric acid solution can lead to quantitative elution of  $Pb^{2+}$  and  $Cd^{2+}$  ions from the 20 mg of SCMNPs-N.

Further tests were performed to assess the regeneration capacity of SCMNPs-N. The adsorbent was used through repeated tests of the adsorption/desorption process with the results showing that the recovery efficiency of the sorbent after four cycles was reduced by only 0.4% and 3.4% for Pb<sup>2+</sup> and Cd<sup>2+</sup>, respectively.

Effect of modification of silica-coated  $Fe_3O_4$  magnetic nanoparticles (SCMNPs) on the Pb<sup>2+</sup> and Cd<sup>2+</sup> ions removal efficiency was investigated. In this order, 20 mg of both SCMNPs and SCMNPs-N were added to 25 mL of 3 mg/L of each ion solutions. The mixed solution was gently shaken at room

temperature for 20 minute. Remarkably, the removal efficiency of both ions was low in unmodified adsorbent (63% for  $Pb^{2+}$  and 59% for  $Cd^{2+}$ ) though it increased in modified adsorbent (100% for  $Pb^{2+}$  and 99% for  $Cd^{2+}$ ). The results indicated that modification of adsorbent with amino functional group would remarkably increase the removal of  $Pb^{2+}$  and  $Cd^{2+}$  ions.

Application of  $Pb^{2+}$  and  $Cd^{2+}$  ion removal from real sample was examined by various wastewater types, including wastewater of pharmaceutical and Battery factory. The initial and residual concentrations of  $Pb^{2+}$  and  $Cd^{2+}$  in the samples were analyzed through the standard addition method, because of the matrix effect. Results (Table 3) revealed that the proposed method could be applied successfully for removal of  $Pb^{2+}$  and  $Cd^{2+}$ ions in wastewater samples with very good efficiency. The proposed adsorbent can remove  $Pb^{2+}$  and  $Cd^{2+}$  ions in low concentrations of ions and complex matrix, whereas most of the adsorbents could not be efficacious in these conditions.

 Table 3. Removal of Pb<sup>2+</sup> and Cd<sup>2+</sup> ions from wastewater samples (contact time: 20 min, volume of sample solution: 25 mL, adsorbent amount: 20 mg)

Samples	Concentration of Pb <sup>2+</sup> (mg/L)	%Removal of Pb <sup>2+</sup>	Concentration of Cd <sup>2+</sup> (mg/L)	%Removal of Cd <sup>2+</sup>
Battery wastewater	5.32	94.7	4.43	88.3
pharmaceutical wastewater	3.79	96.5	2.74	91.6

Adsorbent	Maximum capacity (mg/g)	Removed ions	Ref.
Fe <sub>3</sub> O <sub>4</sub> nanoparticles	9.5 13.8	${ m Pb}^{+2} \ { m Cd}^{+2}$	(Hosseinzadeh et al., 2016)
sulfonated Fe <sub>3</sub> O <sub>4</sub> magnetic nanoparticle	13.8 108.9 80.9	$\begin{array}{c} Cd \\ Pb^{+2} \\ Cd^{+2} \end{array}$	(Chen et al., 2017)
2-(5-bromo-2-pyridylazo)-5-diethylaminophenol Modified Fe <sub>3</sub> O <sub>4</sub>	24.1	$\mathrm{Cd}^{+2}$	(Kakaei & Kazemeini, 2016)
amino-functionalized Fe <sub>3</sub> O <sub>4</sub> nanoparticles	40.1	$Pb^{+2}$	(Tan et al., 2012)
diethylenetriamine functionalized mesoporous SBA-	15 183.0	$Pb^{+2}$	(Hajiaghababaei et al., 2012)
ZnO-Chitosan core-shell nanocomposite	476.1 135.1	$Pb^{+2}$ $Cd^{+2}$	(Saad et al., 2018)
amino functionalized silica coated Fe <sub>3</sub> O <sub>4</sub> magnenergy nanoparticles	etic 1000 454.5	$Pb^{+2}$ $Cd^{+2}$	(This work)

Table 4. Comparison of the proposed method with previous reports

Table 4 compares the maximum capacity of SCMNPs-N and some other previouslyreported adsorbents for  $Pb^{2+}$  and  $Cd^{2+}$  ions removal. Results clearly reveal that the proposed adsorbent was superior to the ones in all former reports in terms of adsorption capacity (Tan et al., 2012; Hajiaghababaei et al., 2012; Hosseinzadeh et al., 2016; Kakaei & Kazemeini, 2016; Chen et al., 2017; Saad et al., 2018). What is noteworthy is that the proposed adsorbent, being the result of Fe<sub>3</sub>O<sub>4</sub> coupling nanoparticles' to amino functionalized mesoporous silica, had very higher adsorption capacity in comparison with the amino-functionalized Fe<sub>3</sub>O<sub>4</sub> nanoparticles (Tan et al., 2012) and diethylenetriamine functionalized mesoporous **SBA-15** (Hajiaghababaei et al., 2012).

### CONCLUSION

The main goal of the present research was to develop a simple, fast, and efficient adsorbent for removal of Pb<sup>2+</sup> and Cd<sup>2+</sup> ions from water and wastewater samples; therefore, it successfully applied amino functionalized silica-coated Fe<sub>3</sub>O<sub>4</sub> magnetic nanoparticles, a novel adsorbent for removal of  $Pb^{2+}$  and  $Cd^{2+}$  ions. Modification of silica-coated Fe<sub>3</sub>O<sub>4</sub> magnetic nanoparticles with amino groups was an efficient tool to improve the efficiency of removal procedure. Pb<sup>2+</sup> and Cd<sup>2+</sup> ions were completely removed at pH  $\geq$ 4 after being stirred for 20 min in 25 mL of 3 mg/L solution of these two ions and by using 20 mg of SCMNPs-N. Isotherm studies indicated that the Langmuir model fitted the experimental data better than Freundlich and Temkin models. The maximum adsorption capacity was 1000.0 and 454.5  $\mu$ g Pb<sup>2+</sup> and Cd<sup>2+</sup> ions per mg SCMNPs-N, respectively. The advantage of the adsorbent turned out to be its very short adsorption time, simple separation process, high adsorption capacity, and reduced channeling results.

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