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Synthesis and Characterization of new modified silica coated magnetite nanoparticles with bisaldeheyde as selective adsorption of Ag (I) from aqueous samples

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Abstract

In this paper, new silica-coated magnetic nanoparticles modified with bisaldeheyde (BISA-APTSCMNPs) was synthesized using a normal method and a vice versa method. The crystal structure of newly obtained nanoparticles was characterized by Fourier Transform Infrared (FT-IR), X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), Vibrating Sample Magnetometry (VSM), Thermogravimetric Analyzes (TGA) and Ultra-Violet Visible (UV-Vis). The surface modification of nanoparticles with bisaldeheyde (BISA-APTSCMNPs) were used to excellent selective removal Ag (I) ion from aqueous mixed metal ion solution containing Cu (II), Co (II), Ni (II), Zn (II) and Pb (II) by syringe and batch techniques. Also, the silver ion desorption efficiency was in HCl.

Keywords: Modified silica coated magnetite nanoparticles, Bisaldehyde, Selective silver adsorption

1. Introduction

Nanotechnology is one of the most important branches of modern science in the preparation and usage of nanoparticles [1]. In recent years, nanomaterials have attracted much interest in the research community due to their large specific surface area and high reactivities [2]. Magnetic nanoparticles are a class of nanoparticle which is commonly composed of magnetic elements such as iron, cobalt, nickel and their respective oxides [3, 4]. Among the various nanostructure materials, iron oxides with many important and diverse applications play a major role in many areas of chemistry, physics and materials science. In particular, various derivatives these nanoparticles such as magnetite (Fe_3O_4), maghemite (γ-Fe_2O_3), and hematite (α-Fe_2O_3) have been investigated intensively for environmental and bio-applications [5]. In addition to convenient magnetic properties and low toxicity and price, iron oxide nanoparticles show high surface to volume ratios, depending on the particle size, shape, and well dispersed in a solvent [6]. The size and shape of magnetite particles are generally controlled by the synthesis methods [7]. To date, numerous chemical methods have been developed to produce magnetite nanoparticles, such as the microemulsion, the chemical co-precipitation, the hydrolysis, the thermal decomposition and the sol–gel technique [8]. Recently, several researchers have used of Schiff base moiety for anchoring different catalytic species on the magnetic nanoparticles [9-13].

Magnetic solid phase extraction developed rapidly in recent years due to its unique advantages, such as easy operation, high extraction efficiency and reusability of sorbent [14]. At present, magnetic nanoparticles (MNPs) have been studied as the solid phase extraction (SPE) sorbents with high magnetic characteristic for the separation and removal of chemical species such as metals, dyes and gases [15]. In many cases, nanoparticles surface functionality with special functional ligands can improve the sorption capacity and efficiency of the extraction [16, 17]. Recently, the number of functionalized Fe_3O_4 nanoparticles has been employed as solid phase extraction (SPE) adsorbents for the removal of metal ions from aqueous solutions. For example, silica-coated magnetic nanoparticles modified with imidazole and quercetin was used for removal of iodine and uranyl ions from aqueous solutions, respectively [18, 19].

In this paper we report the synthesis silica-coated magnetic nanoparticles modified with bisaldeheyde (BISA-APTSCMNPs) by a normal method and a vice versa method. The resulted nanoparticles were employed for selective adsorption Ag (I) ion from aqueous solution in the presence of equal amounts of Cu (II), Co (II), Ag (I), Ni (II), Zn (II) and Pb (II) ions using syringe and batch techniques.

2. Experimantal

2.1. Chemicals and reagents

Ferric chloride hexahydrate ($FeCl_3$. $6H_2O$) with 98% purity, Ferrous chloride tetrahydrate ($FeCl_2$. $4H_2O$) 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 (APTS) with 97% purity and 2-hydroxybenzaldehyde with 99.9% purity were purchased from Sigma-Aldrich, USA. Toluene was bought from Shanghai Experiment Reagent Co., Ltd (Shanghai, China). 1, 3-dibromopropane with 98% purity was purchased from fluka chemicals, Switzerland.

2.2. Instrumentation

FT-IR spectra (Shimadzu prestige-21) were used to determine the identity of the as prepared nanoparticles and to characterize the coated Fe_3O_4 nanoparticles. X-ray powder diffraction measurements were performed using a 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). TEM images of the nanoparticles were obtained with an H-912 transmission electron microscope. Magnetic measurements were performed by means of the vibrating sample magnetometery method, using a VSM 7407 magnetometer, at room temperature. Thermogravimetric analysis (TGA) was performed suing 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 by 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 Ultrasonicaton probe (Karl Deutsch, Germany) was used to disperse the nanoparticles in solution.

2.3. Synthesis of 2, 2'-(propane-1, 3-diylbis (oxy)) bisbenzaldehyde (BISA)

A solution of 1.22 g (0.01 mol) salicyldehyde in hot ethanolic KOH (prepared by dissolving 0.56 g (0.01 mol) KOH in 100 ml of absolute ethanol) was stirred until a clear solution was obtained, which was then evaporated under vacuum. The residue was dissolved in DMF (25 ml) and 0.005 mol of 1, 3-dibromopropan was added. The reaction mixture was refluxed for 5 h, during which KBr was separated out. The solvent was then removed in vacuo and the remaining solid was washed with water and crystallized from ethanol to give high quality crystals (Mp. 393 K) suitable for X-ray analysis in good yield (84%) [20].

2.4. Synthesis of modified magnetite nanoparticles

2.4.1. Synthesis of magnetite nanoparticles (MNPs)

The magnetic nanoparticles (MNPs) were prepared according to Ref. [14] with some little modifications. Briefly, $FeCl_3\cdot6H_2O$ (11.68 g) and $FeCl_2\cdot4H_2O$ (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 bulk solution changed from orange to black immediately. The magnetic precipitates were washed twice with deionized water and once with 0.02 mol L^{-1} sodium chloride. The washed magnetite was stored in deionized water at a concentration of 40 g L^{-1}.

2.4.2. Synthesis of silica-coated magnetic nanoparticles (SCMNPs)

The silica-coated magnetic nanoparticles were synthesized according to previous reported methods with a minor modification [14]. 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^{-1}.

2.4.3. Synthesis of amine-modified silica magnetite (APTSCMNPs)

These nanoparticles were synthesized with some little modifications [14]. The silica coated magnetite nanoparticles was first dispersed with technique of sonication in ethanol (100 ml) and then a solution of 3-aminopropyltrimethoxysilane (APTS, 10% in ethanol) was added to above mixture. After heating at 333 K for 6 h and stir for 12 h at room temperature under dry nitrogen atmosphere, the resulted solid was magnetically separated, washed with ethanol several times to remove the unreacted residue of silylating reagent and then vacuum dried at 353 K.

2.4.4. Synthesis of silica-coated magnetic nanoparticles modified with bisaldeheyde (BISA-APTSCMNPs) using normal method

The amine-modified silica magnetite (APTSCMNPs) (3 g) was dispersed with technique of sonication into 50 mL of distilled water, and 2, 2'-(propane-1, 3-diylbis (oxy)) bisbenzaldehyde (BISA) (1 g, 3.5 mmol) dissolved in to 50 mL absolute ethanol, was added. The resulting mixture was left for stirring for 24 h at room temperature, and was refluxed for 12 h. Then, the formed magnetite nanoparticles was washed with dichloromethane, methanol and chloroform thoroughly and dried under vacuum at 60 °C.

2.4.5. Synthesis of BISA- AP with Schiff base reaction

BISA-AP ligand were synthesized by the reaction of 2, 2'-(propane-1, 3-diylbis (oxy)) bisbenzaldehyde (BISA) (1 g, 3.5 mmol) in 30 ml dry toluene and 3- aminopropyltrimethoxysilane (APTS) (1.26 mL, 7.0 mmol) in 50 ml dry toluene in the presence of 3-4 drops formic acid as a catalyst. The mixtures were stirred for 6 h under N_2-atmosphere at room temperature. The crystals were filtered in vacuum.

2.4.6. Synthesis of silica-coated magnetic nanoparticles modified with bisaldeheyde (BISA-APTSCMNPs) using vice versa method

1 g of the silica coated magnetite nanoparticles (SCMNPs) was first dispersed with technique of sonication in water (100 ml) and BISA-AP ligand (2.13 g, 3.5 mmol) dispersed in water (100 mL) was added to above mixture. After heating at 373 K for 2 h and stir for 24 h at room temperature under dry nitrogen atmosphere, prepared to modified magnetite nanoparticles as “on water reaction” and the resulted solid was magnetically separated, washed with hot ethanol several times to remove the unreacted ligands and then vacuum dried at 353 K.

2.5. Solid phase extraction techniques

2.5.1 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 10^{-4} mol/lit mixture of metal nitrate salts (Pb $(NO_3)_2$, Co $(NO_3)_2$, Zn $(NO_3)_2$, Cu $(NO_3)_2$, Ni $(NO_3)_2$ and Ag (NO_3)) were added to 0.05 gr sorbent (BISA-APTSCMNPs synthesized with a normal method and a vice versa method). The mixtures were shaked at 300 rpm and allowed to complete the extraction process for 1 h. subsequently, an Nd-Fe-B strong magnet (5 cm × 4 cm × 2 cm, 1.4 T) was placed at the bottom of the beakers and the BISA-APTSCMNPs were isolated from the solution. The upper aqueous phase was taken out to measure the remaining metal ion concentration by AAS.

To determine the adsorption capacity, the magnetic adsorbents were separated from the solution washed with 10 ml deionized water. Then, 5 ml eluent solution containing 0.5 M HNO_3, 0.5 M HCl and 0.5 M $S_2O_3^{2-}$ (as prepared in the methanol) was added to the solution and agitation for 15 min by Ultrasonic-50 Hz to separate metal ions from the sorbent. Again, the nanoparticles was isolated from the solution with an Nd-Fe-B strong magnet was placed at the bottom of the beaker and the upper aqueous phase was taken out to measure the remaining metal ion concentration by AAS. The studies of metal ions (Pb (II), Co (II), Zn (II), Cu (II), Ni (II) and Ag (I)) were performed by varying the amount of sorbents BISA-APTSCMNPs (0.01 g and 0.1 g) which produced by normal and vice versa methods. To check the reproducibility, all experimental were done at least in triplicates.

2.5.2. Syringe method

According to the obtained results in the batch method, we have designed a column which checked the rate of adsorption and sorption of Ag (I) ion solution as mobile phase by BISA-APTSCMNPs. For the construction of home-made solid phase extraction syringes, some glass wool was placed at the bottom of the syringe. Afterwards, 0.05 , 0.1 and 0.2 g of BISA-APTSCMNPs were weighed and placed into the syringe and then finally another glass wool was placed at the top of the syringe. The syring with plastic stopper was placed in the mouth of a vacuum flask so that fully coupled with the opening of the Meyer flask to prevent air infiltration. Then, 50 ml burette was placed on top of the column so that the opening is placed on top of the column. The pump was turned on and then the syringes were conditioned with 50 mL water before introducing the sample through the syringes. An aliquot of 50 mL of silver nitrate solution (10^{-4} mol/lit) was applied through the syringe with the flow rates at 1, 3 and 5 ml/min. After completion of the extraction process, the pump was turned off and the resulting solution was analyzed by AAS. The adsorption of the Ag (I) on the BISA-APTSCMNPs was performed by 5 ml HCl (0.5 M), with a flow rate of (1 ml/min). After completed each cycle the eluent directly injected into the nebulizer of the AAS.

3. Results and Discussion

3.1. Preparation of the modified magnetite nanoparticles

In this paper BISA-APTSCMNPs nanoparticles were synthesized by a normal method and a vice versa method and were successfully used as a sorbent for excellent selective removal Ag (I) ion from aqueous mixed metal ion solution containing Cu (II), Co (II), Ni (II), Zn (II) and Pb (II) by syringe and batch techniques. Compared with normal method, the highest sorption percentage of metal ions was obtained with synthesized nanoparticles using vice versa method. In addition, the FT-IR peak of the organic compound was clearer in these nanoparticles. Therefore, it can be concluded that more organic compound onto the surface of these nanoparticles attached. The synthetic procedures of the modified magnetite nanoparticles have been shown in Scheme 1. In normal method, the external surface of magnetite nanoparticles (MNPs) was coated with silica shell to obtain SCMNPs. Reaction of silica-coated magnetic nanoparticles (SCMNPs) with 3-aminopropyltrimethoxysilane (APTS) afforded amine-modified silica magnetite (APTSCMNPs). The next step involves reaction of APTSCMNPs amine groups with bisaldehyde (BISA) to yield the modified magnetite nanoparticles BISA-APTSCMNPs. In vice versa method, the BISA-AP ligands were synthesized from the reaction of bisaldehyde (BISA) and 3-aminopropyltrimethoxysilane (APTS). Then, the reaction of the resulted ligands with silica coated magnetite nanoparticles (SCMNPs) produced nanomaterials, BISA-APTSCMNPs. The crystal structure of newly obtained nanoparticles was characterized by FT-IR, XRD, SEM, TEM, VSM, TGA and UV-Vis.

Scheme 1.

3.2. Characterization of the modified magnetite nanoparticles

3.2.1. FT-IR analysis

Figure 1 shows the FT-IR spectra of all nanoparticles prepared in this work. The presence of magnetite core nanomaterials was confirmed by observation of two broad band's at around 459 cm^{-1} and 573cm^{-1} which correspond to the Fe-O stretching and Fe_2O_3 stretching, respectively (Fig. 1a). The IR spectrum of the silica coating of magnetite nanoparticles (SCMNPs) shows absorption peaks at 1103 and 949 cm^{-1} are due to the Si-O-Si and Si-OH stretching vibration respectively (Fig. 1b). In addition the presence of the anchored propyl groups were confirmed by stretching vibrations appeared at about 2933 cm^{-1} in the FT-IR spectrum of 2, 2'-(propane-1, 3-diylbis (oxy)) bisbenzaldehyde (BISA). The peak corresponding to the CH stretching vibration of ring 2933 cm^{-1} has appeared in the area [13]. In addition, the absorption bands of stretching vibrations of C-O (ether groups) and C = N (imini) bands are observed at 1293 cm^{-1} and 1640 cm^{-1}, respectively. The peak at 1599 cm^{-1} characteristic of bending vibrations of the C=C aromatic ring. The peak at 3427 cm^{-1} belongs to the stretching vibration O-H adsorbed on the surface of the Fe_3O_4 nanoparticles. The broad absorption bands at 3440 cm^{-1} and 1600 cm^{-1} was due to OH stretching vibration, which corresponds to OH groups on the surface of iron oxide and this band can be attributed to the adsorbed water molecules (Fig. 1d and 1e).

Figure 1.

3.2.2. XRD analysis

The crystallinity of as-made magnetic nanoparticles was determined by X-ray diffraction (XRD) using a diffractometer with Cu K_ radiation (40 kV/30 mA). Fig. 2 shows the XRD profiles of the BISA-APTSCMNPs nanoparticles prepared in this work. As shown in figure, the presence of diffraction peaks located at $2\theta = 30.2^\circ$, 35.4°, 37.1°, 43.1°, 53.3°, 57°, and 62.5° corresponded to (2 2 0), (3 1 1), (2 2 2), (4 0 0), (4 2 2), (5 1 1) and (4 4 0), respectively. These results indicated that magnetite (Fe_3O_4) have a face-centered cubic (fcc) structure. Also, we did not observation other iron oxides such as α-Fe_2O_3, β-Fe_2O_3 and γ-Fe_2O_3, which indicate that the Fe_3O_4 was not oxidized to other forms in the synthetic steps. This pattern indicates that organic species are well dispersed on the surface of SCMNPs and there is no any crystalline phase of organic in components the resulted nanomaterials.

Figure 2.

3.2.3. SEM analysis

A scanning electron microscope (SEM) is extremely useful for characterizing the morphological structure and size of the magnetite nanoparticles. The SEM image of the prepared BISA-APTSCMNPs nanomaterials is shown in Fig. 3. SEM images of synthesized nanoparticles clearly show the BISA-APTSCMNPs nanoparticles are spheroidal in shape. As shown in Figure 3a, the diameter of BISA-APTSCMNPs (prepared using normal method) is about 30-45 nm. While, the diameter of synthesized BISA-APTSCMNPs using vice versa method are about 35-50 nm, which is slightly larger than the value of average particle size obtained from normal method (Figure 3b). Also, the SEM images clearly indicate that the sizes of the particles with add of organic compound very slightly changed so that is not sensible.

Figure 3.

3.2.4. TEM analysis

In order to obtain more direct information on particle size and morphology, transmission electron microscopy (TEM) micrographs of the obtained nanoparticles were used. Fig. 4a and 4b illustrates the TEM images of the synthesized BISA-APTSCMNPs. TEM analysis of the nanoparticles indicated that the both BISA-APTSCMNPs (normal method) and BISA-APTSCMNPs (vice versa method) are spherical morphologies. According to TEM images, the mean particle size, is about 45 nm for BISA-APTSCMNPs (normal method) and 50 nm for BISA-APTSCMNPs (vice versa method), which indicate particle size in the vice versa method is slightly larger than the normal method.

Figure 4.

3.2.5. VSM analysis

To study the magnetic properties of magnetite nanoparticles before and after silica coating, we investigated the hysteresis loops of magnetite and functionalized magnetite nanoparticles at room temperature using vibrating sample magnetometry (VSM). Fig. 5 shows the room temperature magnetic hysteresis loops of the prepared magnetite nanoparticles. The VSM results indicate that all the prepared magnetite nanoparticles possess superparamagnetism properties at room temperature, which this is because their small size. On the other hand, surface coating of the magnetite nanoparticles with silica and bisaldehyde (BISA) compunds results in decreasing of the saturation magnetizations (Ms), which this decrease may be due to the superparamagnetic property and the screening effect of the silica layer, since the magnetic silica nanocomposites could be readily and stably dispersed in water and remained in suspension in the absence of an external magnetic field. The saturation magnetization values for the Fe_3O_4 particles, SCMNPs and BISA-APTSCMNPs nanomaterial are 67, 59 and 18 emu/g, respectively. Compared to the Fe_3O_4 microspheres, the slow decrease in the saturation magnetization for the BISA-APTSCMNPs nanoparticles can be attributed to the silica shell.

Figure 5.

3.2.6. TGA analysis

A thermogravimetric analyzer (TGA) was used to confirm the coating formation and to estimate the binding efficacy of bisaldehyde (BISA) on the surface of magnetite nanoparticles. The TGA measurements were carried out by weighting a powder sample of 5–10 mg and loaded into a platinum pan. The mass change under the temperature scan from 30 to 800 °C at a heating rate 20 ˚C/min and under a nitrogen flow was monitored and recorded.

Fig. 6 shows the result of TGA on nanoparticles at the range of 30−800 °C. The TGA curve of the prepared nanoparticles gave two mass loss processes before 600 °C. The mass loss rates are about 1.5% and 10.7%, respectively. The first weight loss rates are about 1.5% with the temperatures below 260 °C is due to the evaporation of water in magnetite BISA-APTSCMNPs nanoparticales, and the second weight loss is about 10.7% between 260 and 450 °C is attributed to the thermal decomposition of the organic species, i.e. aminopropyl groups and bisaldehyde in the nanomaterial. The TGA curve above 600 °C indicates that organic species magnetic composite nanoparticles have completely been decomposed and that the remnant is Fe_3O_4 nanoparticles.

Figure 6.

3.2.7. UV-vis analysis

Light absorption properties of all the synthesized nanomaterials were measured using a UV–vis spectrophotometer (Perkin Elmer Lambda 45) with a wavelength range of 200–700 nm. As shown in Fig. 7, the UV–vis absorption spectrum indicated the absorption peak of bisaldehyde (BISA) in the range 210-285 nm due to π-π* transitions of the (C=C) aromatic ring and imine (C=N) group.

Figure 7.

3.3. Extraction condition optimization

3.3.1. Effect of extraction time

The effect of the extraction time was also studied in the range of 5-60 min for batch method and different flow rates varied from 1.25 ml min^{-1} to 10 ml min^{-1} for syringe method in order to find optimum extraction time for maximum adsorption. Mix standard solutions of Cu (II), Co (II), Ag (I), Ni (II), Zn (II) and Pb (II) (1 mg l^{-1}) were used for all experiments. The adsorption of Ag (I) increased during the first 5 min and then level off as an equilibrium (above 95% sorption) was reached in 5 min. Optimum flow rate of all metal ions were found as 3 ml min^{-1} for syringe method. The rapid adsorption equilibrium indicates the strong affinity between the ligands and the metal ions. This behavior indicates that these ions have a good accessibility through the chelating sites on the modified silica and the binding constant between the metal ion, imine and hydroxyl groups immobilized on the silica surface is possibly high. According to these results, it is suitable for applying the sorbent in a syringe system where shorter extraction time or faster adsorption is required.

3.3.2. Effect of sorbent amount

The amount of sorbent is very important parameter that affects the recovery. Nanoparticles have been used as better sorbents for their high surface areas than conventional sorbents. Therefore, fewer amounts of modified silica coated magnetite nanoparticles (nano-sorbents) can achieve satisfactory results. Optimum sorbent was determined by using batch and syringe methods. 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 5-50 mg for batch method and 25-100 mg for syringe method at pH= 9, respectively. Effect of the adsorbent amount on extraction of metal ions in batch procedure is shown in Fig. 8 and 9. The results for syringe procedure are shown in Table 1. As it is seen from the Fig. 7 and 8, the best sorption percentage and the highest adsorption coefficient values were obtained for Ag (I) ion from water samples with synthesized BISA-APTSCMNPs (0.05 g) using vice versa method. According to results, the synthesized nanomaterial shows excellent silver (I) ion adsorption selectivity at pH=9 in mixed metal ion solution containing Cu (II), Co (II), Ni (II), Zn (II) and Pb (II). Furthermore, the experimental results indicated that 0.05 and 0.1 g of the nano-sorbent is enough for the preconcentration of Ag (I) using the batch and syringe method, respectively. Therefore, 0.05 and 0.1 g of sorbent was used at the subsequent experimental.

Figure 8.

Figure 9.

Table 1.

3.3.3. Effect of elution conditions on recovery

The effect of various acids were used to identify the best eluent for the adsorbed metal ions on solid phase extraction (SPE) with BISA-APTSCMNPs produced by normal and vice versa methods is given in Figure 8 and 9. To obtain a high enrichment factor, a suitable eluent should be used. Diluted hydrochloric acid (HCl), nitric acid (HNO_3) and thiosulfate ($S_2O_3^{2-}$) as prepared in methanol solutions were used for the maximum elution of Cu (II), Co (II), Ag (I), Ni (II), Zn (II) and Pb (II) ions from the nanoparticle-supported complex form as in the literature. An acid solution has been widely used for the elution of metal ions from a sorbent due to the protonation at a chelating site of the sorbent. The experimental results indicated that among of different eluents used, 0.5 M HCl provided higher recovery and reproducibility. Hydrochloric acid (HCl) is commonly suitable and hence replaces the metal ions from binding sites; moreover this acid does not interfere with the subsequent determination by AAS.

3.3.4. Reusability of sorbent

The reusability of the sorbent is very important in order to evaluate its widespread usage in the laboratory. The stability and potential reusability of the adsorbent was investigated through several adsorption-elution cycles. In order to test the reusability, it was subjected to repeated adsorption and desorption operations as follows: 100 mg sorbent was put into the syringe and washed with 0.5 M HCl and water in order to activate the sorbent. 10 ml 1.0 mg l^{-1} Cu (II), Co (II), Ag (I), Ni (II), Zn (II) and Pb (II) mix standard solution was drawn at room temperature. The metal adsorbed ligands were washed with 10 ml 0.5 M HNO_3 and the desorbed metal ions were detected with AAS. Finally, the eluted sorbent was treated with doubly distilled deionized water repeatedly until the supernatant reached neutrality. The absorbance and recovery of Cu (II), Co (II), Ag (I), Ni (II), Zn (II) and Pb (II) were calculated from the adsorption and desorption operations respectively. The results agreed with 95% ± 5 recoveries for all metal ions within 0.1–5% relative error for metal ions in five cycles which fully demonstrates the nanoparticle-supported ligands have desirable stability and reusability.

3.3.5. Effect of Doping of silver ions by column filled with BISA modified nanoparticles

The studies of doping of Ag (I) were performed by varying the concentration of sorbents BISA-APTSCMNPs (0.05 g, 0.1 g and 0.2 g) produced by normal and vice versa methods with a flow rate of (1 ml/min, 3 ml/min and 5 ml/min). Data Tables 1 and 2 shows the doping and adsorption of silver ions. As can be seen from the results, 0.1 g of synthesized BISA-APTSCMNPs using vice versa method are sufficient in the preconcentration of Ag (I) using syringe method and with a flow rate of (3 ml/min).

Table 2.

4. Conclusion

In this paper, aromatic bisaldehyde (BISA) was synthesized by coupling salicylaldehyde with 1, 3-dibromopropan and then nanocomposite material of BISA-APTSCMNPs was synthesized using a normal method and a vice versa method. The newly synthesized nanoparticles were characterized by FT-IR, XRD, SEM, TEM, VSM, TGA and UV-Vis. These nanoparticles were applied as a sorbent for excellent selective removal Ag (I) ion from aqueous mixed metal ion solution containing Cu (II), Co (II), Ni (II), Zn (II) and Pb (II) by syringe and batch techniques. The adsorption mechanism of metal ions onto the surface of BISA-APTSCMNPs is more likely to be templates effects or interaction between metal ions and aromatic rings [21, 22]. The results indicated that the best sorption percentage and the highest adsorption coefficient values were obtained in regard to Ag (I) ion from water samples with synthesized BISA-APTSCMNPs using vice versa method. 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 sample. Also, it was observed that the silver ion desorption efficiency was in HCl. XRD results show that the prepared magnetite nanoparticles have good crystal structure with a face-centered (fcc) structure. The studies of doping of Ag (I) ion showed that 0.1 g of synthesized BISA-APTSCMNPs using vice versa method are sufficient in the preconcentration of Ag (I) using the syringe method at flow rate of (3 mL/min).

Acknowledgements

The authors acknowledge the Payame Noor University, Ardabil, Iran for providing facilities for this work.

Supplementary information

FT-IR sepectra were recorded on Shimadzu prestige-21 FT-IR spectrophotometer in KBr disc. These spectra were used to determine the identity of the as prepared nanoparticles and to characterize the coated Fe_3O_4 nanoparticles. The magnetic properties of the synthesized magnetite nanoparticles were performed by means of the vibrating sample magnetometery method, using a VSM 7407 magnetometer, at room temperature. Light absorption properties of all the synthesized nanomaterials were measured using a UV–Vis spectrophotometer (Perkin Elmer Lambda 45) with a wavelength range of 200–1000 nm.

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Table 1. Doping of silver metal by nanoparticles modified with bisaldeheyde (BISA- APTSCMNPs)

Attraction Ag^{+} 10^{-4} M	1 mL/minute	3 mL/minute	5 mL/minute
BISA-APTSCMNPs (normal method) 0.05 gr	65	61	54
BISA-APTSCMNPs (normal method) 0.1 gr	97	93	74
BISA-APTSCMNPs (normal method) 0.2 gr	99	95	78
BISA-APTSCMNPs (vice versa method) 0.05 gr	71	67	55
BISA-APTSCMNPs (vice versa method) 0.1 gr	H	98	80
BISA-APTSCMNPs (vice versa method) 0.2 gr	H	H	87
Cotton	ND	01	ND

ND. Not detected

Table 2. Desorption of Ag (I) ion from the surface of the nanoparticles modified with bisaldeheyde (BISA- APTSCMNPs)

Pull Ag^+ 10^{-4} M	5 mL HCl 0.5 M	Condensed
BISA-APTSCMNPs (normal method) 0.1 gr	331	33.1
BISA-APTSCMNPs (vice versa method) 0.1 gr	356	35.6

Figure Captions

Figure 1. FTIR spectra of the synthesized magnetite nanoparticles: (a) MNPS, (b) SCMNPs, (c) APTSCMNPs (d) BISA-APTSCMNPs (Normal method) and (e) BISA-APTSCMNPs (Vice versa method).

Figure 2. X-ray diffraction pattern of (a) BISA-APTSCMNPs (Normal method) and (b) BISA-APTSCMNPs (Vice versa method).

Figure 3. SEM images of magnetite nanoparticles: (a) BISA-APTSCMNPs (Normal method) and (b) BISA-APTSCMNPs (Vice versa method).

Figure 4. TEM images of magnetite nanoparticles: (a) BISA-APTSCMNPs (Normal method) and (b) BISA-APTSCMNPs (Vice versa method).

Figure 5. Hysteresis loops of a) MNPS, (b) SCMNPs, (c) APTSCMNPs, d) BISA-APTSCMNPs (Normal method) and (e) BISA-APTSCMNPs (Vice versa method).nanoparticles at room temperature using VSM.

Figure 6. TGA curves of magnetite nanoparticles: (a) BISA-APTSCMNPs (Normal method) and (b) BISA-APTSCMNPs (Vice versa method).

Figure 7. The Uv-vis spectra of MNPS, SCMNPs, APTSCMNPs and BISA-APTSCMNPs nanoparticles

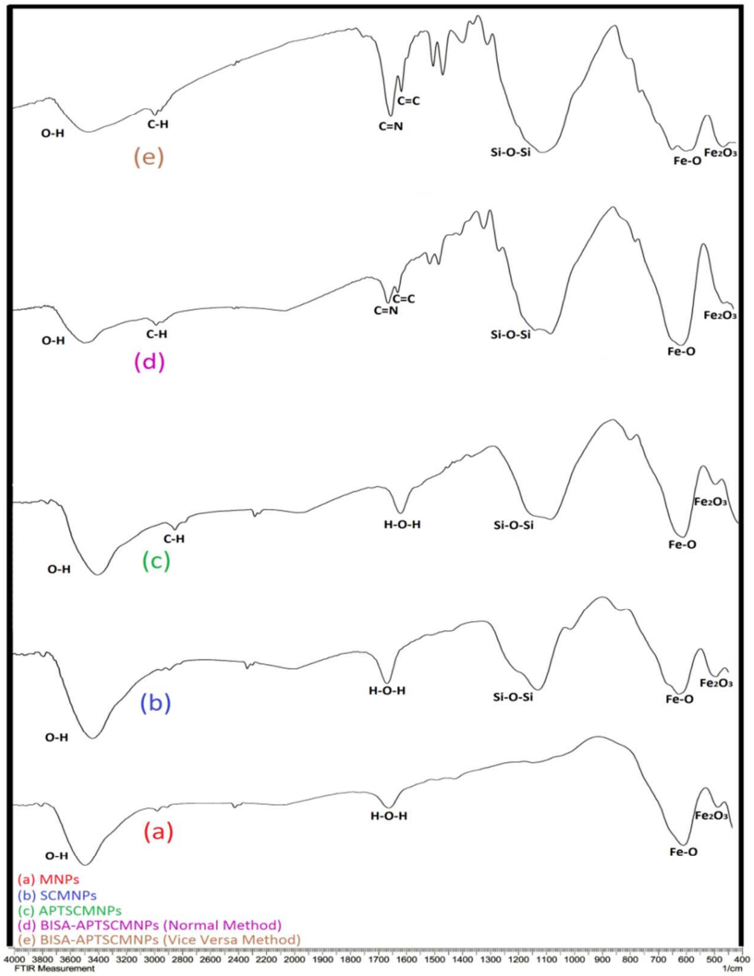
Figure 8. Removal and recovery percentage of metal ions at different amounts of adsorbent obtained with normal method in various eluent.

Figure 9. Removal and recovery percentage of metal ions at different amounts of adsorbent obtained with vice versa method in various eluent.

Scheme captions

Scheme 1. Synthesis of modified magnetite nanoparticles with a normal method and a vice versa method

Figure 1.



O-H
C-H
(e)
C=N
C=C
Si-O-Si
Fe-O
Fe₂O₃
O-H
C-H
(d)
C=N
C=C
Si-O-Si
Fe-O
Fe₂O₃
O-H
C-H
(c)
H-O-H
Si-O-Si
Fe-O
Fe₂O₃
O-H
(b)
H-O-H
Si-O-Si
Fe-O
Fe₂O₃
O-H
(a)
H-O-H
Fe-O
Fe₂O₃
(a) MNPs
(b) SCMNPs
(c) APTSCMNPs
(d) BISA-APTSCMNPs (Normal Method)
(e) BISA-APTSCMNPs (Vice Versa Method)
4000 3800 3600 3400 3200 3000 2800 2600 2400 2200 2000 1900 1800 1700 1600 1500 1400 1300 1200 1100 1000 900 800 700 600 500 400
FTIR Measurement
1/cm

Figure 2.

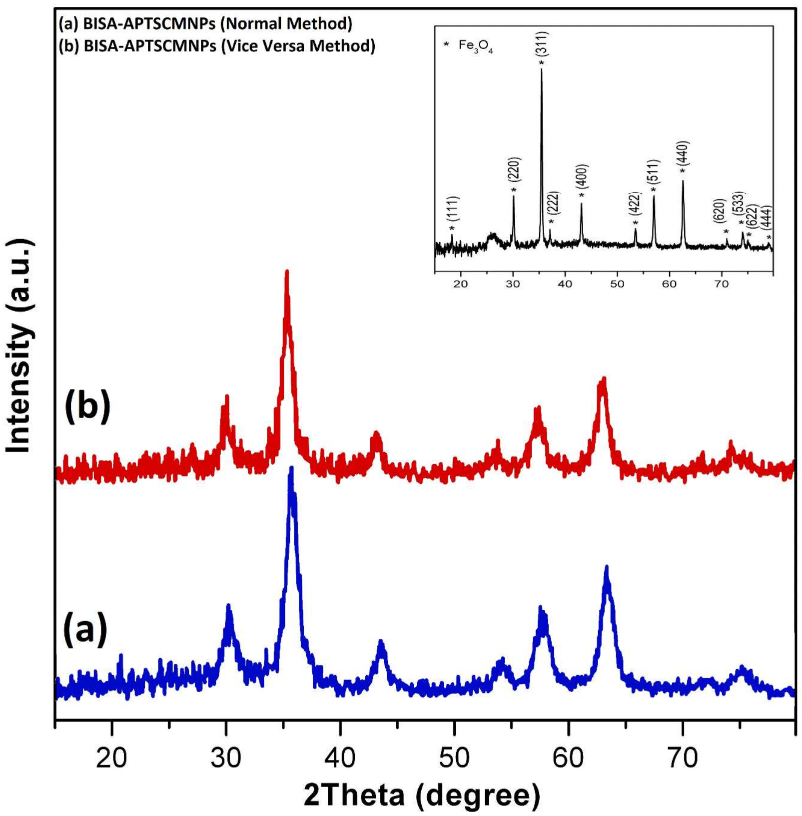

(a) BISA-APTSCMNPs (Normal Method)
(b) BISA-APTSCMNPs (Vice Versa Method)
Intensity (a.u.)
(b)
(a)
20
30
40
50
60
70
2Theta (degree)
* Fe$_3$O$_4$
(111)
(220)
(311)
(222)
(400)
(422)
(511)
(440)
(620)
(533)
(622)
(444)
20
30
40
50
60
70

Figure 3a.

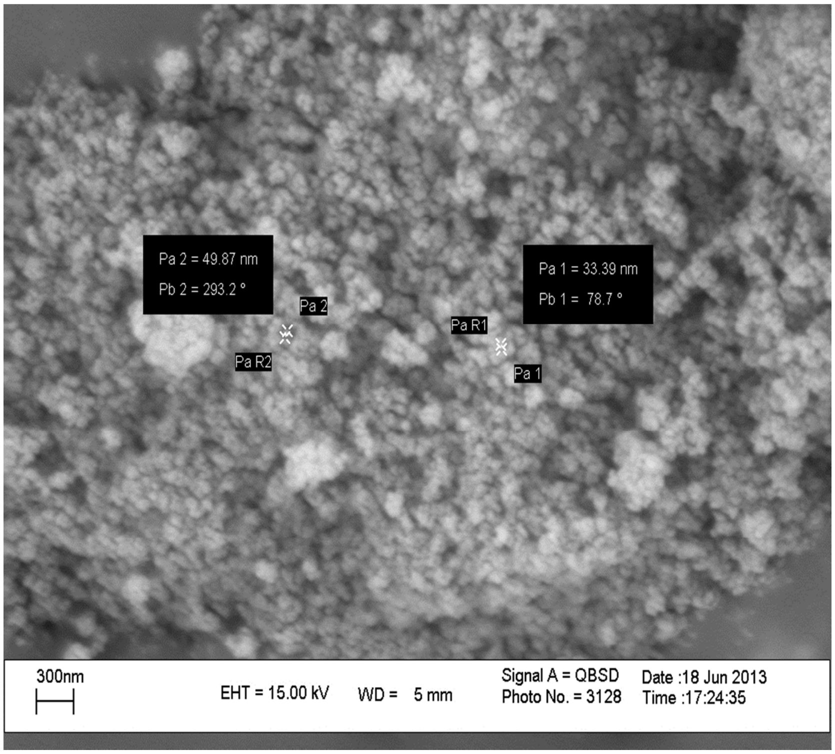

Pa 2 = 49.87 nm
Pb 2 = 293.2 °
Pa 2
Pa R2
Pa R1
Pa 1 = 33.39 nm
Pb 1 = 78.7 °
Pa 1
300nm
EHT = 15.00 kV
WD = 5 mm
Signal A = QBSD
Photo No. = 3128
Date :18 Jun 2013
Time :17:24:35

Figure 3b.

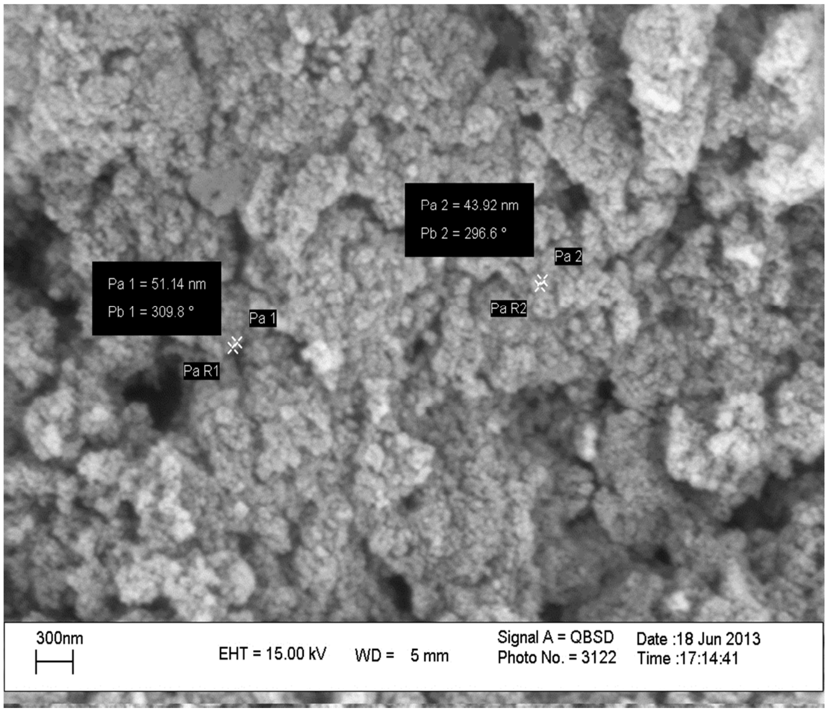

Pa 1 = 51.14 nm
Pb 1 = 309.8 °
Pa 1
Pa R1
Pa 2 = 43.92 nm
Pb 2 = 296.6 °
Pa 2
Pa R2
300nm
EHT = 15.00 kV
WD = 5 mm
Signal A = QBSD
Photo No. = 3122
Date :18 Jun 2013
Time :17:14:41

Figure 4a.

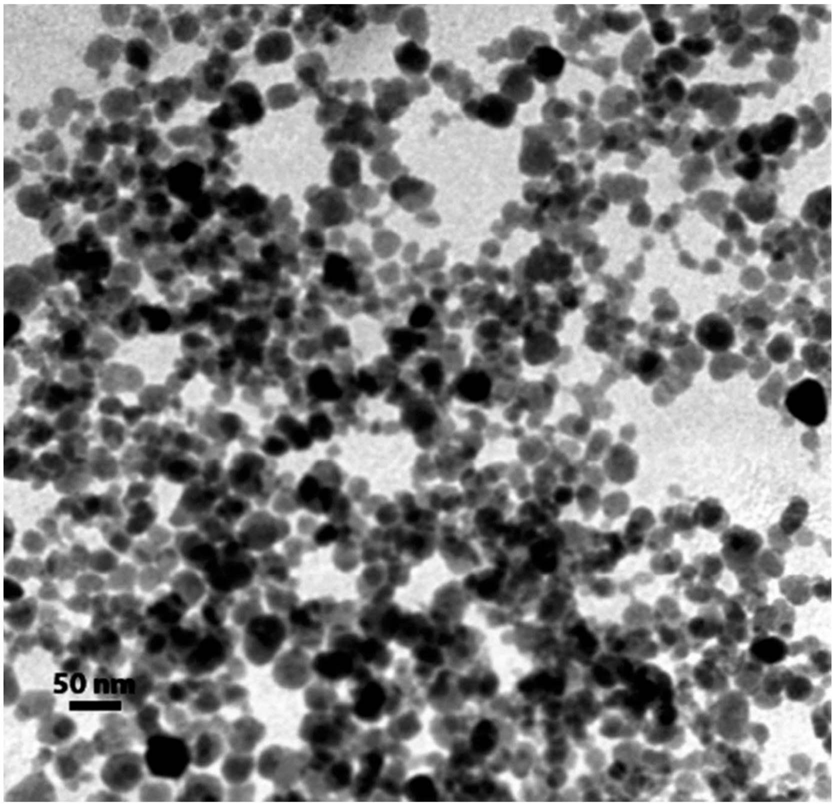


Figure 4b.

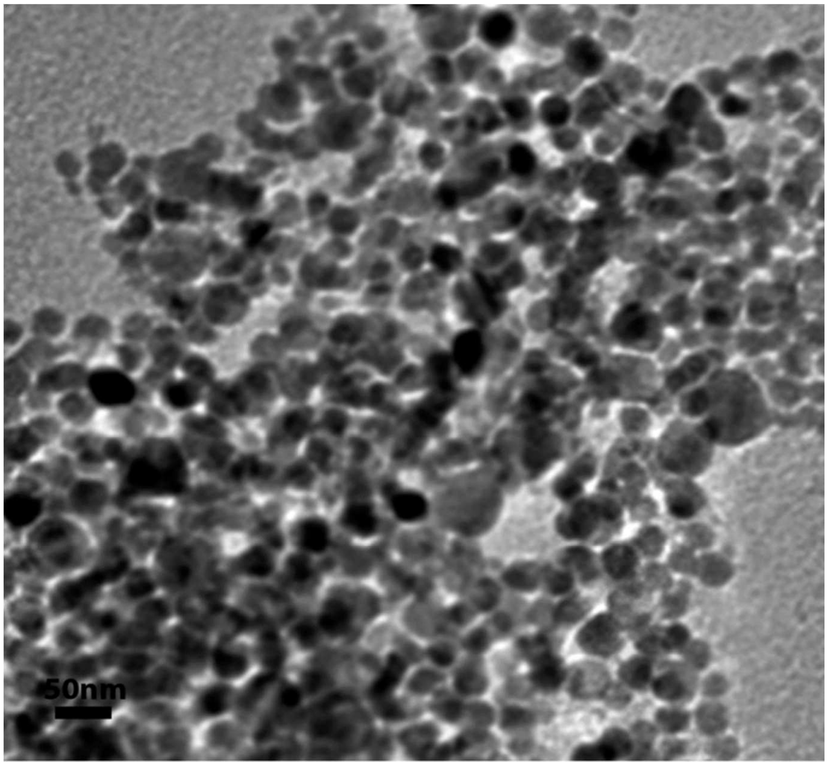


Figure 5.

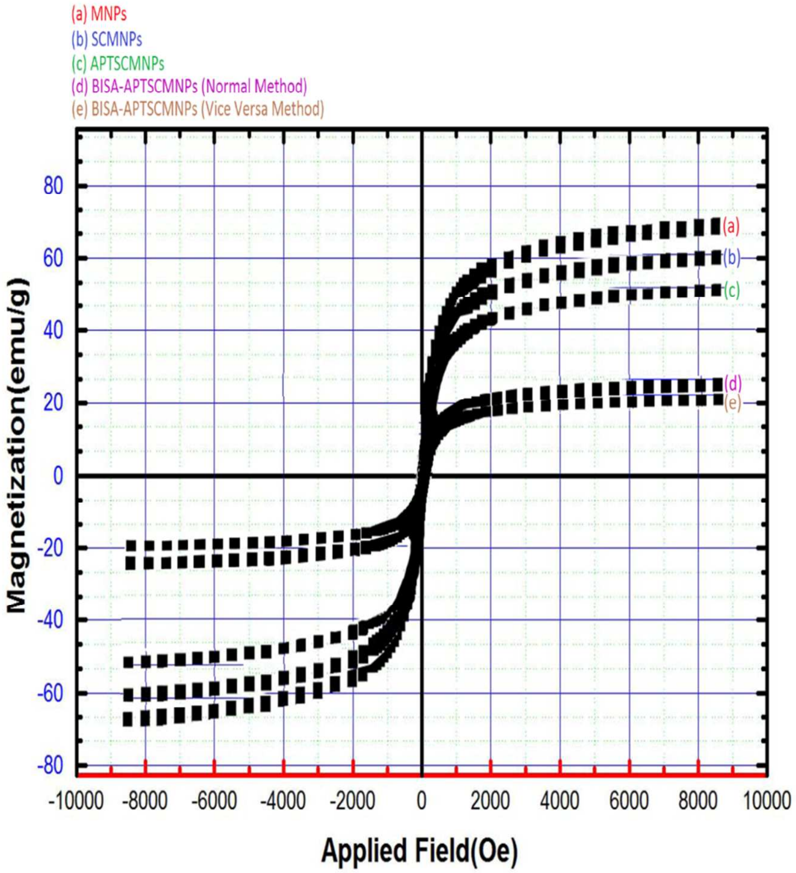

(a) MNPs
(b) SCMNPs
(c) APTSCMNPs
(d) BISA-APTSCMNPs (Normal Method)
(e) BISA-APTSCMNPs (Vice Versa Method)
Magnetization(emu/g)
80
60
40
20
0
-20
-40
-60
-80
-10000
-8000
-6000
-4000
-2000
0
2000
4000
6000
8000
10000
Applied Field(Oe)
(a)
(b)
(c)
(d)
(e)

Figure 6.

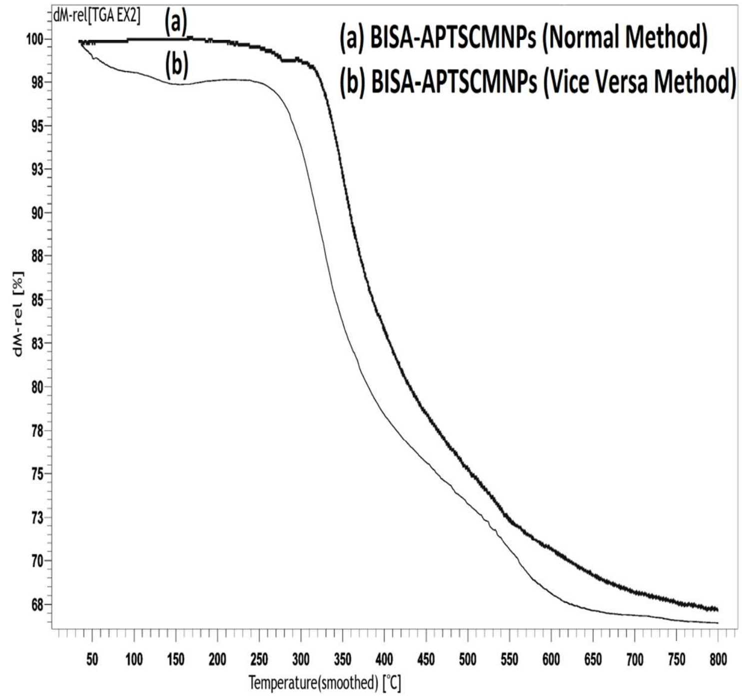

dM-rel[TGA EX2]
(a)
(b)
(a) BISA-APTSCMNPs (Normal Method)
(b) BISA-APTSCMNPs (Vice Versa Method)
dM-rel [%]
100
98
95
93
90
88
85
83
80
78
75
73
70
68
50
100
150
200
250
300
350
400
450
500
550
600
650
700
750
800
Temperature(smoothed) [°C]

Figure 7.

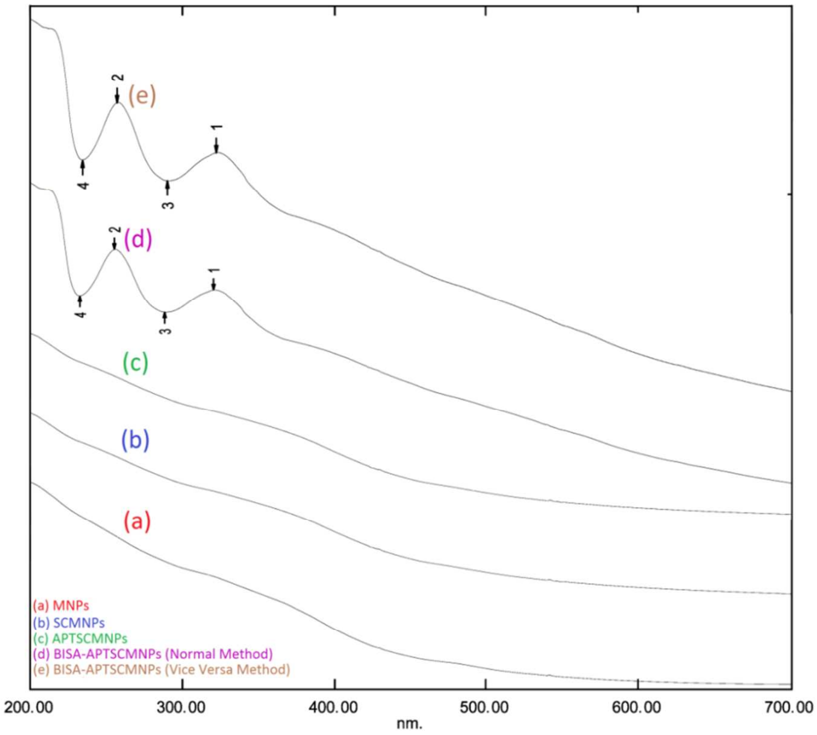

(e)
(d)
(c)
(b)
(a)
1
2
3
4
(a) MNPs
(b) SCMNPs
(c) APTSCMNPs
(d) BISA-APTSCMNPs (Normal Method)
(e) BISA-APTSCMNPs (Vice Versa Method)
200.00
300.00
400.00
500.00
600.00
700.00
nm.

Figure 8.

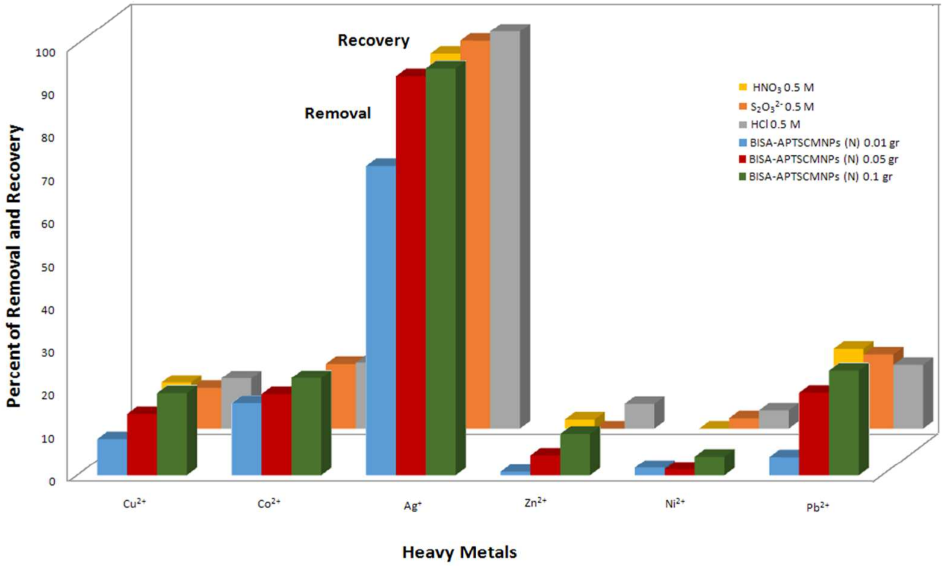
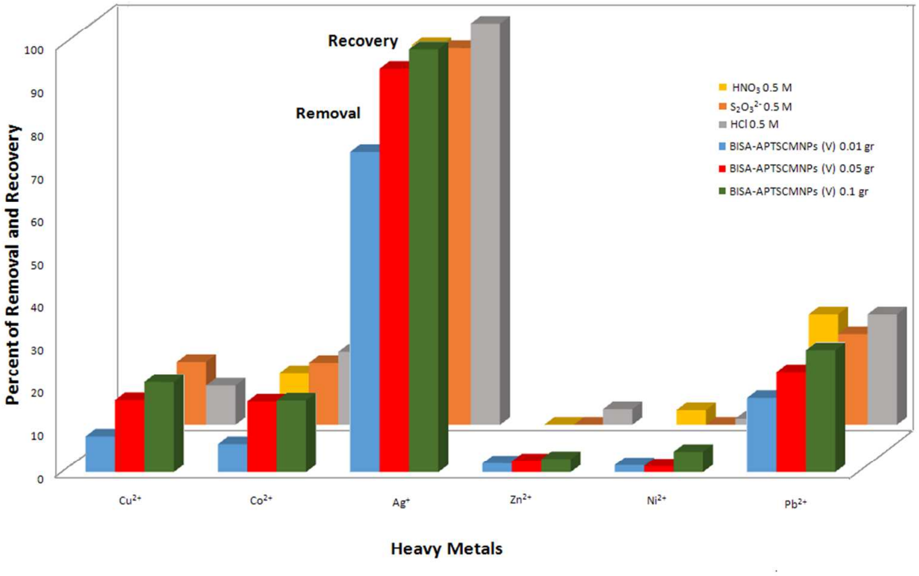
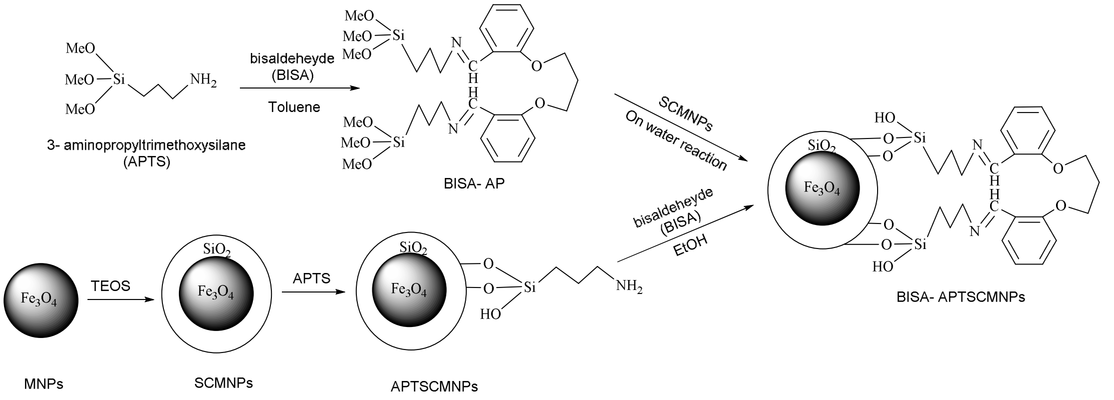

Recovery
Removal
HNO$_3$ 0.5 M
S$_2$O$_3$$^{2-}$ 0.5 M
HCl 0.5 M
BISA-APTSCMNPs (N) 0.01 gr
BISA-APTSCMNPs (N) 0.05 gr
BISA-APTSCMNPs (N) 0.1 gr
Percent of Removal and Recovery
100
90
80
70
60
50
40
30
20
10
0
Cu^{2+}
Co^{2+}
Ag^{+}
Zn^{2+}
Ni^{2+}
Pb^{2+}
Heavy Metals

Figure 9.


Recovery
Removal
HNO$_3$ 0.5 M
S$_2$O$_3^{2-}$ 0.5 M
HCl 0.5 M
BISA-APTSCMNPs (V) 0.01 gr
BISA-APTSCMNPs (V) 0.05 gr
BISA-APTSCMNPs (V) 0.1 gr
Percent of Removal and Recovery
0
10
20
30
40
50
60
70
80
90
100
Cu^{2+}
Co^{2+}
Ag^{+}
Zn^{2+}
Ni^{2+}
Pb^{2+}
Heavy Metals

Scheme 1.


MeO
MeO
MeO
Si
NH$_2$
3- aminopropyltrimethoxysilane
(APTS)
bisaldeheyde
(BISA)
Toluene
N
C
H
O
BISA- AP
SCMNPs
On water reaction
bisaldeheyde
(BISA)
EtOH
HO
SiO$_2$
Fe$_3$O$_4$
BISA- APTSCMNPs
TEOS
APTS
MNPs
SCMNPs
APTSCMNPs