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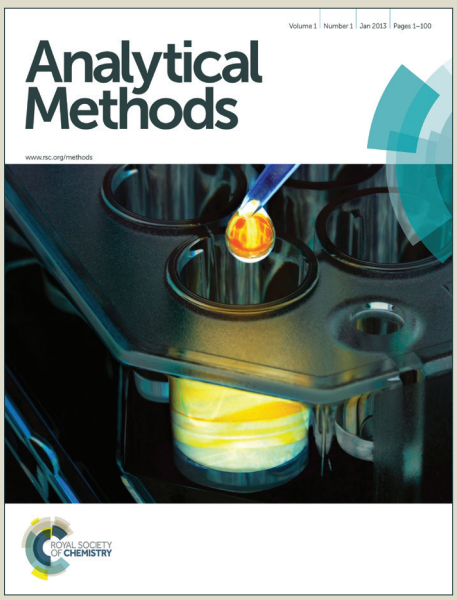

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5-(p-Dimethylaminobenzylidene) Rhodanine-Modified Magnetic Halloysite Nanotubes as a New Solid Phase Sorbent for Silver Ions

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Abstract

In this work, magnetic halloysite nanotubes (MHNTs) were modified with 5-(p-dimethylaminobenzylidene) rhodanine by a facile procedure and the modified MHNTs were used as new and inexpensive magnetic solid phase extraction sorbent for separation and preconcentration of Ag(I) ions form environmental samples. Factors affecting the adsorption of μg L^{-1} levels of silver onto the sorbent were investigated. Quantitative recoveries (>95 %) were obtained for acidic solution (pH=3) using 0.05 g of sorbent. Under the optimum conditions, the calibration graph was linear in the 4.0 - 200 μg L^{-1} concentration range, with a detection limit of 1.6 μg L^{-1}. The selectivity of the method was studied and no serious interference was observed. The method was applied to the determination of trace silver in various water and soil samples.

Keywords: Magnetic Halloysite nanotubes; 5-(p-Dimethylaminobenzylidene) rhodanine; Magnetic Solid phase extraction; Silver

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1. Introduction

Silver is one of industrially important elements, which occurs naturally in the environment as a soft, "silver" colored metal. It is used for making jewelry, silverware, electronic equipment, and dental fillings. It also occurs in powdery white (silver nitrate and silver chloride) or dark-gray to black compounds (silver sulfide and silver oxide). Silver could be found at hazardous waste sites in the form of these compounds mixed with soil and/or water. This, in turn, may cause serious environmental problems. EPA recommends that the concentration of silver in drinking water not exceed 0.1 mg L^{-1} [1]. Therefore, determination of trace amounts of silver is important for many areas of environmental sciences.

In recent years, great attention has been devoted to the application of nano-structure materials in solid phase extraction (SPE) because of large specific surface areas, high adsorption capacity and good chemical and thermal stability [2]. Several nanomaterials such as metallic oxide nanoparticles [3–5], carbonaceous nanomaterials [6], polymer-based nanomaterials [7,8] and nanoclays (NCs) [9,10] have been used as adsorbents in SPE.

Nanoclays are natural sources with at least one dimension in the nanometer scale. The main structure in NCs includes tetrahedral silicate and octahedral aluminum layers, and the diversity in NCs is based on the arrangement of these layers. Halloysite nanotubes (HNTs) are two-layered (1:1) clay with nanotubular structure and molecular formula of $Al_2Si_2O_5(OH)_4 \cdot nH_2O$ which are found in soils of many countries, such as China, France, Belgium and New Zealand. HNTs have an inner diameter of 10–30 nm and an outer diameter of 50–70 nm. The length of HNTs varies in the range of 0.5–1.5 μm. HNTs can adsorb heavy metals via ion exchange process and by formation of inner-sphere and outer-sphere complexes through $Si\text{-}O^-$ and $Al\text{-}O^-$ groups [11–13]. However, they have inherent limitations such as low loading capacity, relatively small metal ion

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binding constants, and low selectivity [14]. To circumvent these limitations, HNTs can be modified with various types of organic compounds and chelating agents [15–17].

By combining the surface properties, nano-scaled and tubular structures of HNTs with magnetic property of Fe_3O_4, magnetic halloysite nanotubes (MHNT) are expected to be ideal candidates for high-performance separation sorbent in magnetic solid phase extraction (MSPE).

In the present study, 5-(*p*-dimethylaminobenzylidene) rhodanine (PDR), a silver specific dye, was used for modification of MHNTs by a simple strategy. The prepared sorbent was applied for separation/preconcentration of silver in different matrices before its determination by flame atomic absorption spectrometry (FAAS). To the best of our knowledge, there is no report on the using of PDR-modified magnetic halloysite nanotubes (MHNTs-PDR) as sorbent for magnetic solid phase extraction.

2. Materials and methods

2.1. Reagents and solutions

All reagents were of analytical-reagent grade and doubly distilled de-ionized water (obtained from Ghazi Serum Co., Tabriz, Iran) was used for the preparation of all solutions. Working solution of silver wase prepared by dilution of 1000 mg L^{-1} standard solution (Merck, Darmstadt, Germany). pH adjustments were performed with 0.1 M HNO_3 and NaOH (Merck). A solution of PDR was prepared by dissolving an appropriate amount of 5-(*p*-dimethylaminobenzylidene) rhodanine (Merck) in hot ethanol. HNTs were purchased from Sigma-Aldrich (St. Louis, USA). $FeCl_3.6H_2O$ and $FeSO_4·7H2O$ were prepared from Merck.

2.2. Instruments

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A Shimadzu model AA-670G atomic absorption spectrometer (Kyoto, Japan) was used for the determination of silver in the following conditions: wavelength, 328.1 nm; lamp current, 4.0 mA; slit width, 0.6 nm; burner height, 6.0 mm; acetylene flow, 2.2 L/min; air flow, 8.0 L/min. A Metrohm model 654 pH meter was used for pH measurements.

The size and structure of MHNTs were determined by a scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDX) (Mira 3 FEG, Tescan Co., Czech Republic). Fourier transform infrared (FTIR) spectra were recorded using a Bruker Tensor-27 spectrometer (Germany). Samples were prepared by mixing 1.0 mg of the powder with 100 mg of KBr and pressing the mixture into a pellet. . An X-ray diffractometer (Siemens D500, Germany) equipped with Cu Kα (λ = 0.154 nm) was used to acquire the XRD patterns of powdered samples. The magnetic properties of nanoparticles were characterized by means of a vibrating sample magnetometer (Meghnatis Kavir Co., Kashan, Iran) at room temperature.

2.3. Preparation of sorbent

2.3.1. Preparation of MHNT

The MHNT composite was synthesized according to the literature with some modifications [18]. A suspension of 0.5 g of HNT in a 200 mL of solution containing 0.582 g $FeCl_3 \cdot 6H_2O$ and 0.300 g $FeSO_4.7H_2O$ refluxed at 70°C for 1.5 h in an oil bath under N_2 atmosphere. $NH_3.H_2O$ solution (25 mL, 4 mol L^{-1}) was added dropwise to prepare iron oxides. The mixtures were aged at 70°C for 1.5 h and then washed 3 times with distilled water. The obtained composites were dried at room temperature for 24 h.

2.3.2. Preparation of MHNT-PDR

PDR- modified MHNTs were prepared as follows: A heterogeneous suspension containing 0.5 g of MHNTs in 100 mL deionized water was sonicated for 10 min. Afterwards, 100 mL of 0.05%

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(w/v) PDR solution in ethanol was added to the suspension and the solution maintained under sonication for 30 min. The resulting solid was isolated by the application of an external magnetic field, washed with water and ethanol and finally dried at room temperature.

2.4. General procedure

An aliquot of 100 mL of aqueous sample or standard solution (containing 4–200 μg L^{-1} silver ion) was placed in a beaker and its pH value was adjusted to 3.0 with 0.1 M HNO_3 and NaOH. Then, 0.05 g of the modified MHNTs was added to the solution and placed in an ultrasonic bath and sonicated for 15 min at 25 °C. Afterwards, a strong magnet (with strength of ~ 0.4 Tesla) was positioned at the bottom of the beaker, and the MHNTs were isolated from the suspension (which takes about 7 min). The preconcentrated silver ions were desorbed with 1.0 mL of 5% thiourea solution under sonication for 1 min. The nanoparticles were isolated by the magnet in a very short time (less than 1 min) and the final solution was analyzed by FAAS.

2.6. Sample preparation

Samples of spring and well water were collected from environs of Tabriz, Iran and tap water was collected from our laboratory (University of Tabriz, Tabriz, Iran). 100 mL of water samples was filtered through a Millipore membrane (with 0.45 μm pore-size) into polyethylene bottles. The samples were analyzed according to the general procedure. Recovery experiments were also conducted by spiking the samples with appropriate amounts of silver, and determining their silver concentration by the developed method.

0.5 g of each soil sample was accurately weighed into a 150-mL beaker, 20 mL of nitric acid (1:3, v/v) was added and the mixture was heated to boiling for about 5 min. After cooling, 5 mL of perchloric acid was added and heated to fume for about 5 min. The mixture was allowed to cool, diluted with about 25 mL deionized water and warmed for a few minutes to dissolve the

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solid. After filtration, the clear sample solution was transferred into a 100-mL volumetric flask and made up to volume with water. Recovery tests were performed by spiking the samples with known amounts of silver before any pretreatment.

3. Results and discussion

For achieving a fast preconcentration, the nanotubular structure of halloysite nanotubes was combined with magnetic property of Fe_3O_4 nanoparticles. Because of inherent limitations of HNTs such as low loading capacity, relatively small metal ion binding constants, and low selectivity, magnetic halloysite nanotubes were modified with a silver specific dye, 5-(*p*-dimethylaminobenzylidene) rhodanine, via a facile procedure without any intermediate molecules. According to the procedure for preparation of magnetic HNT composite, at first Fe(III) and Fe(II) ions adsorbed on HNTs. The attachment could be related to the structures of HNT, such as the large surface area, large pore volume and adequate hydroxyl groups, which enabled metal ions to access and adsorb on the surface. Then coprecipitation with $NH_3.H_2O$ solution makes iron oxides on HNTs[18]. The sorption of an organic chemical on a natural solid is a complicated process and may involves physical, chemical, and electrostatic interactions[19]. PDR is a derivative of rhodanine that is especially suitable as a sensitive and highly selective reagent for silver. The insoluble red chelate formed by reaction of PDR with Ag(I) has a 1:1 composition. An atom of metal replaces H of the imino group and is bonded to S of the thioketo group[20].

3.1. Characterization of prepared sorbent

The proper synthesis of magnetic halloysite nanotubes was confirmed by FT-IR and XRD spectra. FT-IR spectra of HNTs and MHNTs are shown in Fig.2a. In the FT-IR spectrum of HNTs, the peaks at 3696.78 and 3624.62 cm^{-1} are attributed to the stretching vibrations of the

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inner-surface Al–OH groups. Interlayer water is indicated by the bending vibration at 1641.36 cm^{-1}. The 1036.11 cm−1 peak is assigned to the stretching mode of Si-O. The peak at 911.42 cm−1 is attributed to the bending vibration of inner surface hydroxyl groups. The bands observed at 536.99 and 468.90 cm^{-1} are the bending vibration of Al-O-Si and Si-O-Si, respectively [21]. The above mentioned peaks also appeared in FT-IR spectrum of HNT–Fe_3O_4, in which the broad and intense band at 3424.98 cm^{-1} was due to the stretching vibrations of hydroxyl groups from iron oxide. Finally the band related to Al-O-Si of HNT at 536 cm^{-1} and the Fe_3O_4 characteristic peak at around 575.54 cm^{-1} could be overlapped in HNT–Fe_3O_4 [18].

The XRD patterns of the HNT and MHNTs are shown in Fig. 2b. In the powder XRD patterns of MHNTs, there are distinct peaks at 12.15°, 20.11° and 24.60° which can be indexed to halloysite nanotubes. Moreover, the new diffraction peaks at 30.29°, 35.62°, 43.26°, 57.87° and 62.67° can be identified as Fe_3O_4 which illustrates that magnetic Fe_3O_4 nanoparticles are successfully installed on the surface of HNT.

For investigation of morphology and particle size of HNTs and magnetic HNTs, their SEM image was recorded. It can be seen from Fig. 3b that the spherical Fe_3O_4 nanoparticles (about 50 nm) were attached on the wall of HNTs. During SEM observation, we also determined the content of HNTs and MHNTs constituents by EDX (Fig. 3c,d). Fe peaks are seen at 6.2 keV and 7 keV at EDX pattern of MHNTs. The untagged peak at 2.2 keV belongs to Au element which coated on sample prior to SEM imaging for enhancing the conductive property of sample. The amount of Fe element in the magnetic HNTs sample was obtained as 25 wt%.

The successful coating of PDR on MHNTs was proved by FT-IR spectra (Fig.1a). Compared to MHNTs, certain features of PDR can be noticed in the spectrum of MHNTs-PDR. The strong peak at 1616.61 cm^{-1} can be assigned to C=O stretching vibration and the peaks at 3236.17,

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3415.03, 3475.85 and 3549.25 cm^{-1} is caused by the C-H and N-H stretching vibrations of PDR which interfere with the O-H stretching vibration of MHNTs. All of these observations indicate that MHNTs-PDR was prepared successfully.

Fig. 4 shows the magnetization of MHNTs as a function of the applied magnetic field at 298 K. Magnetization increased with an increase in the magnetic field. MHNTs possessed good magnetic properties with the saturation magnetization (25.38 emu/g) and exhibited an extremely small hysteresis loop and low coercivity, as is a typical characteristic of superparamagnetic particles. The magnetization curve of MHNTs-PDR was also recorded. Almost no changes can be seen in the saturation magnetization of MHNTs as a result of modification with PDR.

3.2. Optimization of experimental conditions

3.2.1. Effect of PDR amount

For optimization of PDR amount in the sorbent preparation process, several sorbents with variable concentration of PDR solution (0.01% - 0.07% (w/v)) were prepared. Then 50 mg of each sorbent was added to 25 mL of 20 mg L^{-1} Ag(I) solution at pH=3 and sonicated for 30 min. After centrifugation, the concentration of the Ag(I) ions in the solution was determined by FAAS and the adsorbed amount of Ag(I) was calculated. According to the results (Fig. 5a), adsorption percentage of Ag(I) increased with increasing PDR concentration up to 0.05% and then remained constant. It could be considered that the surface of MHNTs was saturated by ligand at this concentration.

3.2.2. Effect of pH

The effect of pH on the sorption of silver ion was studied in the range of 1.0–6.0 using HNO_3 and NaOH for pH adjustment. For this purpose aliquots of 100 mL of 50 µg L^{-1} silver ion solutions

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containing 0.05 g sorbent at different pH values were sonicated for 15 minutes. The results, shown in Fig. 5b, revealed that a quantitative recovery achieves at the pH range of 3.0–4.0. As Ag(I) is more stable at acidic pH values, pH 3.0 was chosen as the optimum pH for further studies.

3.2.3. Effect of sonication time

The effect of sonication time on the adsorption of silver ions onto the sorbent was investigated in the range of 2 to 30 min. As shown in Fig. 5c, recovery decreased by increasing the time beyond 15 min. Thus, a sonication time of 15 min was selected for subsequent experiments.

3.2.4. Desorption conditions

In order to choose the most effective eluent, 1.0 mL of several eluents with different concentrations was used for desorption of 5 µg silver ion. The eluents included HNO_3, HCl, HCl in acetone, sodium thiosulfate, potassium thiocyanate, thiourea, thiourea in HCl and thiourea in HNO_3. The obtained results (Table 1) showed that 1.0 mL of 5% thiourea is the best eluent. In order to achieve complete desorption of analyte, sorbent was sonicated for 60 s during desorption process. The sorbent can be reused after being regenerated with 10 mL distilled water and is stable up to four adsorption-elution cycles without significant decrease in the recovery of silver.

3.2.5. Effect of sample volume

The effect of sample volume on the adsorption of silver ion onto 0.05 g of sorbent was studied by using samples with volumes in the range of 25–250 mL containing 2.5 µg of silver ion (Fig. 5d). The sample volume did not affect the adsorption of silver up to 100 mL while at higher volumes the recovery was decreased.

3.3. Adsorption capacity

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In order to determine the adsorption capacity of the magnetic nanocomposite, 10 mg of the adsorbent (in a beaker) was added to 25 mL of an aqueous solution containing 100 mg L^{-1} Ag(I) at pH=3.0. After sonicating for 45 min and decantation of the sorbent by applying an external magnetic field, the retained silver ions in the supernatant portion solution were determined by using FAAS. The adsorption capacity was found to be 16.2 mg g^{-1}.

3.4. Interference study

Several potentially interfering ions were added to 100 mL of 25 µg L^{-1} Ag(I) solution and analysis was performed according to the general procedure. The following excess of ions did not interfere in the determination (i.e., caused a relative error of less than 5%): 1000-fold of Na^{+}, Ca^{2+}, Mg^{2+}, K^{+}, Ni^{2+}, Co^{2+}, Mn^{2+}, Pb^{2+}, Fe^{3+}, Cr(III), Cr(IV), As(V) and SO_4^{2-} ,NO_3^{-} and Cl^{-}; 750-fold of $Al^{3+,}$ Cd^{2+} and Zn^{2+}; 500-fold of Pd^{2+}, Pt(IV), CO_3^{2-}, PO_4^{3-}, CH_3COO^{-}; 200-fold of Au^{3+}, 20-fold of Hg^{2+}. According to these results, the developed method is selective for preconcentration and determination of silver(I) ions in different matrices.

3.5. Analytical figures of merit

Calibration graph was obtained both with and without preconcentration. While the linear range without preconcentration was 0.5-22 mg L^{-1}, the calibration graph after preconcentration by using the proposed method was linear in the range of 4.0 - 200 µg L^{-1} with a correlation coefficient of 0.999. The limit of detection (LOD) of the proposed method based on three times the standard deviations of the blank (3s) was found to be 1.6 µg L^{-1}. The precision of the method, evaluated as the relative standard deviation (RSD), for five replicate determinations of 50 µg L^{-1} Ag (I) in 100 mL solution, was about 2.6%. The amount of Ag(I) ions in 100 mL was measured

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after elution of adsorbed ions by 1.0 mL of eluent, therefore the maximum preconcentration factor for this method is 100.

3.6. Analytical applications

In order to confirm the applicability of the proposed method for real samples, it was applied for the determination of silver in several water and soil samples. The accuracy of the proposed method was checked by spiking samples with known amounts of silver before any pretreatment. The obtained results are given in Table 2. As can be seen, the recoveries are between 98 and 102.0%, which confirm the accuracy of the method.

4. Conclusions

MHNTs were modified with 5-(*p*-dimethylaminobenzylidene) rhodanine by a fast and very simple procedure. The modified MHNTs were successfully applied as inexpensive and natural sorbent for solid-phase extraction and preconcentration of Ag(I) ions. The main advantages of this sorbent compared to other sorbents (Table 3) include its magnetic feature which simplifies extraction process, high selectivity, simplicity of sorbent modification method, acidic working pH, re-usability and applicability for several types of samples because of low matrix effect.

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Table 1. Effect of eluent type and concentration on the recovery of Ag(I), pH=3.0.

Eluent type	Recovery (%)
HNO_3 (1.0 M)	40
HNO_3 (5.0 M)	46
HCl (5.0 M)	36
HCl (1.0 M) in aceton	40
Thiourea (1%)	83
Thiourea (1%) in 1.0 M HCl	95
Thiourea (1%) in 1.0 M HNO_3	97
Thiourea (5%)	100
Potassium thiocyanate (5%)	83
Sodium thiosulfate	92

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Table 2. Results obtained for silver determination in various water and soil samples.

Sample	Added [a]	Found [b]	Recovery (%)	t-Statistic [c]
Soil 1	0	2.6±0.1	-	-
	1.0	3.61±0.08	102	0.43
	10.0	12.8±0.15	102	2.19
Soil 2	0	1.42±0.07	-	-
	1.0	2.43±0.07	100	0.24
	10.0	11.48±0.15	100.2	0.35
Soil 3	0	4.02±0.04	-	-
	1.0	5.0±0.07	98	0.49
	10.0	14.18±0.13	101	1.59
Tap water	0	ND [d]	-	-
	10.0	10.0±0.6	100	0
	100.0	100.0±1.0	100	0
Spring water	0	ND	-	-
	10.0	9.8±0.3	98	1.22
	100.0	99.8±0.7	101	0.62
Well water	0	ND	-	-
	10.0	10.0±0.5	100	0
	100.0	99.8±0.3	99	1.38

[a] The added and found values have μg L^{-1} unit in the case of water samples and μg g^{-1} unit in the case of soil samples.
[b] Averages of three determinations ± standard deviation.
[c] Critical t-value at %95 confidence level is 4.30.
[d] Not detected.

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Table 3. Comparison of the developed MSPE - FAAS method with some other methods.

Sorbent	LDR[a] (µg L^{-1})	DL[b] (µg L^{-1})	PF [c]	Sample Volume (mL)	Adsorption capacity (mg g^{-1})	Ref.
3,4-Dihydroxybenzaldehyde- nanoporous MCM-41	1-180	0.5	667	2000	160	[22]
Poly(DPMAAm-co-DVB-co-AMPS)[d]chelating resin	10-1000	2.4	43	10.4	-	[23]
Ethylene glycol bis-mercaptoacetate- TMSP[e]-Fe_3O_4	-	0.07	240	250	29.8	[24]
2-Mercaptobenzothiazole-MWCNTs	-	0.21	160	800	5.40	[25]
Benzothiazolecalix[4]arene-silica	12.5-62.5	0.44	40	10	12.2	[26]
BNAS[f]- octadecyl silica membrane disk	-	0.01	160	2500	17.14	[27]
2-Mercaptobenzothiazole–silica gel	-	-	300	300	0.34	[28]
Eggshell membrane	40-300	27	2	20	1.7	[29]
PDR-Sepabeads SP207	50-10000	0.13	200	1000	5.40	[20]
Magnetic halloysite nanotubes-PDR	4-200	1.6	100	100	16.2	This work

[a] Linear dynamic range
[b] Detection limit
[c] Preconcentration factor
[d] Poly(N,N0-dipropionitrilemetha- crylamide-co-divinylbenzene-co-2-acrylamido-2-methyl-1-propanesulfonicacid)
[e] 3-(Trimethoxysilyl)-1-propanethiol
[f] Bis[5-((4-nitrophenyl)azosalicylaldehyde)]

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Figure captions

Fig.1. Molecular structure of 5-(*p*-Dimethylaminobenzylidene) rhodanine.

Fig.2. (a) FTIR spectra of Fe_3O_4, HNTs, MHNT and MHNT-PDR. (b) XRD patterns of HNTs and MHNT.

Fig.3. SEM image of (a) HNTs (b) MHNTs and EDX spectrum of (c) HNTs (d) MHNTs.

Fig.4. Magnetization curve of MHNT and MHNT-PDR at room temperature.

Fig.5. Effect of (a) concentration of PDR on the adsorption of the Ag(I) ions (20 mg L^{-1}), pH:3.0, amount of sorbent:50 mg (b) Effect of pH of sample solution on the analyte recovery; Ag: 50 µg L^{-1}; sonication time: 20 min, sample volume: 100 mL (c) Effect of sonication time on the analyte recovery; Ag: 50 µg L^{-1}; pH: 3; sample volume: 100 mL (d) Effect of volume of sample on analyte recovery; Ag: 2.5 µg; pH: 3, sonication time: 15 min.

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Fig.1

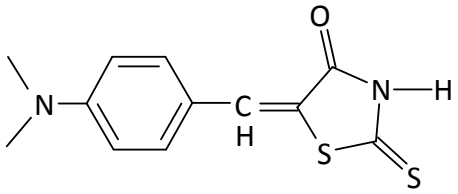

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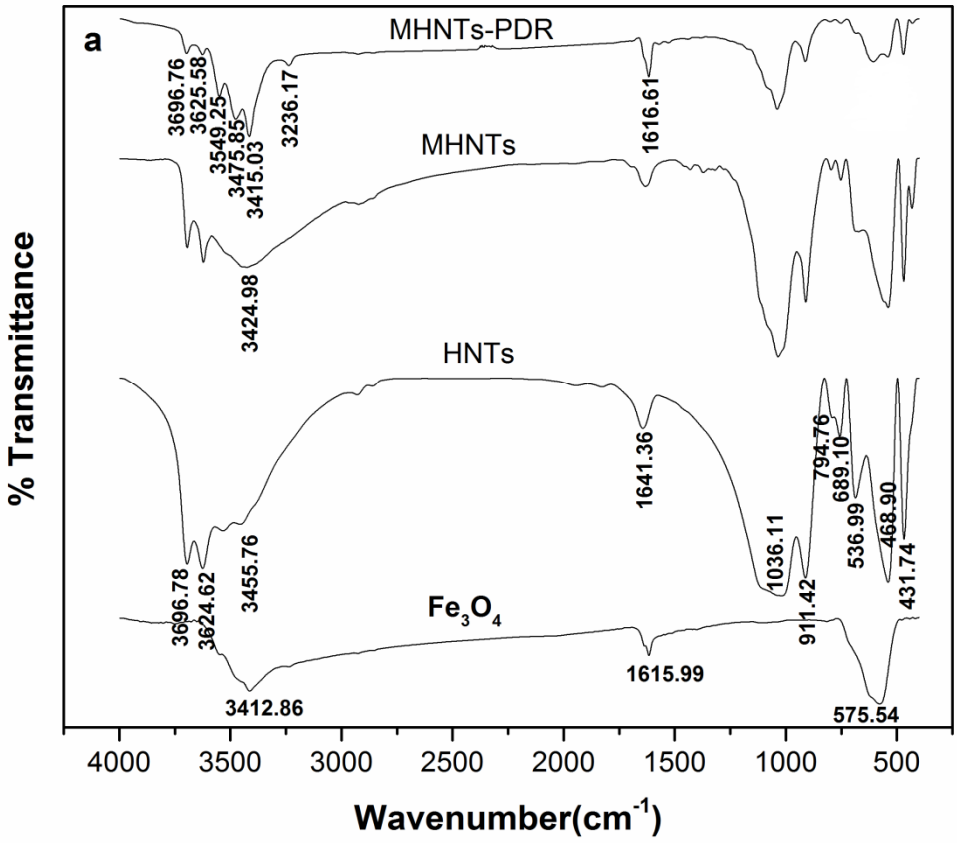
Fig.2



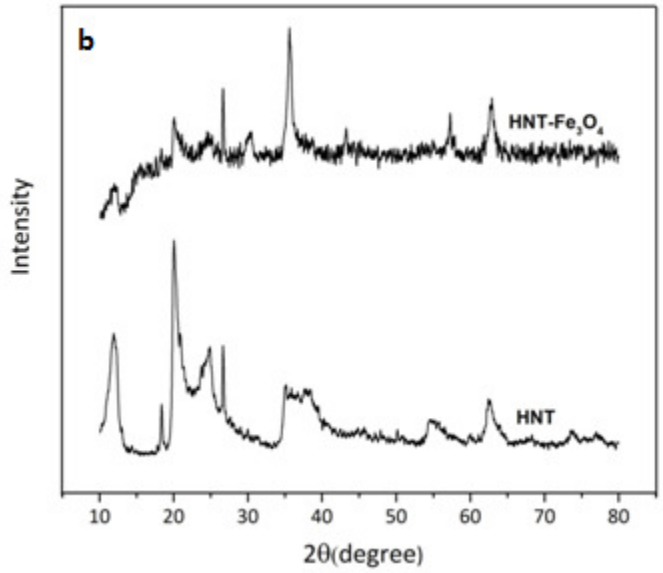


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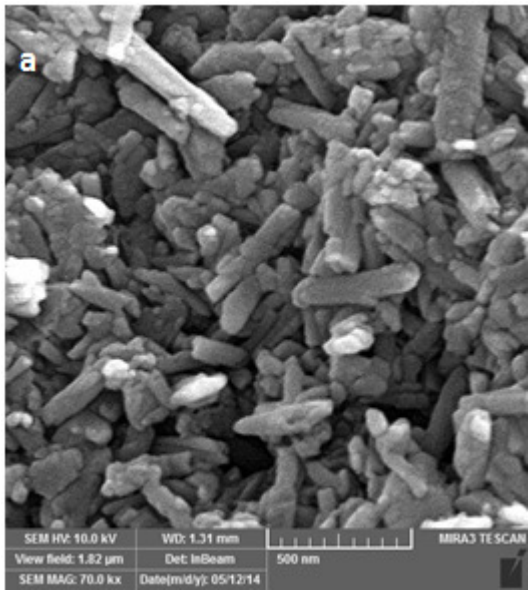
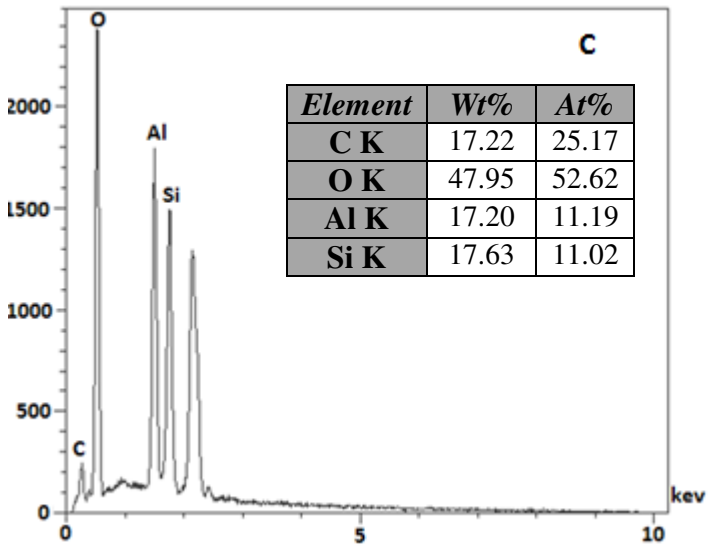
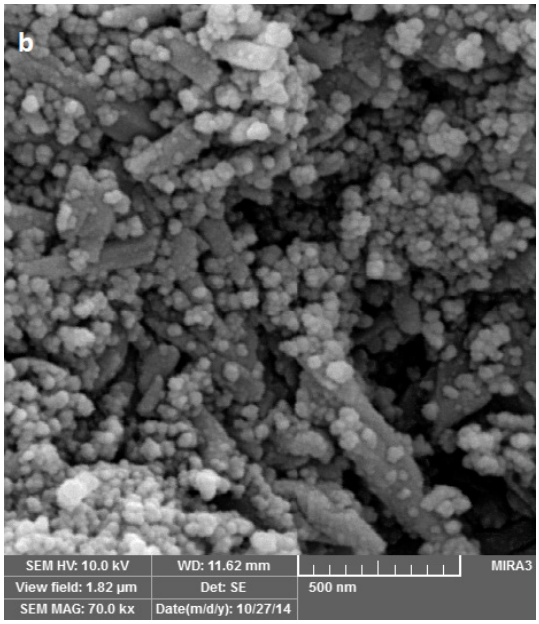
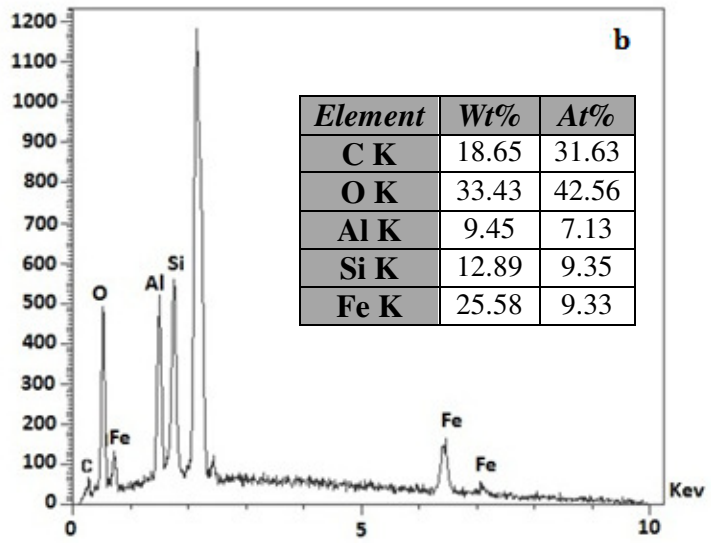
Fig.3





Element	Wt%	At%
C K	17.22	25.17
O K	47.95	52.62
Al K	17.20	11.19
Si K	17.63	11.02





Element	Wt%	At%
C K	18.65	31.63
O K	33.43	42.56
Al K	9.45	7.13
Si K	12.89	9.35
Fe K	25.58	9.33

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Fig4.

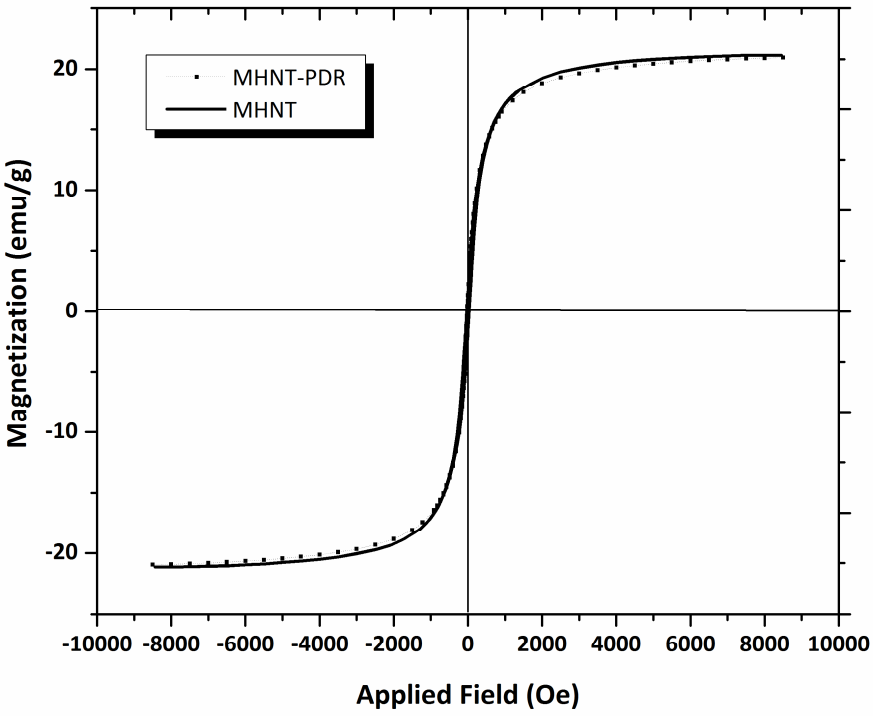

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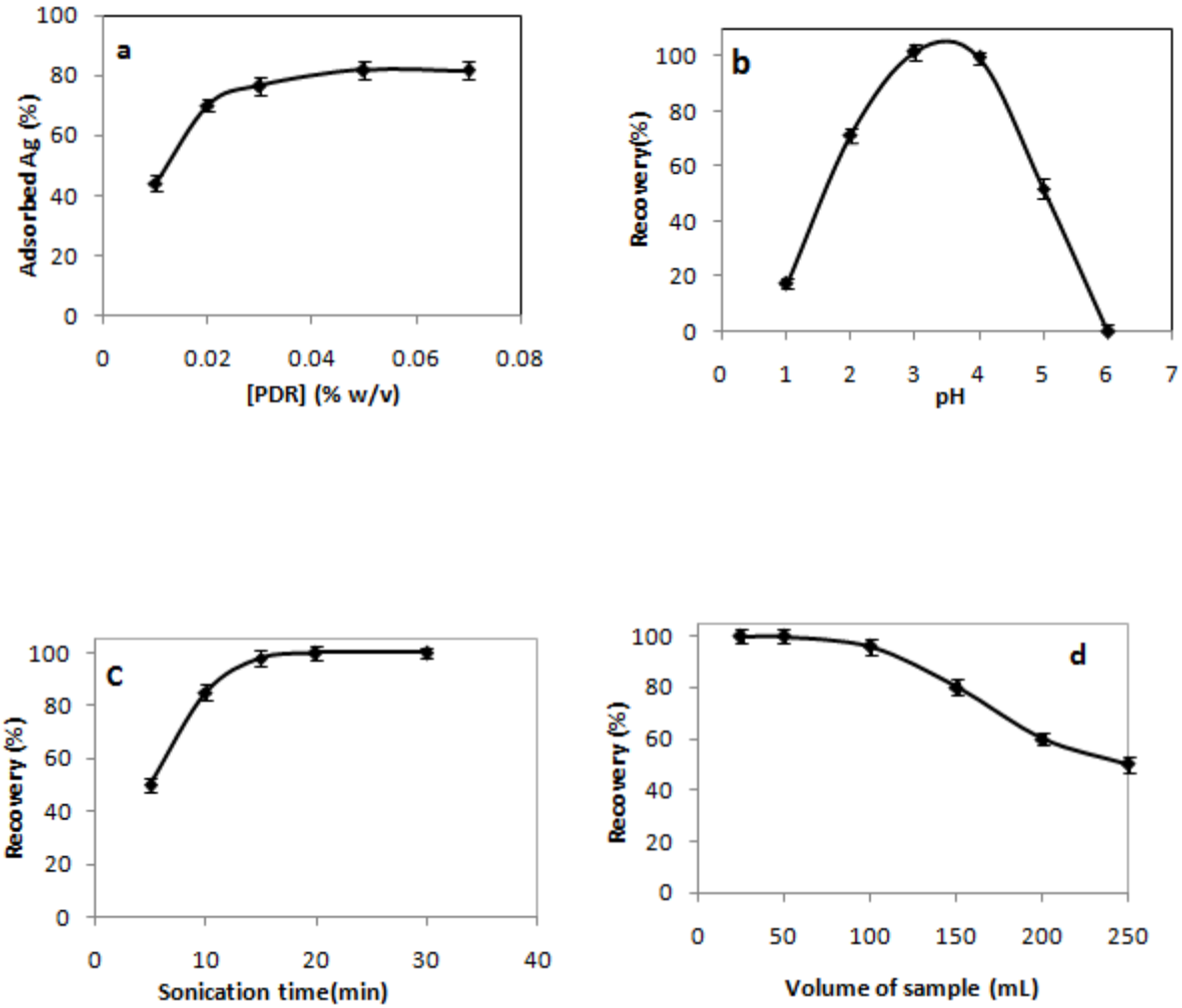
Fig.5



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