# Preparation of Silica-Coated Magnetite Nanoparticles with Thiophosphoramide 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) phosphonamide dithioic acide 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) phosphonamide dithioic acide 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 ($S_2O_3^{2-}$).*

## 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 $\gamma$-Fe$_2$O$_3$, Co - $\gamma$-Fe$_2$O$_3$,

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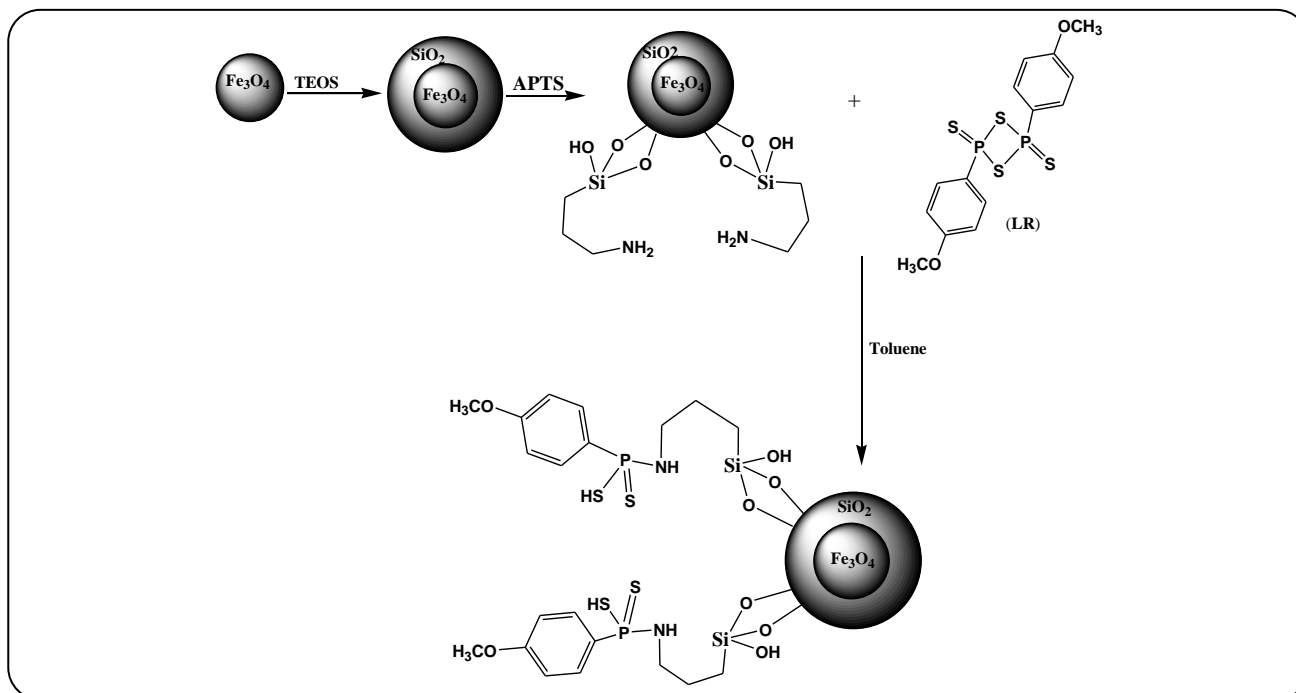
*Fig. 1: Synthesis of Fe3O4@SiO2-NH2–LR magnetic nanoparticles.*

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 (FeCl$_3$.6H$_2$O) with 98% purity, ferrous chloride tetrahydrate (FeCl$_3$.4H$_2$O) with 98% purity, absolute ethanol, glycerol with 99% purity, and ammonia (NH$_3$) 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 Fe$_3$O$_4$ 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 (Fe₃O₄)

The magnetic nanoparticles were prepared according to [23] with minor modifications. Briefly, $FeCl_3.6H_2O$ (11.68 g) and $FeCl_2.4H_2O$ (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 Fe₃O₄@SiO₂

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 Fe₃O₄@SiO₂-NH₂

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 Fe₃O₄@SiO₂–NH₂–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 $Fe_3O_4@SiO_2$ with 3-aminopropyltrimethoxysilane afforded amine-modified silica magnetite $Fe_3O_4@SiO_2$-$NH_2$. The next step involves the reaction of the $Fe_3O_4@SiO_2$-$NH_2$ amine groups with Lawesson reagent (LR) to yield the modified magnetite nanoparticles, $Fe_3O_4@SiO_2$-$NH_2$-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 $Fe_3O_4@SiO_2$ (Fig. 2b) belongs to the Si–O–Si and Si–OH stretching vibrations, respectively. In addition, the presence of the peaks at 2929 $cm^{-1}$ ($v_s$ $CH_2$), 1535 $cm^{-1}$ (bending vibration $CH_2$), and 1390 $cm^{-1}$ ($v_{as}$ 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 $Fe_3O_4@SiO_2$-$NH_2$-LR nanomaterials are shown in Fig. 3. As it is indicated in Fig. 3 the diameters of $Fe_3O_4$ and Fe3O4@$SiO_2$-$NH_2$-LR are about 26-32 and 47–54 nm respectively. No considerable increase in the particle size was observed after the final reaction.
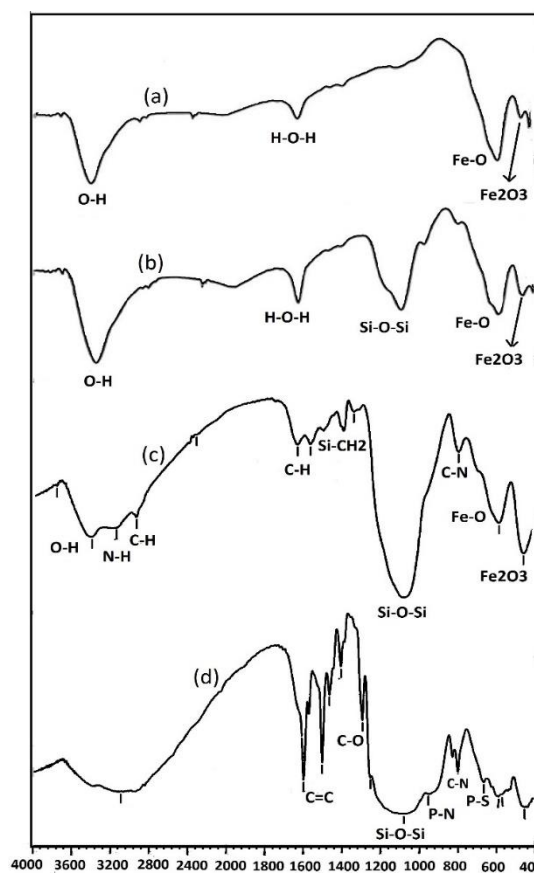


*Fig. 2: FT-IR spectra (KBr) of (a) Fe₃O₄, (b) Fe₃O₄@SiO₂, (c) Fe₃O₄@SiO₂-NH₂, (d) Fe₃O₄@SiO₂-NH₂-LR.*

The crystallinity of the as-prepared magnetic nanoparticles was determined by X-Ray Diffraction (XRD) using a diffractometer with Cu Ka radiation (40 kV/30mA). The XRD pattern of the $Fe_3O_4@SiO_2$-$NH_2$–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 $Fe_3O_4@SiO_2$-$NH_2$-LR is also estimated *via* Debye–Scherer equation D= $0.9\lambda/\beta\cos\theta$ (D is the average size, $\lambda$ is the X-ray source wavelength (1.54 Å), $\beta$ is the full width at half maximum (FWHM) of the diffraction peak and $\theta$ 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
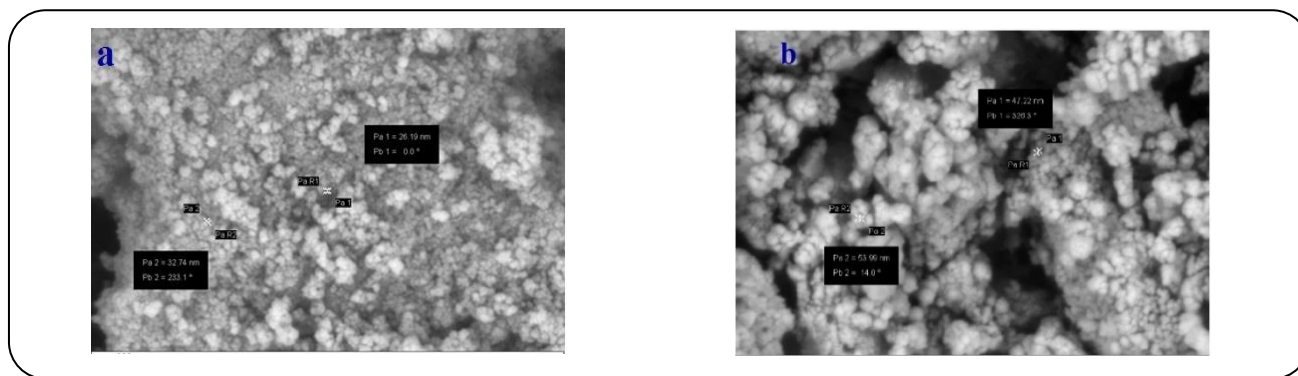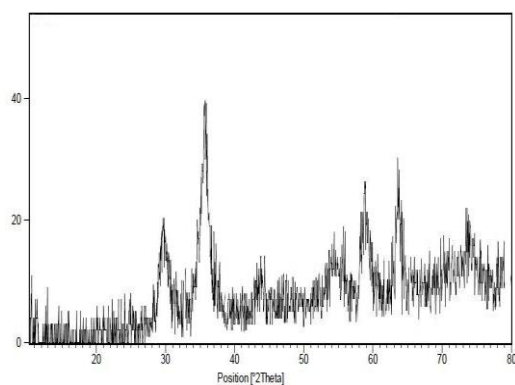
Fig. 3: SEM images of the a) $Fe_3O_4$ b) $Fe_3O_4$ @ $SiO_2$-$NH_2$–LR nanoparticles.



Fig. 4: XRD patterns of the $Fe_3O_4$ @$SiO_2$-$NH_2$–LR nanoparticles.
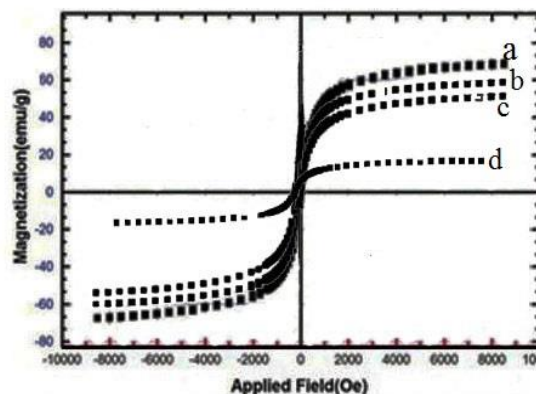


Fig. 5: Hysteresis loops of (a) $Fe_3O_4$, (b) $Fe_3O_4$ @ $SiO_2$, (c) $Fe_3O_4$@$SiO_2$ -$NH_2$, (d) $Fe_3O_4$@$SiO_2$ -$NH_2$-LR nanoparticles at room temperature using VSM.

of the $Fe_3O_4$, $Fe_3O_4$@$SiO_2$, $Fe_3O_4$@$SiO_2$-$NH_2$, and $Fe_3O_4$@$SiO_2$-$NH_2$-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 $Fe_3O_4$ 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 $Fe_3O_4$ particles, $Fe_3O_4$@$SiO_2$, $Fe_3O_4$@$SiO_2$-$NH_2$, and $Fe_3O_4$@$SiO_2$-$NH_2$-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 $Fe_3O_4$@$SiO_2$-$NH_2$–LR is 3.58%. At the temperature range of 250-500°C, TGA curve of $Fe_3O_4$@$SiO_2$-$NH_2$–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 $CH_4$.

*Table 1: Five cycles of adsorption-desorption of different metal ions onto the Fe₃O₄@SiO₂-NH₂–LR.*

| Adsorbent | Metal ions | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|---|
| Fe₃O₄@SiO₂-NH₂–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 |
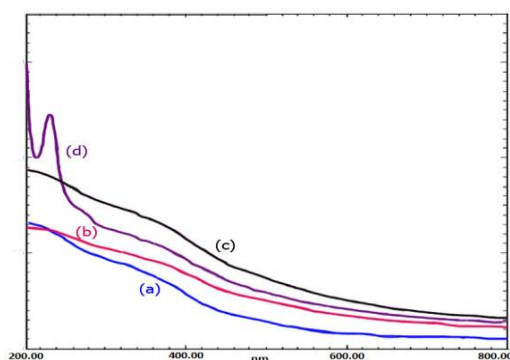


Fig. 6: The UV-vis spectra of (a) Fe₃O₄, (b) Fe₃O₄@SiO₂, (c) Fe₃O₄@SiO₂-NH₂, (d) Fe₃O₄@SiO₂-NH₂-LR.
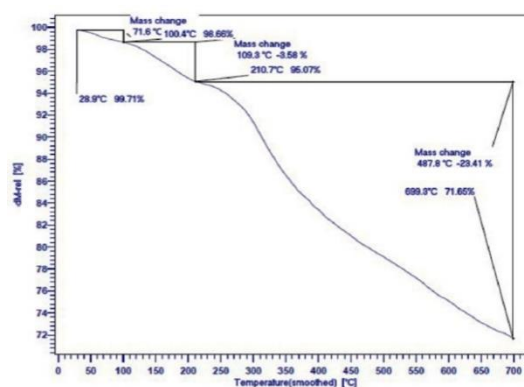


Fig. 7: TGA curves of magnetite Fe₃O₄ @ SiO₂ -NH₂–LR nanoparticles.

### 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 Fe₃O₄@SiO₂-NH₂–LR produced. The effects of these acids are shown in Fig. 9. An acid solution has been widely used for the elution of

metal ions from a sorbent due to protonation at the chelating sites of the sorbent. Diluted thiocyanate (SCN⁻), thiourea (CS(NH₂)₂) and thiosulfate (S₂O₃²⁻) [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 S₂O₃²⁻ 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] |
| $Fe_3O_4@SiO_2$-$NH_2$–LR | Ag(I) | 225 | This work |
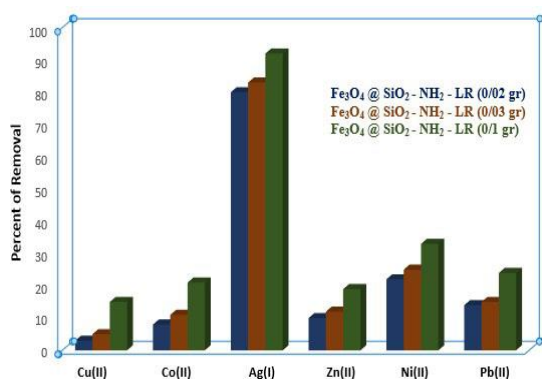


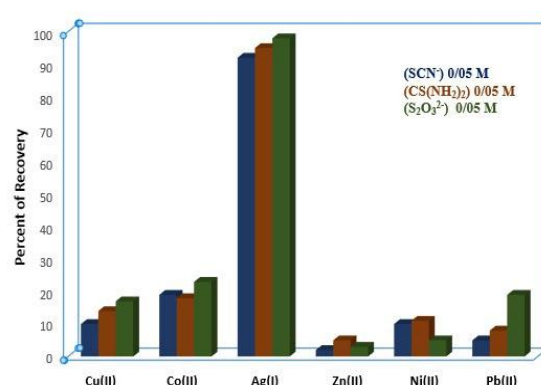*Fig. 8: Removal percentage of metal ions at different amounts of adsorbent.*



*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 $Fe_3O_4@SiO_2$-$NH_2$–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 acide were synthesized. The synthesized nanoparticles were characterized by FT-IR, XRD, SEM, VSM, TGA and UV-vis. SEM suggested the $Fe_3O_4@SiO_2$-$NH_2$–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 $Fd\overline{3}m$ 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

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