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Synthesis and Application of Novel Modified Magnetic Nanocomposite for Solid Phase Extraction of Thallium(I) Ions

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In this paper, a magnetically multiwalled carbon nanotube (MMWCNT) nanocomposite modified by methyl-2-[2-(2-[2-(methoxycarbonyl) phenoxy] ethoxyethoxy) ethoxy] benzoate was applied for magnetic solid-phase extraction (MSPE) of thallium(I) ions. Fourier transform infrared (FT-IR) spectroscopy, field emission scanning electron microscopy (FE-SEM), X-ray diffraction (XRD) spectrometry and vibrating sample magnetometer (VSM) were used to characterize the magnetic sorbent. The effects of pH, sample volume, eluent, and interfering ions were studied. Under the optimized conditions, the preconcentration factor of 100 and the linear response over 3-280 $\mu\text{g l}^{-1}$ were obtained. The detection limit of the suggested procedure (LOD, $3S_b/m$) was found to be 0.59 $\mu\text{g l}^{-1}$. The relative standard deviation for six replicate detections of 100 $\mu\text{g l}^{-1}$ of Tl(I) was $\pm 1.9\%$. Finally, the developed method was utilized for the determination of thallium(I) ions in different real samples with recoveries in the range of 96.9-102.2% for the spiked samples. The proposed MSPE method exhibited some advantages, such as simplicity, rapidity, high sensitivity and excellent precision. In addition, the mechanism of thallium extraction by the modified nanocomposite was proposed.

Keywords: Magnetic solid phase extraction, Nanocomposite, Thallium(I), Multiwalled carbon nanotubes, Flame atomic absorption spectrometry, Heavy metals

INTRODUCTION

The determination of hazardous elements in environmental samples can provide important information concerning pollution, since they are usually released in the environment from anthropogenic sources, such as agricultural and industrial activities [1]. Thallium (Tl) is widely used in industrial applications such as catalyst, alloys, nuclear medicine and pigments [2]. Thallium is toxic for many biological systems even more than mercury, cadmium, lead and copper [3]. It is extremely toxic to humans, plants and animals and plays no role in their metabolisms. From this point of view, trace analysis of thallium is necessary. Some analytical techniques are available for determination of trace amounts of thallium in geological and environmental samples such as flame atomic

absorption spectrometry (FAAS) [4], spectrometry [5], inductively coupled plasma mass spectrometry (ICP-MS) [6], inductively coupled plasma atomic emission spectrometry (ICP-AES) [7], electrothermal atomic absorption spectrometry (ETAAS) [8] and electrochemical methods [9]. However, it is difficult to determine directly the extremely low concentration of thallium in the presence of a relatively high concentration of other diverse ions. Hence, separation and preconcentration methods have been routinely used to eliminate matrix effects. Currently, the widely used techniques for preconcentration and separation of trace amount of thallium include solid phase extraction (SPE) [10], liquid-liquid extraction (LLE) [11], cloud point extraction (CPE) [12] and dispersive liquid-liquid microextraction (DLLME) [13]. Among them, SPE is the most common technique because it offers many practical and operating advantages such as simple operation, high extraction efficiency, rapid phase separation and the ability

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of combination with different detection techniques [14]. In SPE procedure, the choice of an appropriate adsorbent is a critical factor to obtain full recovery and high selectivity [15]. Recently, a novel SPE procedure, based on the use of magnetic or magnetisable materials called MSPE, has also been developed [16]. A distinctive superiority of this technology is that solid-liquid separation can be easily achieved by the action of an external magnetic field instead of tedious and time-consuming centrifugation or filtration procedures which simplify the sampling and collection processes [17,18]. Obviously, the best adsorbents must have high specific surface area, good selectivity, suitable chemical and physical stability, and high extraction efficiency [19]. To date, various adsorbents such as activated carbon (AC), cellulose, modified silica gel, nanoadsorbents materials, chelating resins and multiwalled carbon nanotubes (MWCNTs) have been widely used in SPE. Among them, MWCNTs have attracted considerable interest due to their strong adsorption ability, exceptional mechanical properties, high chemical stability, and a large specific surface area [20]. However, disadvantages such as small size and poor dispersion in aquatic phase, limit the application of MWCNTs [21]. The combination of magnetic properties into MWCNTs has the advantages of high adsorption capacity for heavy metal ions and the separation convenience of magnetic materials [22].

In this paper, a magnetically multiwalled carbon nanotube (MMWCNT) nanocomposite was prepared by a wet chemical method at room temperature. However, the obtained MMWCNT nanocomposite was not selective and not suitable for complicated matrix of real samples. For this reason, MMWCNT nanocomposite was modified by methyl-2-[2-(2-2-[2-(methoxycarbonyl) phenoxy] ethoxyethoxy) ethoxy] benzoate. The proposed modified adsorbent has a high selectivity and good adsorption capacity under the optimized experimental conditions.

EXPERIMENTAL

Materials and Instrumentation

All reagents used were of analytical grade and utilized without further purification. Ferrous sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), and ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) sodium hydroxide (NaOH), were obtained

from Sigma-Aldrich (St. Louis, MO, USA). Thallium(I) stock solution (1000 mg l^{-1}) and acetonitrile (ACN) were purchased from Merck (Merck, Darmstadt Germany). A Spectr AA 220 atomic absorption spectrometer (Varian, Australia) equipped with a computer processor was used for measuring the thallium(I) ions. FT-IR spectra were recorded in the range of $4000\text{-}500 \text{ cm}^{-1}$ on a Spectrum One FT-IR spectrometer (PerkinElmer, Norwalk, CT, USA). The morphology of the sorbents was also determined by field emission scanning electron microscope (FE-SEM) (CARL ZEISS-AURIGA 60 microscope, Jena, Germany), operated at 15 kV. X-ray diffraction (XRD) patterns of MWCNTs and MMWCNTs nanocomposite were obtained on a powder X-ray diffraction system from PANalytical model X'Pert PRO (PANalytical B.V., Almelo, The Netherlands). The magnetic property was analyzed by using a vibrating sample magnetometer (VSM) (Meghnatis Daghigh Kavir Co., Kashan, Iran). Zeta-potential measurements were performed with a Zeta Plus Zeta Potential Analyzer (Brookhaven, USA).

Preparation of Ligand

Noncyclic crown-type polyether, methyl-2-[2-(2-2-[2-(methoxycarbonyl) phenoxy] ethoxyethoxy) ethoxy] benzoate was synthesized and purified in our laboratory according to the following procedure [23]. Briefly, a mixture of 1,2-bis(2-bromoethoxy)ethane (0.1 mol) and methyl 2-hydroxybenzoate (0.2 mol) in acetone (500 ml) containing potassium carbonate (20 g) was refluxed for 7 days. The mixture was cooled, the solid was filtered and solvent evaporated. Chloroform (400 ml) was added, and the organic layer was washed with cold 10% aqueous sodium hydroxide solution ($2 \times 100 \text{ ml}$) and then with waters ($2 \times 100 \text{ ml}$) and was dried with anhydrous magnesium sulphate. The solvent was evaporated to give a yellow viscous oil of the corresponding ligand. A schematic representation of the synthesized polyether ligand is shown in Fig. 1.

Preparation of Adsorbent

At the first step, the MWCNTs were purified and pretreated to remove amorphous carbon, graphitic nanoparticles and catalyst impurities. After that, they were functionalized with carboxylic acid groups according to a

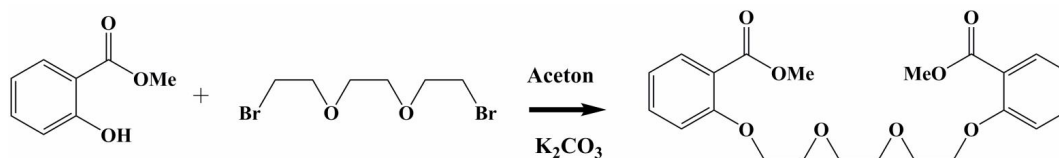


Fig. 1. Synthesis procedure of methyl-2-[2-(2-2-[2-(methoxycarbonyl) phenoxy] ethoxyethoxy) ethoxy] benzoate.

general procedure in the literature [24]: Raw MWCNTs were heated at 300 °C for 40 min to remove amorphous carbon and then were refluxed in concentrated nitric acid at 60 °C for 5 h. Subsequently, the mixture was filtered and rinsed with deionized water to be neutral, and then dried at 80 °C overnight to achieve treated MWCNTs.

The MMWCNT nanocomposite was prepared according to the previous work reported by our lab [25]. In brief, 0.5 g oxidized MWCNTs were added to 100 ml solution containing FeSO₄·7H₂O (1.49) and FeCl₃·6H₂O (0.765 g), and the mixture was sonicated under N₂ atmosphere at 70 °C. After 10 min, ~7.5 ml NaOH solution (0.5 M) was added dropwise to this mixture until final pH ripened to 10.0 ± 0.5. Then, the resultant product was collected by filtration, followed by repeated washing with deionized water and absolute ethanol (99.5%), and then dried at 100 °C for 6 h.

Methyl-2-[2-(2-2-[2-(methoxycarbonyl) phenoxy] ethoxyethoxy) ethoxy] benzoate loaded MMWCNT nanocomposite was prepared by dissolving 0.5 ml of ligand in 100 ml of ACN while stirring; then 0.5 g of MMWCNT nanocomposite was added to the mixture. The mixture was stirred at room temperature for 24 h. The resulting solid phase was separated using a magnet, washed with ethanol and water, and then dried at 60 °C overnight.

Magnetic Solid-phase Extraction Procedure

In the sorption step, 50 ml aqueous sample solution containing 50 µg l⁻¹ Tl(I) was transferred to a 100 ml Erlenmeyer flask; pH value was adjusted to 6.0. Then, the solution was shaken for 5 min to facilitate adsorption of Tl(I) onto the modified MMWCNT nanocomposite (0.02 g). Subsequently, the sorbent was separated using a magnet and the clear supernatant was decanted immediately. The magnet was removed, and the adsorbed analyte ions were eluted with 1.0 ml of 0.1 M hydrochloric acid solutions for

7 min. Finally, the modified magnetic nanocomposite was settled again using a magnetic field, and the eluent was transferred into a test tube for the determination of Tl(I) by FAAS.

Preparation of Real Samples

Two water samples, including; tap water (Kerman drinking water, Kerman, Iran) and well water (Islamic Azad University, Kerman, Iran) were selected. These samples were filtered to remove suspended particulate matters. For determination of Tl(I) content, to 45 ml of the sample, 2 ml of hydroxylamine hydrochloride (0.1 M) was added, and the pH was adjusted to 6 with sodium hydroxide solution. The solution was diluted to 50 ml and was treated according to the given procedure.

The nail sample was rinsed with acetone and doubly distilled water, and was dried at 60 °C. Then, 1g dried nail was placed in a 50 ml beaker and 5 ml concentrated HNO₃ were added. The content of the beakers were heated on a hot plate (initially at 100 °C for 45 min and then at 150 °C for 15 min) after dissolution, the solution was cooled to 70 °C and 2 ml of 30% H₂O₂ was added. The mixture was heated to dryness at 200 °C to yield a white residue. Approximately 10 ml of 0.1 M HNO₃ was added to the beakers and the contents were heated at 100 °C for several minutes. Then, 2 mL hydroxylamine hydrochloride (0.1 M) was added, the content was diluted to 50 ml and pH was adjusted to 6. The thallium content was determined according to the given procedure.

For accuracy evaluation, a synthetic mixture containing of different cations (composition: Zn(II) = 200.0, Mg(II) = 200.0, Ag(I) = 200.0, Co(II) = 200.0, Ni(II) = 100.0, Pb(II) = 75.0, Cd(II) = 75.0 and Tl(I) = 40.0 µg l⁻¹) was prepared and the proposed procedure was applied to the determination of thallium(I) ions.

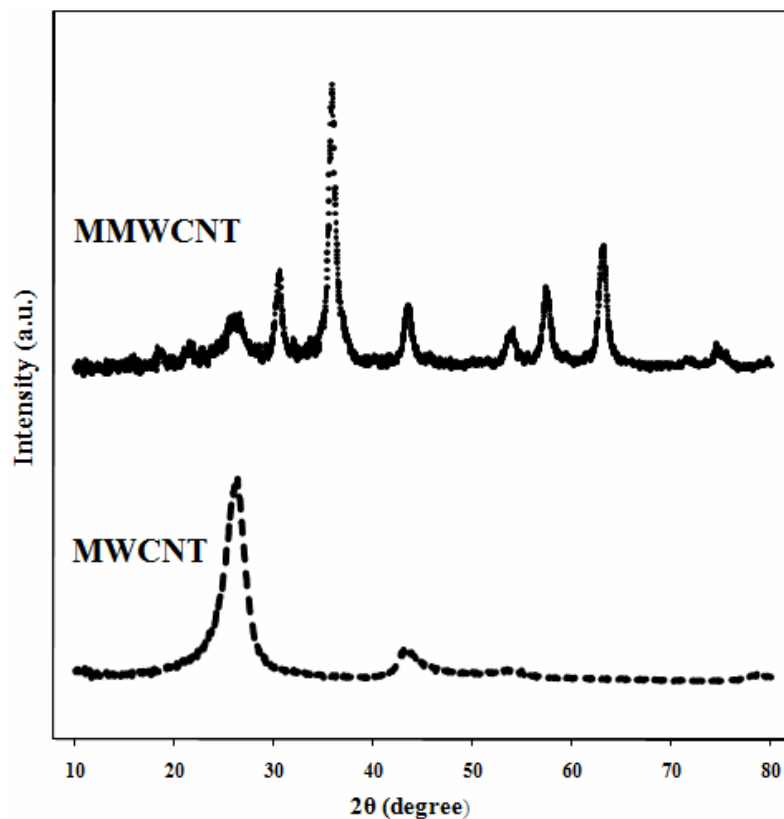


Fig. 2. XRD patterns of MWCNT and magnetic MWCNT (MMWCNT) nanocomposite.

RESULTS AND DISCUSSIONS

Characterization

The XRD pattern of treated MWCNT and MMWCNT composite are shown in Fig. 2. The diffraction peak at $2\theta = 26.2^\circ$ corresponds to 002 planes of MWCNT, which was observed for both pure MWCNTc and magnetic composite. On the contrary, the XRD pattern of the synthesized MMWCNTs composite shows six characteristic Fe_3O_4 peaks at 30.51° (220), 35.85° (311), 43.54° (400), 53.84° (422), 57.46° (333) and 63.06° (440). Based on the XRD patterns, it can be postulated that the resultant Fe_3O_4 nanoparticles in the composite were pure Fe_3O_4 with a spinel structure [26].

FT-IR spectra were acquired for oxidized MWCNT, MMWCNT, and modified MMWCNT. The main functional groups of the predicted structure can be identified through corresponding IR absorption bands. As shown in Fig. 3, a

wide band in the region $800\text{-}1200\text{ cm}^{-1}$ is attributed to the stretching of C=C in MWCNT. The broad band at 3439 cm^{-1} is attributed to the stretching vibration of dissociative O-H stretching and mode of hydroxyl groups. The peaks ranged from $2852\text{-}2921$ are attributed to the stretching vibration of -CH and the peak at 1632 cm^{-1} is due to C=O stretching vibration [27]. In MMWCNT spectrum the characteristic peak around 558 cm^{-1} corresponding to the stretching vibration of Fe-O bond illustrate that Fe_3O_4 is successfully bound to the MWCNT [28]. In modified MMWCNT, the new peaks in the region of $1000\text{-}1300\text{ cm}^{-1}$ are due to C-O stretching vibration of ligand. Also, the band at 1076 is due to the characteristic vibrations of C=O groups in organic ligand. Consequently, the above experimental results suggest that MMWCNTs are successfully modified by the ligand.

Scanning electron microscopy was employed to explore the morphology of the treated MWCNT, synthesized

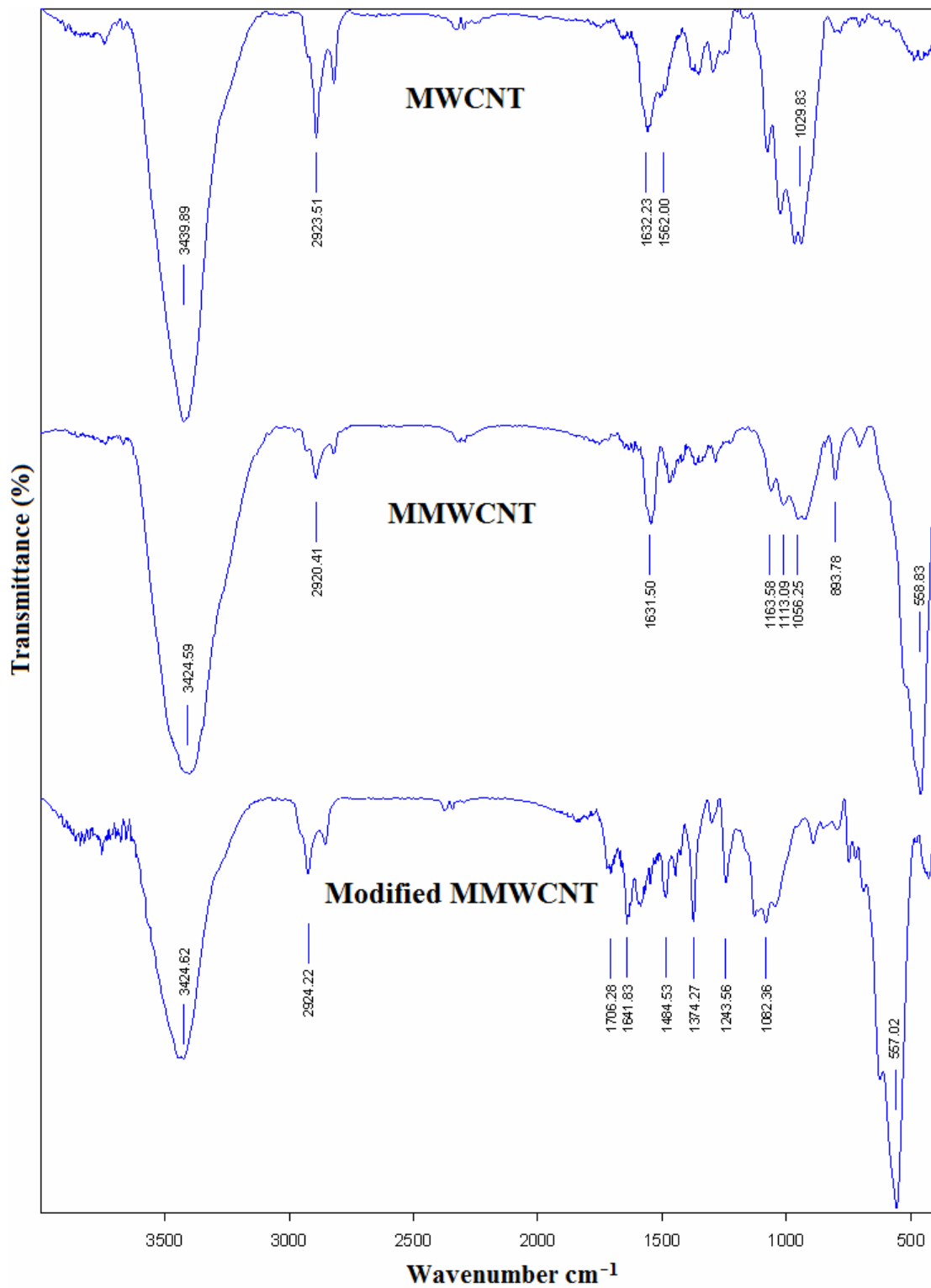


Fig. 3. FT-IR spectra of MWCNT, MMWCNT and modified MMWCNT nanocomposite.

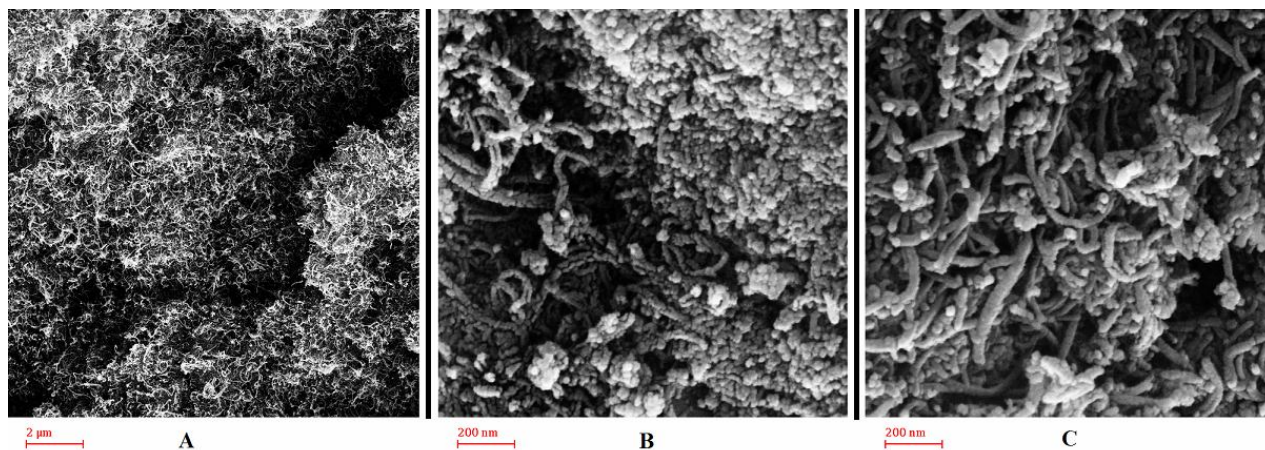


Fig. 4. FE-SEM images of (A) MWCNT, (B) MMWCNT and (C) modified MMWCNT nanocomposite.

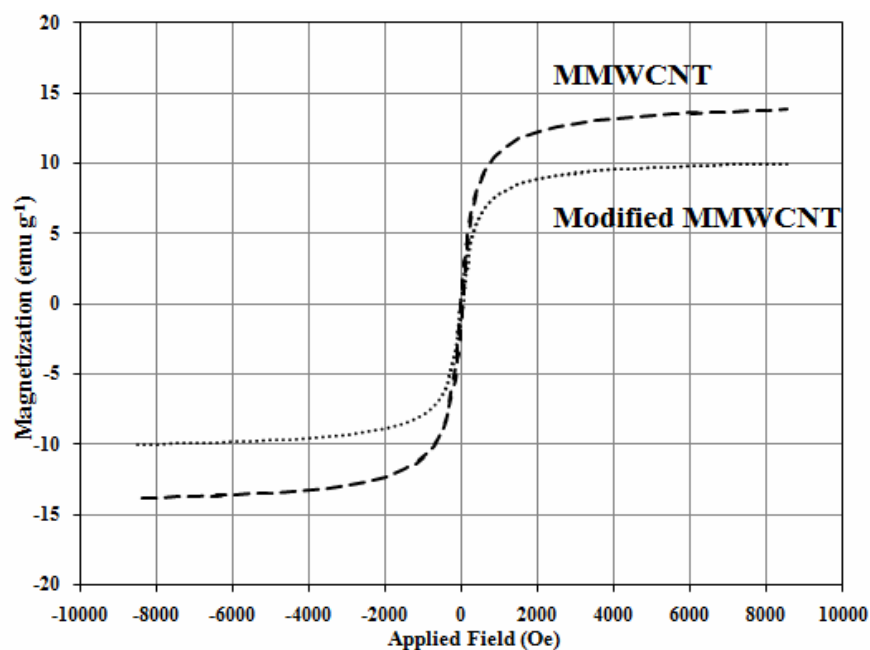


Fig. 5. Magnetic hysteresis curves of MMWCNT and modified MMWCNT.

MMWCNT composite and modified MMWCNT adsorbent (Fig. 4). Before the surface modification, the SEM image of the treated MWCNT is smooth and tidy (Fig. 4A). The surface of the MWCNT is much rougher as a result of in situ deposition of Fe_3O_4 nanoparticles (Fig. 4B). The magnetic nanoparticles exhibit a broad distribution of sizes

ranging from 20-60 nm. The average particle diameter, based on measurement of 40 nanoparticles, was found to be 36.7 ± 1.7 nm. The combination of the treated MWCNTs with Fe_3O_4 nanoparticles and then, modification with methyl-2-[2-(2-2-[2-(methoxycarbonyl) phenoxy] ethoxyethoxy) ethoxy] benzoate (Fig. 4C), showed a

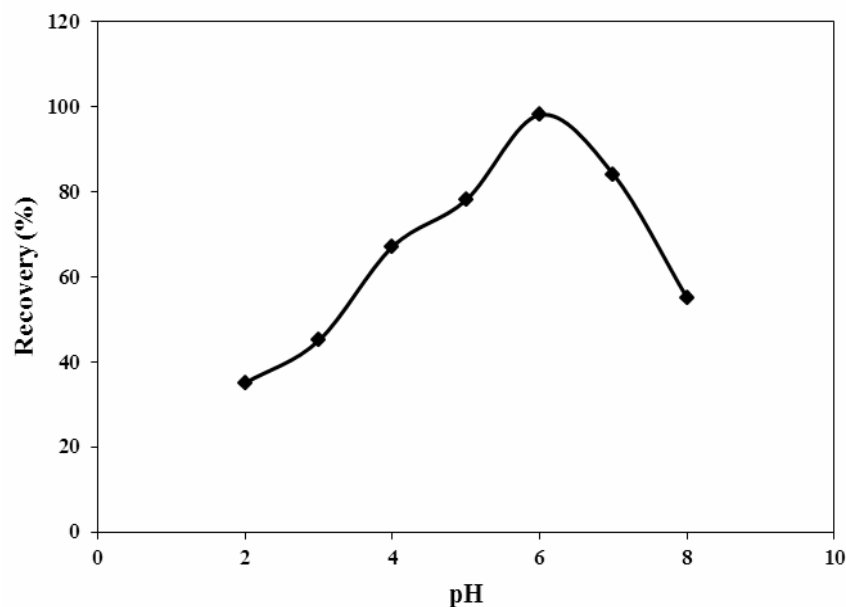


Fig. 6. The effect of sample solution pH.

Table 1. Influence of the Type and Concentration of Eluent on the Recovery of Tl(I) Ions

Eluent	Concentration (M)	Recovery (%)
Nitric acid	0.1	76.7
Acetic acid	0.1	50.6
Hydrochloric acid	0.1	98.4
Phosphoric acid	0.1	79.8
Thiourea	0.1	21.3
Hydrochloric acid	0.01	47.9
Hydrochloric acid	0.05	87.6
Hydrochloric acid	0.5	96.2
Hydrochloric acid	1.0	91.5

nanocomposite with rough surface.

The magnetic hysteresis loops of MMWCNT and modified MMWCNT are illustrated in Fig. 5. The magnetization of the modified MMWCNT was measured as

9.8 emu g⁻¹, less than that for the MMWCNT composite (13.6 emu g⁻¹).

The point of zero charge (pH_{PZC}) of the adsorbent is known to be an important characteristic. The pH_{PZC} of

MWCNT, MMWCNT and modified MMWCNT were found to be 2.78, 5.11 and 5.37, respectively.

Optimization of MSPE Parameters

Effect of pH. An appropriate pH is not only important for the extraction of the metal ions but also important for the selectivity behaviour [29]. To determine the optimal pH, the effect of pH on the adsorption of Tl(I) ions was studied over the range of 2.0-8.0 and the results are shown in Fig. 6. As can be seen, the sorption ability of Tl(I) ions by the as-prepared nanocomposite is significantly dependent on the pH value of the aqueous solution. The thallium recovery increased with increasing pH from 2.0 to 6.0 and then gradually decreased when the pH increased further to 8.0. The observed dependence of recovery efficiency on pH may be attributed to the changes in the surface of the adsorbent with pH, consistent with the pH-dependent zeta-potential of modified MMWCNTs. At $\text{pH} < \text{pHpzc}$, the surface of the adsorbent is positively charged and therefore adsorption of Tl(I) ion at the adsorbent decreases. Above this pH, the sorbent is negatively charged. Also, the decrease in thallium recovery at higher pH (>6.0) is due to the competition of the hydroxide with the chelating agent in the formation of a complex with thallium ions. A pH of ~ 6 was selected in subsequent studies.

Effect of type and concentration of eluent. To elute the thallium ions from the modified MMWCNT nanocomposite, a series of eluents including nitric acid, hydrochloric acid, acetic acid, phosphoric acid and thiourea were investigated. The results (Table 1) showed that with 0.1 M hydrochloric acid desorption was nearly completed. Then, the effect of the hydrochloric acid concentration on the desorption efficiency was studied by varying its concentration in the range of 0.01-1.0 M. As can be seen in Table 1, at concentrations more than 0.1 M hydrochloric acid quantitative recovery of thallium ions could be obtained. Therefore, a concentration of 0.1 M hydrochloric acid was employed in subsequent studies.

Effect of sample volume. The sample volume is an important parameter in preconcentration procedure [30]. Due to the magnetically assisted separation of the modified MMWCNT, it is possible to collect the adsorbent from larger volumes of the sample solution. To study the effect of sample volume on the extraction of 15 μg of thallium ions,

various sample volumes in the range of 20-200 ml were used (Fig. 7). It was found that extraction of thallium ions were almost constant up to 100 ml of the aqueous phase. So, the preconcentration factor (PF) was calculated as 100 by the ratio of the highest sample volume (100 ml) and the eluted volume (1 ml).

Effect of sorption and desorption time. To investigate the sorption and desorption time, shaking times in the range of 1-10 min were investigated. According to the experimental results, thallium ions can be adsorbed on the modified MMWCNT nanocomposite within 5 min and also desorbed quantitatively ($>99\%$) with eluent in 7 min.

Effect of the amount of adsorbent. To study the optimum amount of adsorbent, different weights in the range from 5-30 mg were used for thallium extraction. From the experimental results, the minimum amount of 20 mg of the modified MMWCNT nanocomposite was enough for the quantitative recovery of the thallium ions.

Sorbent Capacity

The capacity of the synthesized sorbent, defined as the maximum amount of the analyte retained by the certain amount of magnetic nanocomposite was investigated. For this purpose, 50 mg of the MMWCNT (or modified MMWCNT) nanocomposite was added to 50 ml of Tl(I) solution (50 mg l^{-1}) under optimum conditions. After 60 min, the sorbent was separated and the concentration of the thallium in the supernatant solution was determined. The capacity of the sorbent for the thallium was determined through the differences in the amount of thallium in the initial and final solutions. The capacity of the MMWCNT and modified MMWCNT nanocomposite was found to be 26.1 mg g^{-1} and 34.8 mg g^{-1} , respectively.

Interference Study

Under optimized conditions, the interference of coexisting ions on the recovery of thallium ion was investigated. For doing so, a solution of $0.3 \mu\text{g ml}^{-1}$ of thallium containing the corresponding interfering ions was prepared and operated according to the recommended procedure. The criterion for the interference of each species was set at $\pm 5.0\%$ in the analytical signal obtained for a solution containing Tl(I). Table 2 shows the substances studied and their maximum tolerable amounts. The recovery of Tl(I) was not less than those in the absence of coexisting

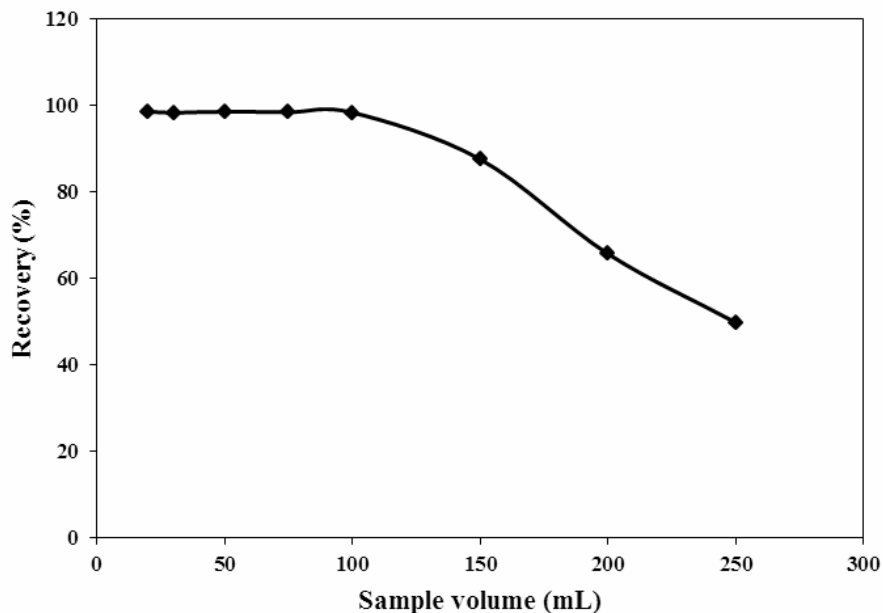


Fig.7. Effect of sample volume on the recovery of Tl(I).

Table 2. Tolerance Limits of Diverse Ions for the Determination of Thallium(I)

Foreign ion	Molar ratio (ion/Tl(I))	Recovery (%)
Ba ²⁺	700	96.7
Mg ²⁺	1000	100.0
Cd ²⁺	700	99.2
Ni ⁺	900	102.1
Zn ²⁺	800	99.8
Pb ²⁺	500	95.9
Cu ²⁺	900	98.4
Ag ⁺	900	100.5
Co ²⁺	1000	97.9
SO ₄ ²⁻	1000	103.2
NO ₃ ⁻	2000	101.9
I ⁻	1000	97.2
Br ⁻	1000	102.3

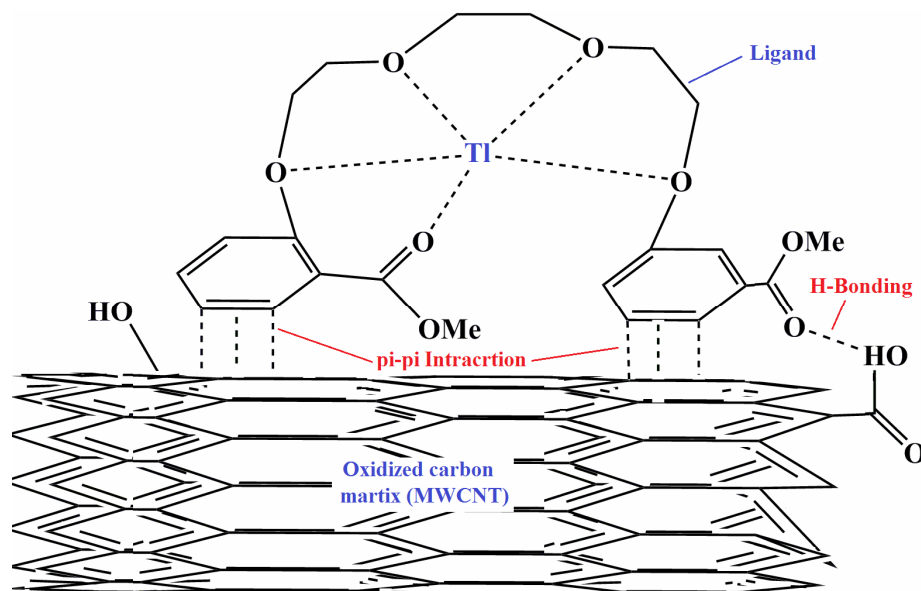


Fig. 8. Proposed mechanisms for ligand and Tl(I) adsorption onto the prepared nanocomposite.

Table 3. Comparative Data from Previously Reported Method for Determination of Thallium(I) Ions

Method	Material	Linear range ($\mu\text{g l}^{-1}$)	LOD ($\mu\text{g l}^{-1}$)	R.S.D (%)	PF	Ref.
IL/USA/DLLME-FAAS	DCH-18-crown-6	5-400	0.64	1.43	98.2	[31]
MCPE-DPASV	Graphene-OPFP-L	3.0-240	0.76	2.7	-	[32]
SPE-FAAS	Immobilized oxine on SDS-coated alumina	20-200	2.5	2.6	77	[33]
DSPE-FAAS	$\text{Fe}_3\text{O}_4/\text{SiO}_2$ /palmitic acid	4-150	0.85	3.2	298	[34]
MSPE-FAAS	Modified MMWCNTs	3-280	0.59	1.9	100	This work

Abbreviations: IL/USA/DLLME: Ionic liquid ultrasound assisted dispersive liquid-liquid microextraction, DCH-18-crown-6: dicyclohexyl-18-crown-6, MCPE: Modified carbon paste electrode, DPASV: Differential pulse anodic stripping voltammetry, OPFP: 1-(2,4-Dichlorophenyl)-3,3,3-triphenylpropan-1-one, SPE: Solid-phase extraction, SDS: Sodium dodecyl sulfate FAAS: Flame atomic absorption spectrometry, DSPE: dispersive solid phase extraction.

ions, indicating that modified MMWCNT had a high selectivity towards Tl(I) and could present a potential to apply in real samples analysis.

Adsorption Mechanism and Reusability

It is necessary to investigate the state of donor groups of ligand distributed on the surface of MMWCNT

Table 4. Determination of Thallium in Different Real Samples

Sample	Added ($\mu\text{g l}^{-1}$)	Found ($\mu\text{g l}^{-1}$) ^a	Recovery (%)
Tap water ^b	0	N.D. ^b	-
	20.0	19.6 ± 0.7	98.0
Well water ^d	0	N.D.	-
	20.0	19.5 ± 0.9	97.5
Synthetic sample	-	40.9	102.2
Nail	-	$0.12^c \pm 0.03$	-
	0.20	0.31 ± 0.05	96.9

^aMean \pm Relative Standard Deviation (n = 3). ^bNot Detected. ^c $\mu\text{g g}^{-1}$.

nanocomposite. As can be seen in Fig. 8, the mechanism of interactions between carbon matrix and noncyclic crown-type polyether is the p-p stacking and hydrogen bonding. As a result, Tl(I) ions are thus favourably adsorbed onto the surfaces of the modified MMWCNT nanocomposite.

The reusability of the prepared magnetic sorbent was examined by subsequent sorption and desorption cycles. The experimental results showed that the modified MMWCNTs can be reused for at least four successive extraction processes with thallium recovery efficiency higher than 95%. From these results, it can be postulated that the modified nanocomposite had a good reusability and stability manner.

Analytical Figure of Merit

To investigate the superiority of the proposed method, the modified MMWCNT was applied for the preconcentration and determination of thallium under the optimized conditions. The linearity range for thallium ions was between 3 and 280 $\mu\text{g l}^{-1}$, with a correlation coefficient of 0.9981. The limit of detection (LOD) defined as $3S_b/m$ (where S_b is the standard deviation of the blank signals and m is the slope of the calibration curve) was 0.59 $\mu\text{g l}^{-1}$. The relative standard deviation (RSD) for six replicate measurements at 100 $\mu\text{g l}^{-1}$ of Tl(I) was found $\pm 1.9\%$. Table 3 compares the characteristic data of the current method with other methods [31-34] for determination of thallium.

As can be seen, from several points of view, the comparison is favourable to the procedure here discussed.

Analytical Applications

To demonstrate the feasibility of the method, the proposed procedure was successfully applied to the determination of trace amount of Tl(I) ions in different real samples. According to Table 4, the proposed procedure can be used for the analysis of Tl(I) in environmental water and nail samples. The procedure was also applied to determine thallium in a synthetic sample with thallium concentration of 40.0 $\mu\text{g l}^{-1}$. It is obvious that satisfactory agreement is achieved between the obtained results and accepted value (Table 4). Evidently, the obtained results show that the procedure is suitable for the thallium analysis in environmental samples.

CONCLUSIONS

In this work, a novel magnetic nanocomposite (MMWCNT) was successfully synthesized and used as MSPE agent for separation and preconcentration of trace amounts of thallium ions prior to the determination by FAAS. The synthesized adsorbent was characterized by XRD patterns, FT-IR spectra, FE-SEM images, VSM and elemental analysis. Under the optimal conditions, the maximum adsorption capacity of the prepared magnetic

sorbent and LOD of the proposed method were calculated to be 34.8 mg g⁻¹ and 0.59 µg l⁻¹, respectively. The preconcentration factor of 100 was achieved in this technique. The simple and rapid determination of thallium with high sensitivity and reproducibility are the advantages of the proposed MSPE method. The obtained results clearly show that the MSPE based on the prepared modified MMWCNT can be used for trace thallium determination in different real samples.

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