

Preparation of Silica-Coated Magnetite Nanoparticles with Thiophosphoramidate for Removal of Heavy Metals from Aqueous Solutions

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ABSTRACT: In this study, new silica-coated magnetic nanoparticles modified with *p*-(4-methoxy phenyl)-*N*-(3-triethoxy silyl) phosphoramidate dithioic acid were synthesized using a normal method. The structure of the newly obtained nanoparticles was characterized by Fourier Transform InfraRed (FT-IR) spectroscopy, X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Vibrating Sample Magnetometry (VSM), and ThermoGravimetric Analysis (TGA). The surface of the nanoparticles modified with *p*-(4-methoxy phenyl)-*N*-(3-triethoxy silyl) phosphoramidate dithioic acid showed to be an effective adsorbent for the selective extraction of the ion of Ag (I) from aqueous mixed metal ions solution also containing Co(II), Cu(II), Ni(II) and Pb(II). Moreover, the silver ion desorption was most efficient in thiosulfate ($S_2O_3^{2-}$).

KEYWORDS: Silica-coated Magnetic Nanoparticles; Phosphoramidate Dithioic Acid; SEM; Ag(I) ion.

INTRODUCTION

In recent years, nanomaterials have attracted considerable interest in the research community due to their large specific surface areas and high reactivities [1]. Magnetic nanoparticles are a class of nanoparticles that is commonly composed of magnetic elements such as iron, cobalt, nickel, and their respective oxides [2, 3]. Magnetic nanoparticles are abundant in nature and are found in many biological objects [4]. Magnetic nanomaterials are used in information recording and storage systems, in new permanent magnets, in magnetic cooling systems, as magnetic sensors, catalysts in organic reactions, etc. [5, 13]. Currently, powders with micron-size γ -Fe₂O₃, Co - γ -Fe₂O₃,

Fe or Fe - Co grains are used most often in magnetic tapes or discs as media for magnetic recording [14]. Recently, researchers have used magnetic iron oxides at the nanometric scale to remove toxic heavy metal ions and organic pollutants from water [15]. It is believed that these magnetic nanoparticles exhibit amphoteric surface activity, easy dispersion ability, and, thanks to their very small dimensions, a high surface-to-volume ratio, resulting in a high metal adsorption capacity [16- 20]. Traditional adsorbents show poor recovery of the target metal ions from large volumes of solution due to low binding capacity, diffusion limitations, and the lack of active

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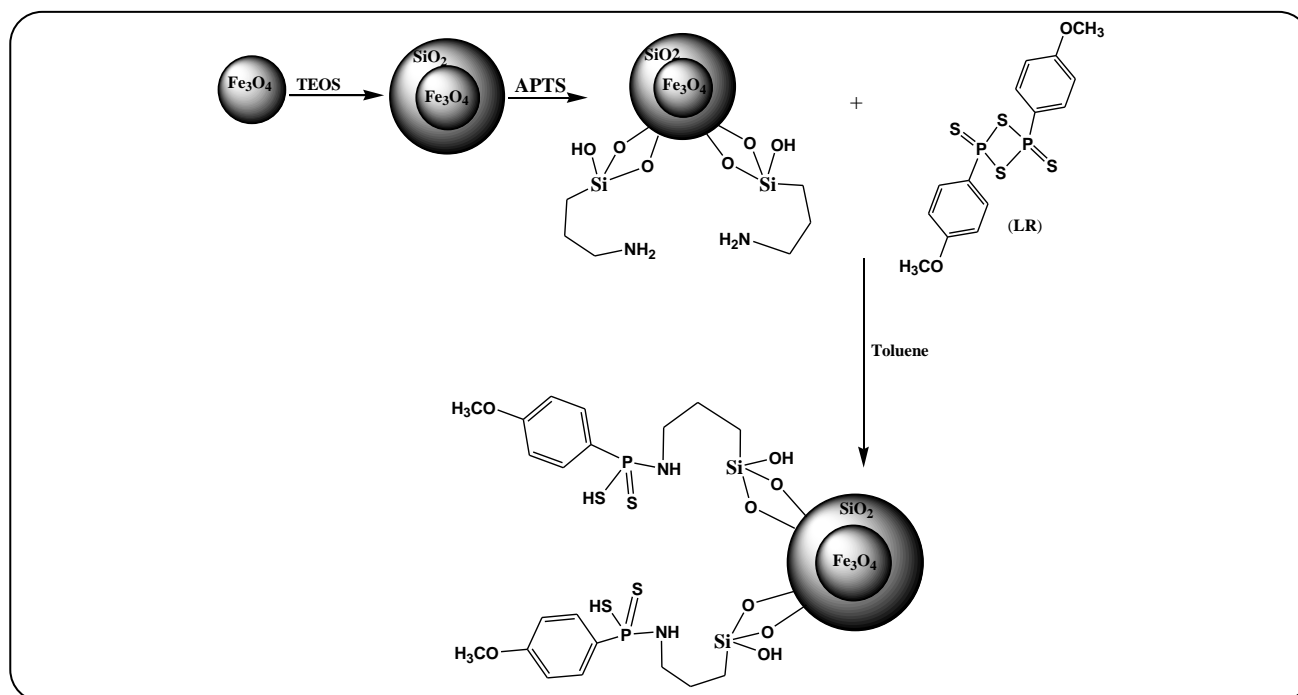


Fig. 1: Synthesis of Fe₃O₄@SiO₂-NH₂-LR magnetic nanoparticles.

surface sites. The search for new adsorbents has been important in recent years. Nanometer-sized materials have attracted substantial interest in the scientific community because of their special properties. The use of magnetic nanoparticles for separation and preconcentration in analytical chemistry provides a new methodology that is faster, simpler, and more precise than those used traditionally. The greatest advantage of this method is that desired materials are separated from the solution by a simple and compact process while fewer secondary wastes are produced. Other advantages are represented by a large active surface area for a given mass of particles and the ability to process a solution that contains suspended solids [21]. In this study, we report the synthesis of silica-coated magnetic nanoparticles modified with *p*-(4-methoxy phenyl)-*N*-(3-triethoxy silyl) phosphonamide dithioic acid (Fig. 1). The resulting nanoparticles were employed for the selective adsorption of Ag (I) ion from an aqueous solution in the presence of equal amounts of Co(II), Zn(II), Ni (II), Cu (II) and Pb(II).

EXPERIMENTAL SECTION

Chemicals and reagents

Ferric chloride hexahydrate (FeCl₃.6H₂O) with 98% purity, ferrous chloride tetrahydrate (FeCl₃.4H₂O) with

98% purity, absolute ethanol, glycerol with 99% purity, and ammonia (NH₃) with 25% purity were purchased from Merck, Germany. Tetraethyl orthosilicate (TEOS) with 99.8% purity, 3-aminopropyltrimethoxysilane with 97% purity. Lawesson reagent was prepared as described in the literature [22].

Instrumentation

FT-IR spectra (Shimadzu prestige-21) were used to determine the identity of the as-prepared nanoparticles and to characterize the coated Fe₃O₄ nanoparticles. X-ray powder diffraction measurements were performed using an X-Ray Diffractometer (XRD) (Perkin Elmer) at ambient temperature. The surface morphology of the silica-supported ligands was identified with a scanning electron microscope (LECO SEM, Michigan, USA). Magnetic measurements were performed by means of the vibrating sample magnetometry method, using a VSM 7407 magnetometer, at room temperature. ThermoGravimetric Analysis (TGA) was performed using a Perkin Elmer thermogravimetric analyzer. UV-visible spectra in the 200–1000 nm range were obtained in DMF solvent on a Perkin Elmer Lambda 45 spectrophotometer. The concentration of metal ions in the solution was measured using a flame atomic absorption spectrophotometer

(FAAS, GBC 932 AA, Victoria, Australia). A Jenway model 4510 pH meter was used for pH measurements by use of a combined electrode. An ultrasonication probe (Karl Deutsch, Germany) was used to disperse the nanoparticles in the solution.

Synthesis of magnetite nanoparticles (Fe_3O_4)

The magnetic nanoparticles were prepared according to [23] with minor modifications. Briefly, $FeCl_3 \cdot 6H_2O$ (11.68 g) and $FeCl_2 \cdot 4H_2O$ (4.30 g) were dissolved in 200 mL deionized water under nitrogen gas with vigorous stirring at 85 °C. Then, 20 mL of 30% aqueous ammonia was added to the solution. The color of the bulk solution changed from orange to black immediately. The magnetic precipitates were washed twice with deionized water and once with 0.02 mol/L sodium chloride. The washed magnetite was stored in deionized water at a concentration of 40 g/L.

Synthesis of silica-coated magnetic nanoparticles $Fe_3O_4@SiO_2$

The silica-coated magnetic nanoparticles were prepared according to [23] with minor modifications. The magnetite suspension prepared above (20 mL) was placed in a 250 mL round-bottom flask and allowed to settle. The supernatant was removed, and an aqueous solution of tetraethylorthosilicate (TEOS, 10% (v/v), 80 mL) was added, followed by glycerol (60 mL). The pH of the suspension was adjusted to 4.6 using glacial acetic acid, and the mixture was then stirred and heated at 90 °C for 2 h under a nitrogen atmosphere. After cooling to room temperature, the suspension was washed sequentially with deionized water (3×500 mL), methanol (3×500 mL), and deionized water (5×500 mL). The silica magnetite composite was stored in deionized water at a concentration of 40 g/L.

Synthesis of amine-modified silica magnetite $Fe_3O_4@SiO_2-NH_2$

These nanoparticles were synthesized according to previously reported methods with minor modifications [23]. The silica-coated magnetite nanoparticles were first dispersed by sonication in ethanol (100 mL); a solution of 3-aminopropyltrimethoxysilane (APTS, 10% in ethanol) was then added to the above-mentioned mixture. After heating at 60 °C for 6 h and stirring for 12 h at room temperature under a dry nitrogen atmosphere, the resulting solid was magnetically separated, washed with ethanol

several times to remove the unreacted residue of silylating reagent and then vacuum dried at 80 °C.

Synthesis of silica-coated magnetic nanoparticles modified with lawesson reagent using normal method $Fe_3O_4@SiO_2-NH_2-LR$

To a suspension of the silica-coated magnetite nanoparticles (1 g) in dry toluene (30 ml), Lawesson's reagent (LR) was added (1.4 g, 3.5 mmol). After heating at 100 °C for 2 h and stirring for 24 h at room temperature under a dry nitrogen atmosphere, the modified magnetite nanoparticles were prepared, the resulting solid was magnetically separated, washed with hot toluene several times to remove the unreacted ligands and dried under vacuum.

Solid phase extraction (Batch method)

All adsorption experiments were carried out at room temperature in a gas bath shaker. To determine the sorption capacity, 20 mL of aqueous solution containing a 10^{-4} mol/L mixture of metal nitrate salts $Zn(NO_3)_2$, $Co(NO_3)_2$, $Cu(NO_3)_2$, $Pb(NO_3)_2$, $Ni(NO_3)_2$ and $Ag(NO_3)$ were added to 0.05 g sorbent. The mixtures were shaken at 300 rpm and the extraction process was allowed to proceed for 1 h. Subsequently, an NdFeB strong magnet was placed at the bottom of the beaker and $Fe_3O_4@SiO_2-NH_2-LR$ were isolated from the solution. To determine the adsorption capacity, the magnetic adsorbents were separated from the solution and washed with 10 mL of deionized water. Then, 5 mL eluent solution containing 0/05M (SCN^-), 0/05M ($CS(NH_2)_2$), and 0/05M ($S_2O_3^{2-}$) (prepared in methanol) was added to the solution and agitated for 15 min by an Ultrasonic-50 Hz to separate the metal ions from the sorbent. In addition, the nanoparticles were isolated from the solution with an NdFeB strong magnet placed at the bottom of the beaker, and the upper aqueous phase was removed to measure the remaining metal ion concentration.

RESULTS AND DISCUSSION

Preparation of the modified magnetite nanoparticles

In this study, $Fe_3O_4@SiO_2-NH_2-LR$ nanoparticles were synthesized and were successfully used as a sorbent for the highly selective removal of Ag (I) ion from an aqueous mixed metal ion solution containing Co(II), Cu(II), Ni(II) of active and Pb(II). In addition, the FT-IR peak of the organic

the compound was clearer in the spectrum of these nanoparticles. Therefore, it can be concluded that more organic compounds are attached to the surface of these nanoparticles. The synthetic procedures of the modified magnetite nanoparticles are shown in Fig. 1. Reaction of the silica-coated magnetic nanoparticles $\text{Fe}_3\text{O}_4@ \text{SiO}_2$ with 3-aminopropyltrimethoxysilane afforded amine-modified silica magnetite $\text{Fe}_3\text{O}_4@ \text{SiO}_2\text{-NH}_2$. The next step involves the reaction of the $\text{Fe}_3\text{O}_4@ \text{SiO}_2\text{-NH}_2$ amine groups with Lawesson reagent (LR) to yield the modified magnetite nanoparticles, $\text{Fe}_3\text{O}_4@ \text{SiO}_2\text{-NH}_2\text{-LR}$. The structures of the newly obtained nanoparticles were characterized by FT-IR, XRD, SEM, VSM, TGA, and UV-Vis.

Characterization of the modified magnetite nanoparticles

The FT-IR spectra of all the nanoparticles are shown in Fig. 2. Two broad bands at around 456 and 584 cm^{-1} confirmed the magnetite core nanomaterial, which corresponds to the Fe_2O_3 and Fe-O stretching, respectively (Fig. 2a). The appearance of transmittance bands at 1062 and 1122 cm^{-1} in the IR spectrum of the silica coating of magnetite nanoparticles $\text{Fe}_3\text{O}_4 @ \text{SiO}_2$ (Fig. 2b) belongs to the Si-O-Si and Si-OH stretching vibrations, respectively. In addition, the presence of the peaks at 2929 cm^{-1} ($\nu_{\text{as}} \text{CH}_2$), 1535 cm^{-1} (bending vibration CH_2), and 1390 cm^{-1} ($\nu_{\text{as}} \text{Si-CH}_2$) in Fig. 2c reveal the progress of condensation reaction between the silica-coated magnetite nanoparticles and 3-aminopropyltrimethoxysilane and the formation of magnetite nanoparticles with a core-shell structure. From the FT-IR spectra presented in Fig. 2d, the absorption peak at 667 cm^{-1} belongs to the stretching vibration mode of P-S. Also, the presence of vibration bands in 1598 cm^{-1} (C=C bending), 1280 cm^{-1} (C-O stretching), and 952 cm^{-1} (P-N stretching) is a confirmation of yielding the final product. The peak at 3478 cm^{-1} belongs to the stretching vibration of O-H adsorbed on the surface of the Fe_3O_4 nanoparticles.

The SEM images show more or less significant alterations in the size of the Fe_3O_4 nanoparticles after silica-coated and LR modification. The SEM images of the Fe_3O_4 and $\text{Fe}_3\text{O}_4@ \text{SiO}_2\text{-NH}_2\text{-LR}$ nanomaterials are shown in Fig. 3. As it is indicated in Fig. 3 the diameters of Fe_3O_4 and $\text{Fe}_3\text{O}_4@ \text{SiO}_2\text{-NH}_2\text{-LR}$ are about 26-32 and 47-54 nm respectively. No considerable increase in the particle size was observed after the final reaction.

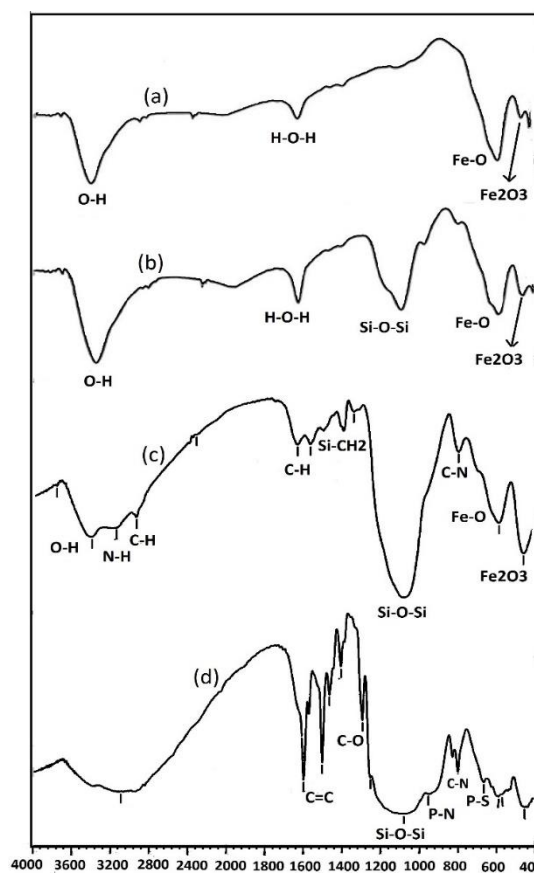


Fig. 2: FT-IR spectra (KBr) of (a) Fe_3O_4 , (b) $\text{Fe}_3\text{O}_4@ \text{SiO}_2$, (c) $\text{Fe}_3\text{O}_4@ \text{SiO}_2\text{-NH}_2$, (d) $\text{Fe}_3\text{O}_4@ \text{SiO}_2\text{-NH}_2\text{-LR}$.

The crystallinity of the as-prepared magnetic nanoparticles was determined by X-Ray Diffraction (XRD) using a diffractometer with $\text{Cu K}\alpha$ radiation (40 kV/30mA). The XRD pattern of the $\text{Fe}_3\text{O}_4@ \text{SiO}_2\text{-NH}_2\text{-LR}$ nanoparticles is shown in Fig. 4. Six characteristic peaks for Fe_3O_4 were observed in all the samples. These peaks correspond to the (220), (311), (400), (422), (511), and (440) planes, indicating the formation of cubic magnetite nanoparticles in the $Fd\bar{3}m$ space group [24]. The average size of $\text{Fe}_3\text{O}_4@ \text{SiO}_2\text{-NH}_2\text{-LR}$ is also estimated *via* Debye-Scherrer equation $D = 0.9\lambda / \beta \cos\theta$ (D is the average size, λ is the X-ray source wavelength (1.54 Å), β is the full width at half maximum (FWHM) of the diffraction peak and θ is the Bragg's angle) to be approximately 58 nm.

The magnetic moment of the prepared magnetite nanoparticles was measured over a range of applied fields between 8500 and -8500 Oe. The magnetization curves

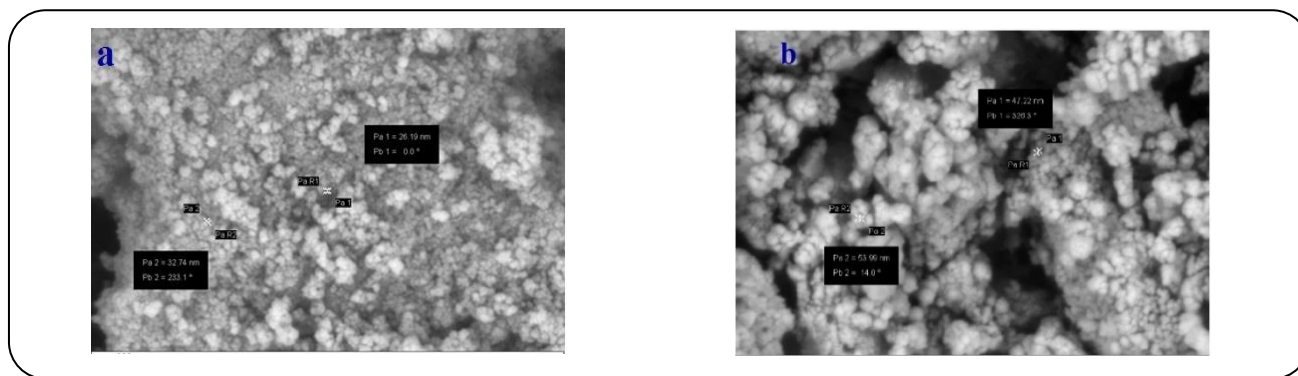


Fig. 3: SEM images of the a) Fe₃O₄ b) Fe₃O₄@SiO₂-NH₂-LR nanoparticles.

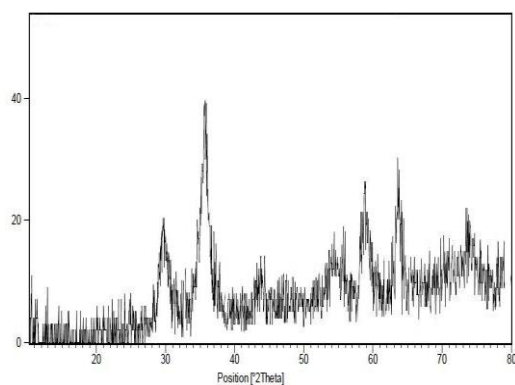


Fig. 4: XRD patterns of the Fe₃O₄@SiO₂-NH₂-LR nanoparticles.

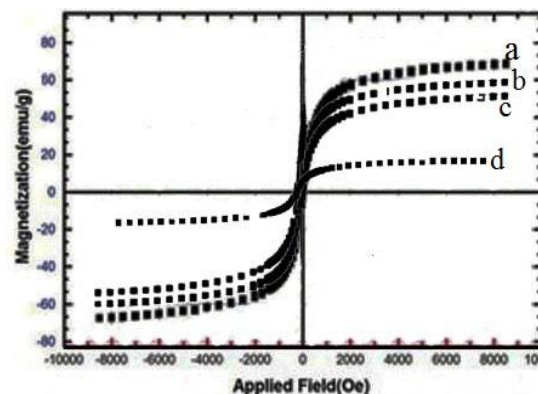


Fig. 5: Hysteresis loops of (a) Fe₃O₄, (b) Fe₃O₄@SiO₂, (c) Fe₃O₄@SiO₂-NH₂, (d) Fe₃O₄@SiO₂-NH₂-LR nanoparticles at room temperature using VSM.

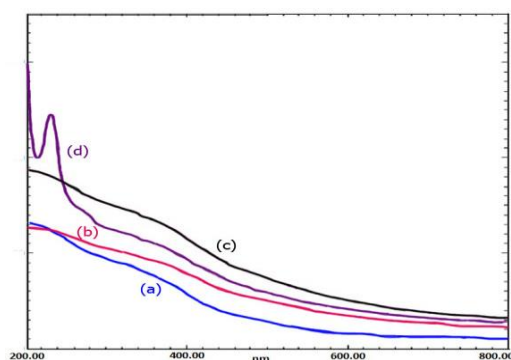
of the Fe₃O₄, Fe₃O₄@SiO₂, Fe₃O₄@SiO₂-NH₂, and Fe₃O₄@SiO₂-NH₂-LR at room temperature are shown in Fig. 5. The VSM results indicate coating the surface of the magnetite nanoparticles with silica and LR leads to a decrease in the saturation magnetization. This is due to the presence of LR on the surface of Fe₃O₄ nanoparticles which may generate a magnetically dead layer so any crystalline disorder within the surface layer causes to a significant decrease in the saturation magnetization of nanoparticles [25]. The saturation magnetization values for the Fe₃O₄ particles, Fe₃O₄@SiO₂, Fe₃O₄@SiO₂-NH₂, and Fe₃O₄@SiO₂-NH₂-LR nanomaterials were 68, 60, 55, and 15 emu g⁻¹, respectively.

The light absorption properties of all the synthesized nanomaterials were measured using a UV-Vis spectrophotometer with a wavelength range of 200–800 nm. As shown in Fig. 6. The UV-vis absorption spectrum showed an absorption peak in the range of 220–245 nm due to the π - π^* transitions of the (C=C) aromatic ring group [26, 27].

ThermoGravimetric Analysis (TGA) was conducted on modified magnetite nanoparticles at temperatures from 40–700°C. Fig. 7 shows that there are three stages of weight loss in the TGA curve. In the first stage, degradation occurs at a temperature of 30–100°C, the second stage of 100–250°C, the third stage of 250–700°C. In Fig. 7 is observed that a sample of coated magnetite lost weight at a temperature of 30–100 °C (<100 °C). The weight loss is related to the removal of water molecules adsorbed physically, which removal of water molecules is continued at the temperature of 100–220°C [28, 29]. Fig. 7 shows that the weight loss in the second stage at that temperature range (100–250°C), for Fe₃O₄@SiO₂-NH₂-LR is 3.58%. At the temperature range of 250–500°C, TGA curve of Fe₃O₄@SiO₂-NH₂-LR the weight loss is 23.41%. The weight loss is linked to the decay of the organic part of a silica network. At that temperature, the decomposition of organic parts, including LR bound to the silica network produces CO and CH₄.

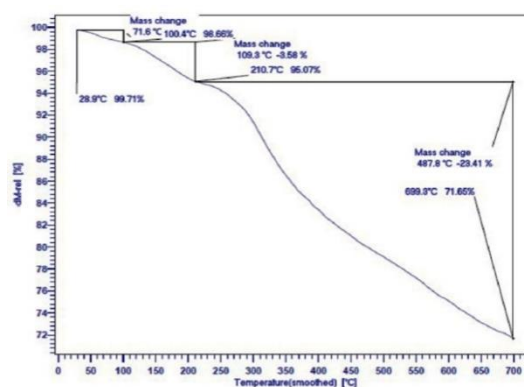
Table 1: Five cycles of adsorption-desorption of different metal ions onto the $Fe_3O_4@SiO_2-NH_2-LR$.

Adsorbent	Metal ions	1	2	3	4	5
$Fe_3O_4@SiO_2-NH_2-LR$	Cu(II)	97	96	96	94	91
	Zn(II)	94	94	92	91	89
	Co(II)	96	94	92	92	90
	Ag(I)	97	96	95	93	91
	Pb(II)	96	95	93	91	90
	Ni(II)	95	93	93	92	90

**Fig. 6: The UV-vis spectra of (a) Fe_3O_4 , (b) $Fe_3O_4@SiO_2$, (c) $Fe_3O_4@SiO_2-NH_2$, (d) $Fe_3O_4@SiO_2-NH_2-LR$.**

Extraction condition optimization

The influence of the sorbent amount for the quantitative extraction of Cu(II), Co(II), Ag(I), Ni(II), Zn(II) and Pb(II) from an aqueous sample was tested in the range of 20–100 mg at pH 9. The effects of the adsorbent amount on the extraction of metal ions are shown in Fig. 8. According to these results, the synthesized nanomaterial shows excellent silver(I) ion adsorption selectivity at pH= 9 in a metal ion solution containing Cu(II), Co(II), Ni(II), Zn(II) and Pb(II). Silver(I) binds strongly with sulfur. These species are important in the inorganic and biological reactions involving Ag(I) [30]. Furthermore, the experimental results indicated that 0.02-0.1 g of the nanosorbent is enough for the preconcentration of Ag(I) using the batch. Therefore, 0.02 and 0.1 g of sorbent were used in the subsequent experiments. Various acids were used to identify the best eluent for the adsorbed metal ions in solid phase extraction with $Fe_3O_4@SiO_2-NH_2-LR$ produced. The effects of these acids are shown in Fig. 9. An acid solution has been widely used for the elution of

**Fig. 7: TGA curves of magnetite $Fe_3O_4 @ SiO_2 -NH_2-LR$ nanoparticles.**

metal ions from a sorbent due to protonation at the chelating sites of the sorbent. Diluted thiocyanate (SCN^-), thiourea ($CS(NH_2)_2$) and thiosulfate ($S_2O_3^{2-}$) [31] as prepared in methanol solutions were used for the maximum elution of Cu(II), Zn(II), Co(II), Ag(I), Pb(II) and Ni(II) ions from the nanoparticle-supported complex. The experimental results indicated that among the different eluents used, 0.5 M $S_2O_3^{2-}$ provided higher recovery and reproducibility.

Reusability of the adsorbent

For the reusing possibility study, the adsorbed metal ions on the adsorbent were transferred to a flask containing 100 mL of desorbing agent such as HCl (0.5 M). The mixture was stirred at room temperature for 3 h and the desorbed metal ions concentration in the solution was determined by spectrophotometer. The desorption process was done consecutively in five cycles. The ability of reusing the adsorbent was tested in several steps of adsorption and desorption. The result is shown in Table 1.

Table 2: Comparison for the adsorption of Ag(I) ion by batch method.

Adsorbents	Ions	Adsorption capacity (mg/g)	References
MCM-41 modified with 3,4-dihydroxybenzaldehyde	Ag(I)	160	[32]
Cellulose filter paper grafted with polymer chains bearing thiocarbamate moieties	Ag(I)	27	[33]
polyethylene glycol diacrylate-3-sulfopropyl methacrylate potassium salt (PEGDA-SMP)	Ag(I)	227	[34]
polyethylene-graft-polystyrene sulfonic acid (PE-g-PSSA)	Ag(I)	49.9	[35]
$\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NH}_2\text{-LR}$	Ag(I)	225	This work

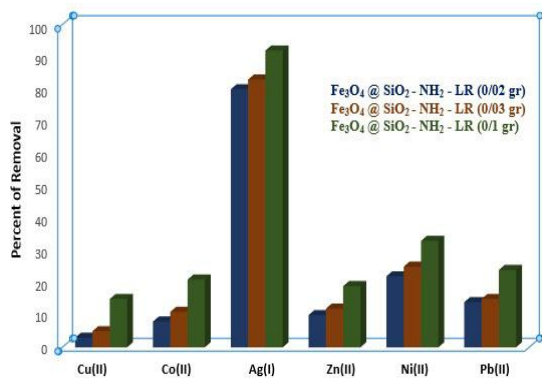


Fig. 8: Removal percentage of metal ions at different amounts of adsorbent.

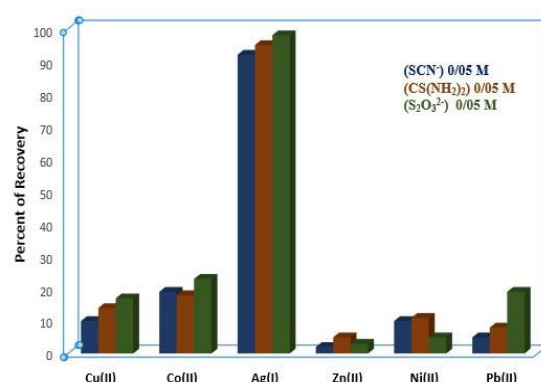


Fig. 9 Recovery percentage of metal ions in various eluents.

Comparison with other adsorbents

The results obtained by comparing this adsorbent with other established adsorbents for Ag(I) are shown in Table 2. Table 2. demonstrates, that the $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NH}_2\text{-LR}$ had an acceptable adsorption capacity for Ag(I) ion in comparison with other adsorbents. Different factors such as types of functional groups on the surface, amount of the Ag(I) ion, surface area of the adsorbent, initial concentration of the Ag(I) ion, amount of the adsorbent used and the kind of adsorption mechanism.

CONCLUSIONS

In this work, the silica-coated magnetic nanoparticles modified with p-(4-methoxy phenyl)-N-(3-triethoxy silyl) phosphonamide dithioic acid were synthesized. The synthesized nanoparticles were characterized by FT-IR, XRD, SEM, VSM, TGA and UV-vis. SEM suggested the $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NH}_2\text{-LR}$ nanoparticles were spherical in shape, of particle size 45–55 nm. The VSM results indicate coating the surface of the magnetite nanoparticles with silica and LR leads to a decrease in the saturation magnetization. XRD results showed that the prepared

magnetite nanoparticles have good crystal structures with $Fd\bar{3}m$ space group. These nanoparticles were applied as a sorbent for the highly selective removal of Ag(I) ion from an aqueous mixed metal ion solution containing Cu(II), Co(II), Ni(II), Zn(II), and Pb(II). According to these results, we can say the novel modified magnetite nanoparticles may be used as an alternative sorbent for the removal of Ag(I) from water samples.

Acknowledgments

We are grateful to University of Ardabil Payamenoor and Islamic Azad Gerni University for supporting this research.

Received : Jan. 19, 2022 ; Accepted : May 30, 2022

REFERENCES

- [1] Baig N., Kammakam I., Falath W., *Nanomaterials: A Review of Synthesis Methods, Properties, Recent Progress, and Challenges, Mater. Adv.*, **2**: 1821-1871 (2021).

- [2] Aser A., Garg S. K., Nayak A., Sanket K., Ahsan J., **Magnetic Nanoparticles: Magnetic Nano-technology Using Biomedical Applications and Future Prospects**, *Int. J. Pharm. Sci. Rev. Res.*, **31(2)**: 119-131 (2015).
- [3] Indira T. K., Lakshmi P. K., **Magnetic Nanoparticles**, *Int. J. Pharm. Sci. Nanotechnol.*, **3(3)**: 1035–1042 (2010).
- [4] Wallyn J., Anton N., Vandamme T. F., **Synthesis, Principles, and Properties of Magnetite Nanoparticles for in Vivo Imaging Applications—A Review**, *Pharmaceutics*, **11(11)**: 601 (2019).
- [5] Gubin S.P., Koksharov Y., Khomutov G., Yurkov G.Y., **Magnetic Nanoparticles: Preparation, Structure and Properties**, *Russian Chemical Reviews*, **74(6)**: 539-574 (2005).
- [6] Mirhosseini-Eshkevari B., Ghasemzadeh M. A., Safaei-Ghomi J., **An efficient and Green One-Pot Synthesis of Indazolo [1,2-b]-phthalazinetriones via Three-Component Reaction of Aldehydes, Dimedone, and Phthalhydrazide Using Fe₃O₄@SiO₂ Core–Shell Nanoparticles**, *Research on Chemical Intermediates*, **41(10)**: 7703-77141 (2015).
- [7] Esmaeilpour M., Javidi J., Nowroozi Dodeji F., Zahmatkesh S., **Solvent-Free, Sonochemical, One-Pot, Four-Component Synthesis of 2H-indazolo[2,1-b]phthalazine-triones and 1H-pyrazolo[1,2-b]phthalazine-diones Catalyzed by Fe₃O₄@SiO₂-imid-PMAn Magnetic Nanoparticles**, *Research on Chemical Intermediates*, **47(6)**: 2629-2652 (2021).
- [8] Akkoç M., Buğday N., Altın S., Kiraz N., Yaşar S., Özdemir I., **N-heterocyclic Carbene Pd(II) Complex Supported on Fe₃O₄@SiO₂: Highly Active, Reusable and Magnetically Separable Catalyst for Suzuki-Miyaura Cross-Coupling Reactions in Aqueous Media**, *Journal of Organometallic Chemistry*, **94321**:121823 (2021).
- [9] Farhadi S., Ghasemzadeh M. A., Aghaei S. S., **NiCo₂O₄@Ni(BDC) Nano-Porous Metal–Organic Framework as a Novel Catalyst for the Synthesis of Spiro[indene[1,2-d] Pyrimidine-Ones and Investigation of their Antimicrobial Activities**, *Chemistry Select*, **4(2)**: 729-73617 (2019).
- [10] Uruş S., Eskalen H., Çaylar M., Akbulut M., **Highly Effective Aldose Reductase Mimetics: Microwave-Assisted Catalytic Transfer Hydrogenation of D-Glucose to D-Sorbitol with Magnetically Recoverable Aminomethylphosphine-Ru(II) and Ni(II) Complexes**, *Journal of Molecular Structure*, **12375**: 130313 (2021).
- [11] Ghasemzadeh M. A., Azimi-Nasrabad M., **Nano-Fe₃O₄ -Encapsulated Silica Particles Bearing Sulfonic Acid Groups as a Magnetically Separable Catalyst for the Green and Efficient Synthesis of 14-aryl14H-dibenzo[a,i]xanthene-8,13-dione Derivatives**, *Res. Chem. Intermed.*, **42(2)**: 1057-10691 (2016).
- [12] Nesarvand M., Azarifar D., Ebrahimias H., **One-pot and Green Synthesis 1H pyrazolo [1,2 b] Phthalazine 5,10 Dione and dihydropyrano[3,2 c] Chromene Derivatives by Fe₃O₄@SiO₂ Imine/ Phenoxy Cu(II) as an Efficient and Reusable Catalyst**, *Research on Chemical Intermediates*, **47(9)**: 3629-3644 (2021).
- [13] Chipurici P., Vlaicu A., Călinescu I., Vinătoru M., Busuioc C., Dinescu A., Ghebur A., Rusen E., Voicu G., Ignat M., Diacon A., **Magnetic Silica Particles Functionalized with Guanidine Derivatives for Microwave Assisted Transesterification of Waste Oil**, *Scientific Reports*, **11(1)**: 17518 (2021).
- [14] Shokrollahi H., **A Review of the Magnetic Properties, Synthesis Methods and Applications of Maghemite**, *Journal of Magnetism and Magnetic Materials*, **426**: 74-81 (2017).
- [15] Liang X., Xi B., Xiong S., Zhu Y., Xue F., Qian Y., **Porous Soft Magnetic Material: The Maghemite Microsphere with Hierarchical Nanoarchitecture and its Application in Water Purification**, *Mater. Res. Bull.*, **44**: 2233-2239 (2009).
- [16] Shen Y. F., Tang J., Nie Z. H., Wang Y. D., Ren Y., Zuo L., **Preparation and Application of Magnetic Fe₃O₄ Nanoparticles for Wastewater Purification**, *Sep. Purif. Technol.*, **68**: 312–319 (2009).
- [17] Nassar N., **Kinetics, Equilibrium and Thermodynamic Studies on the Adsorptive Removal of Nickel, Cadmium and Cobalt From Wastewater by Superparamagnetic Iron Oxide Nanoadsorbents**, *Can. J. Chem. Eng.*, **9999**: 1–8 (2011).
- [18] Tratnyek P. G., Johnson R. L., **Nanotechnologies for Environmental Cleanup**, *Nano Today*, **1**: 44–48 (2006).
- [19] Sun S. H., Zeng H., **Size-Controlled Synthesis of Magnetite Nanoparticles**, *J. Am. Chem. Soc.*, **124**: 8204–8205 (2002).
- [20] Wan S. R., Huang J. S., Yan H. S., Liu K. L., **Size Controlled Preparation of Magnetite Nanoparticles in the Presence of Graft Copolymer**, *J. Mater. Chem.*, **16**: 298–303 (2006).

- [21] Khajeh M., Khajeh A., [Synthesis of Magnetic Nanoparticles for Biological and Water Applications](#), *Int. J. Green Nanotechnol. Phys. Chem.*, **1**(1): 51–56 (2009).
- [22] Clausen K., El Barbary A., Lawesson S., [Studies on Organophosphorus Compounds—XXXV¹: A New Route to 4-methoxyphenylphosphonothioic Diamides from 2,4-bis\(4-methoxyphenyl\)-1,3,2,4-Dithiadiphosphetane-2,4-disulfide and Amines](#), *Tetrahedron*, **37**: 1019-1025 (1981).
- [23] Huang C., Hu B., [Silica-coated Magnetic Nanoparticles Modified with \$\gamma\$ -Mercaptopropyltrimethoxysilane for Fast and Selective Solid Phase Extraction of Trace Amounts of Cd, Cu, Hg, And Pb In Environmental and Biological Samples Prior to their Determination by Inductively Coupled Plasma Mass Spectrometry](#), *Spectrochim. Acta Part B*, **63**: 437–444 (2008).
- [24] Hanawalt J. D., Rinn H. W., Frevel L. K., [Chemical Analysis by X-Ray Diffraction](#), *Ind. Eng. Chem. Anal. Ed.*, **10**: 457–512 (1938).
- [25] Gui-yin L., Jiang Yu-ren J., Huang K., Ding P, Chen J., [Preparation and properties of Magnetic Fe₃O₄-Chitosan Nanoparticles](#), *Journal of Alloys and Compounds*, **466**(1-2):451-6 (2008).
- [26] Shokry A., A. Khalil M. M., Ibrahim H., Soliman M., Ebrahim S., [Highly Luminescent Ternary Nanocomposite of Polyaniline, Silver Nanoparticles and Graphene Oxide Quantum Dots](#), *Scientific Reports*, **9**:16984 (2019).
- [27] Ali Maleki, Rahmatollah Rahimi, Saied Maleki, [Preparation and Characterization of Magnetic Chlorochromate Hybrid Nanomaterials with Triphenylphosphine Surface-Modified Iron Oxide Nanoparticles](#), *Journal of Nanostructure in Chemistry*, **4**:153–160 (2014).
- [28] Shajesh P., Smitha S., Aravind P. R., Warriar K. G. K., [Effect of 3-glycidoxypropyltrimethoxysilane Precursor on the Properties of Ambient Pressure Dried Silica Aerogels](#), *J. Sol-Gel Sci. Technol.*, **50**(3): 353–358 (2009).
- [29] Sun Z. H., Xu D., Wang X. Q., Zhang G. H., Yu G., Zhu L. Y., Fan H. L., [Growth and Characterization Of the Nonlinear Optical Crystal: L-arginine Trifluoroacetate](#), *Cryst. Res. Technol*, **42**: 812–816 (2007).
- [30] Adams N. W. H., Kramer J.R., [Reactivity of Silver\(I\) Ion with Thiol Ligands in the Presence of Iron Sulfide](#), *Environmental Toxicology and Chemistry*, **17**:625–629 (1998).
- [31] Awadalla F. T., Ritcey G. M., [Recovery of Gold from Thiourea, Thiocyanate, or Thiosulfate Solutions by Reduction-Precipitation with a Stabilized Form of Sodium Borohydride](#), *separation science and technology*, **26**(9): 1207-1228 (1991).
- [32] Behbahani M., Najafi F., Amini M. M., Sadeghi O., Bagheri A., Hassanlou P. G., [Solid Phase Extraction Using Nanoporous MCM-41 Modified with 3,4-dihydroxybenzaldehyde for Simultaneous Preconcentration and Removal of Gold\(III\), Palladium\(II\), Copper\(II\) and Silver\(I\)](#), *J. Ind. Eng. Chem.*, **20**(4): 2248–2255 (2014).
- [33] Awual M. R., [Solid Phase Sensitive Palladium\(II\) Ions Detection and Recovery Using Ligand Based Efficient Conjugate Nanomaterials](#), *Chem. Eng. J.*, **300**: 264–272 (2016).
- [34] Dharmapriya T. N., Li D. Y., Chung Y., Huang P., [Green Synthesis of Reusable Adsorbents for the Removal of Heavy Metal Ions](#), *ACS Omega*, **6**: 30478–30487 (2021).
- [35] Nasef M. M., Saidi H., Ujang Z., Dahlan K. Z. M., [Removal of Metal Ions from Aqueous Solutions Using Crosslinked Polyethylene-graft-polystyrene Sulfonic Acid Adsorbent Prepared by Radiation Grafting](#), *J. Chil. Chem. Soc.*, **55**: 4 (2010).