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Magnetic multi-wall carbon nanotube nanocomposite as an adsorbent for preconcentration and determination of lead (II) and manganese (II) in various matrices

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ABSTRACT

Magnetic multi-wall carbon nanotube (MMWCNT) nanocomposite was synthesized and used as an adsorbent for preconcentration and determination of lead (II) and manganese (II). The properties of MMWCNT were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), Energy dispersive X-ray spectrometry (EDS) and fourier transform infrared spectrophotometer (FT-IR). This adsorbent was found to be advantageous over conventional solid phase extraction (SPE) in terms of operational simplicity and low time-consuming. MMWCNT, carrying target metals, was easily separated from the aqueous solutions with the help of an external magnet; so, no filtration or centrifugation was necessary. After extraction and collection of MMWCNT, the adsorbed analytes were eluted and analyzed by flame atomic absorption spectrometry (FAAS). Experiments were carried out to investigate the influence of different sorption/desorption parameters. Under the optimized conditions, detection limits and enhancement factors of the proposed method for Pb and Mn were 1.0 and 0.6 $\mu g\,L^{-1}$, 390 and 697 respectively. The presented procedure was successfully applied for determination of Pb(II) and Mn (II) contents in lipstick, rice samples and accuracy was evaluated analyzing a certified reference material Seronorm™ Urine LOT NO2525.

1. Introduction

The determination of Pb and Mn at trace level is an important issue in the context of environmental protection, human health, food and agricultural chemistry as well as high purity materials [1,2]. Manganese is an essential element to man, playing an important role in tissue and bone formation in reproductive functions in carbohydrate and lipid metabolisms [2]. Lead is classified as prevalent toxic metal, which constitutes a major environmental problem [1]. Although major sources of lead contamination from leaded gasoline, Pb-based paints, Pb in public water systems and Pb solder for sealing canned foods have been reduced through various regulatory actions, public concerns still exist over possible sources of Pb contamination. Pb from gasoline and paint can remain in soil and dust for many years, and imported foods and cosmetics may contain unsafe levels of Pb [3]. The determination of heavy metals is of particular relevance to human health [4]. They are normally present at low concentration, therefore sensitive, reproducible and accurate analytical methods are required for their determination [5]. Considering the spectroanalytical

techniques, flame atomic absorption remains popular technique for trace element determination due to high selectivity, speed and low operational cost. However, direct determination of metal ions in complex matrices is limited due to their usually low concentrations and matrix interferences. In trace analysis, preconcentration or separation is necessary to improve sensitivity and selectivity of determination [5]. Several methods have been proposed for separation and preconcentration of trace amounts of lead and manganese such as dispersive liquid–liquid microextraction (LLME), cloud point extraction (CPE), liquid–liquid extraction (LLE), and solid-phase extraction (SPE) [6]. Among these techniques, the SPE procedures, either off-line or on-line, are considered superior to the other procedures for their simplicity, consumption of small volumes of organic solvents, capability to eliminate undesirable matrix components, and their ability to achieve a higher enrichment factors. In SPE, the sorbent plays key role in obtaining higher enrichment efficiency of analytes [6].

Carbon nanotubes (CNTs) have been proposed as a novel solid phase extractant for various inorganic and organic compounds at trace levels. In recent years, CNTs have attracted great attention due to its high surface area and good electrical, chemical, mechanical and conducting properties [7]. CNTs are one of the most commonly used building blocks of nanotechnology [8]. According to the graphene layer, CNTs can be classified into single-wall CNTs

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(SWCNTs) and multi-wall CNTs (MWCNTs). Hexagonal sheets of graphite rolled into cylindrical tubes called SWCNTs and MWCNTs are several concentric SWCNTs similar to a lowered telescopic antenna. CNTs are characterized by high surface area, narrow pore size distribution, low density and the ability of binding functional groups [9].This combination of physicochemical properties makes CNT a very attractive choice for solid phase extraction (SPE).

CNTs have been proven to possess great potential as superior adsorbents for removing many kinds of organic and inorganic contaminants including 1, 2-dichlorobenzene [10], trihalomethanes [11], microcystines [12], nickel [13] and arsenate [14]. The pristine CNTs are difficult to separate from the aqueous solution by using traditional methods such as centrifugation and filtration due to their small size and poor dispersion [15]. The other major drawback of CNT when used as SPE sorbent is resistance to flow of water sample, especially if it contains suspended particles. It restricts the use of large volumes of water samples and hampers the enrichment of trace quantities of analytes. The use of SPE in conventional column form becomes inconvenient when the sample is either dirty (causes plugging of sorbent column) or its volume is high (sample loading consumes lots of time). To optimize the potential applications of CNTs, it is essential to modify them with functional groups and/or nanoparticles in order to integrate the CNTs into desired structures or attach suitable nanostructures to them [16]. The analytical capabilities of CNT can be further increased by surface modification. One such approach is the magnetization of CNT with iron oxide nanoparticles.

In recent years, much research has been conducted towards decorating CNTs with iron oxide and preparing magnetic carbon nanomaterials due to the potential of these as modified CNTs in applications such as electrical devices, magnetic data storage and heterogeneous catalysis [17,18]. The prepared magnetic CNT can be well dispersed in water and easily separated from the medium with the help of a magnet [7]. The application of magnetic particle technology to solve environmental problems has received considerable attention in recent years. Magnetic particles can be used to adsorb contaminants from aqueous or gaseous effluents [19]. These MMWCNTs were used for removal of Ni (II) and Sr (II) [19], Pb (II) and Cu (II) [20], Co (II) [21] and cationic dyes [8]. Pardasani et al. used them for the dispersive SPE of nerve agents from water [7]. Thus, magnetic CNT have an edge over conventional SPE in which sorbents are used in column form.

Taking into account the properties of the MMWCNT and the sensitivity of FAAS, a study was undertaken to develop a method to determine Pb and Mn at trace levels. To this aim, we report the use of MMWCNT for the preconcentration and determination of these metal ions that formed stable complexes with amine and 1-(2-pyridilazo)-2-naphtol (PAN) and the formed complexes were adsorbed on MMWCNT in a batch extraction procedure. The MMWCNT were then collected using an external magnetic field. Afterward, the extracted metal ions were washed from the surface of the adsorbent and determined by FAAS. To the best of our knowledge, this methodology has not been employed previously in the extraction and determination of trace amounts of Pb and Mn from aqueous samples.

2. Experimental

2.1. Chemicals and materials

MWCNTs of 95% purity with average diameter 3–20 nm and length 1–10 μm, number of walls 3–15 were purchased from PlasmaChem GmbH (Berlin, Germany). Reagent grade PAN was used as chelating agent (Merck) without further purification. A 100 mg L^{-1} solution of PAN in methanol was prepared by dissolving proper amount of the reagent. Standard metal solutions used for the experiments as well as for the interference study were prepared by sequential dilution of 1000 mg L^{-1} of standard solutions (Merck) in ultra-pure water. Other reagents including ammonium ferric sulfate and ammonium ferrous sulfate, ammonium hydroxide 28%, methanol, nitric acid, hydrogen peroxide 30% and ammonia were purchased from Merck. The pH of solutions was adjusted by NH$_3$ (0.5 mol L^{-1}) and drop wise addition of HNO3 (0.5 mol L^{-1}). Water was purified using Milli-Q purification system.

The certified reference material Seronorm™ Trace Elements Urine LOT NO2525 was obtained from Sero As (Billingstad, Norway) for method validation.

2.2. Apparatus

Measurements were performed with a Perkin-Elmer model AAnalyst 400 flame atomic absorption spectrometer equipped with a deuterium background corrector and air-acetylene burner. The manganese and lead hollow cathode lamps (Perkin-Elmer) were employed as the radiation sources. The wavelengths used were 217 nm and 279.5 nm using a spectral bandwidth of 0.7 nm and 0.2 nm and the lamp currents were 10 mA and 20 mA for Pb and Mn, respectively. The instrumental parameters were used according to the manufacturer's recommendations. The pH of solutions were determined and adjusted using a pH meter model 823 Metrohm with a combined glass-calomel electrode. Magnetic separation was done by a strong magnet with 1 T magnetic fields (10 × 3 × 2). A Heidolph motor stirrer (Schwabach, Germany) was applied for stirring of solutions with a glassware stirrer. X-Ray powder diffraction (XRD) measurements were performed using a STADI-MP from a STOE company (Germany) with monochromatized Cu K$_\alpha$ radiation. The FT-IR spectra (4000–400 cm^{-1}) were recorded using KBr pellets by Bruker Vector 22 FT-IR spectrophotometer (Bruker, Germany). The MMWCNTs were characterized by scanning electronic microscope (SEM) (Philips XL30, Eindhoven), The Netherlands with gold coating. Energy dispersive X-ray spectrometry (EDS) was performed by Oxford ED-2000 (England).

2.3. Preparation of MMWCNT

MMWCNT was prepared as reported by Qu et al. [22]. Typically, MWCNT was dispersed in concentrated nitric acid and stirred at 60 °C overnight. Purified MWCNT thus obtained, was washed with copious amount of water followed by ethanol and dried at 110 °C for 6 h. The MMWCNT nanoparticle nanocomposite was prepared by the in situ chemical coprecipitation of Fe^{+2} and Fe^{+3} in the alkaline solution in the presence of CNTs. The molar ratio of Fe^{+2}: Fe^{+3} were 1:2. The magnetic composite was prepared by suspending 0.5 g purified CNT in 200 mL of solution containing 0.85 g (NH$_4$)$_2$Fe(SO$_4$)$_2$.6H$_2$O and 1.255 g NH$_4$Fe (SO$_4$)$_2$•12 H$_2$O at 50 °C under argon atmosphere. After the solution was sonicated for 10 min, 20 mL of 8 M NH$_4$OH aqueous solution was added drop wise to precipitate the iron oxides while the mixture solution was sonicated. The pH of the final mixture was controlled in the range of 10–11. To promote the complete growth of the nanoparticle crystals, the reaction was carried out at 50 °C for 30 min. The suspension was cooled to room temperature and MMWCNT was isolated from the mixture with the help of a permanent magnet. Separated MMWCNT was washed thrice with deionized water followed by ethanol. Finally, MMWCNT was dried under vacuum. 0.5 g of obtained MMWCNT was dispersed in 100 mL deionized water.

2.4. Sample preparation

(a) Cosmetic sample: 1.0 g of lipstick sample (MERO, no. 1667-8) was accurately weighed and placed in a furnace, heated slowly to 450 °C, remaining in this temperature until produced white ashes without carbon. After that the sample was cooled and dissolved in diluted nitric acid solution followed by addition of deionized water to 50 mL.

(b) Rice sample: 10.0 g of rice sample that was purchased from a local supermarket in North of Iran was thoroughly washed with deionized water sample and milled to a fine powder. The homogenized sample was dried in oven at 110 °C. The dried sample was placed in a furnace, heated to 450 °C, followed by adding a drop concentrated nitric acid each 2 h until produced white ashes without carbon. After that, the sample was dissolved in diluted nitric acid solution followed by addition of deionized water to 50 mL in a proper volumetric flask.

(c) Urine sample: ultrasonic digestion of Urine certified reference material (CRM) namely, Seronorm LOT NO2525 powder was performed in a reaction vessel containing 2 mL of 1% nitric acid and 2 mL of hydrogen peroxide 30% and was placed in an ultrasonic bath for 30 min. Then the solution was diluted to 5 mL using deionized water. Each vial of CRM, is 5 mL, so we added two of them together to reach 10 mL. Then the following procedure was done on 10 mL of CRM.

2.5. Procedure

40 mL of sample solutions containing 50 μg L^{-1} of Pb and 20 μg L^{-1} of Mn were taken in a 50 mL conical capped tube and the pH of sample solutions was adjusted at 9 by drop wise addition of 0.5 M ammonia. Then 120 μL of the PAN solution (100 mg L^{-1}) as chelating agent and 2 mL of MMWCNT suspension (containing 10 mg of the adsorbent in deionized water) were added into the sample solution and final volume of the solutions was adjusted at 50 mL using deionized water. The mixture was stirred using a glassware stirrer (400 rpm) and allowed to complete the extraction process within 5 min. The samples were treated with a magnet to separate the MMWCNT nanocomposite adsorbents from the solution. After about 2 min, the solutions became limpid and the supernatant solutions were completely decanted. 200 μL of 2 M HNO$_3$ in ethanol (eluent solution) was added to the isolated adsorbent and the obtained mixture was shaked and again exposed on the strong magnet and the clear solution of eluent was injected into FAAS for determination of Pb and Mn concentrations.

3. Results and discussion

3.1. Characterization of the MMWCNT nanocomposite

SEM, EDS, XRD and FT-IR instruments, characterized MMWCNT nanocomposite. The morphologies of the oxidized MWCNT and the synthesized MMWCNT adsorbent were obtained by SEM (Fig. 1). It was observed that iron oxide nanoparticles were successfully coated on the surface of MWCNTs to form MMWCNTs (Fig. 1b). These nanocomposites were explored as adsorbents for preconcentration and extraction of Mn and Pb from aqueous solutions. A typical EDS spectrum taken from the MMWCNT is presented in Fig. 1c, where peaks associated with Fe, C and O can be distinguished. The quantitative analysis gives weight ratios of Fe (14.02%), C (63.92%) and O (22.06%).

Fig. 2 shows the XRD patterns of oxidized MWCNT and MMWCNT nanocomposite. It was observed that the peak corresponding to the structure of MWCNT (Fig. 2b) also exist in the XRD pattern of the MMWCNT nanocomposite (Fig. 2a). Under the reaction conditions employed, there are four types of iron oxides commonly formed including magnetite (Fe$_3$O$_4$), maghemite (γ-Fe$_2$O$_3$), hematite (α-Fe$_2$O$_3$) and goethite FeO(OH). Among them only magnetite and maghemite are magnetic. Six characteristic
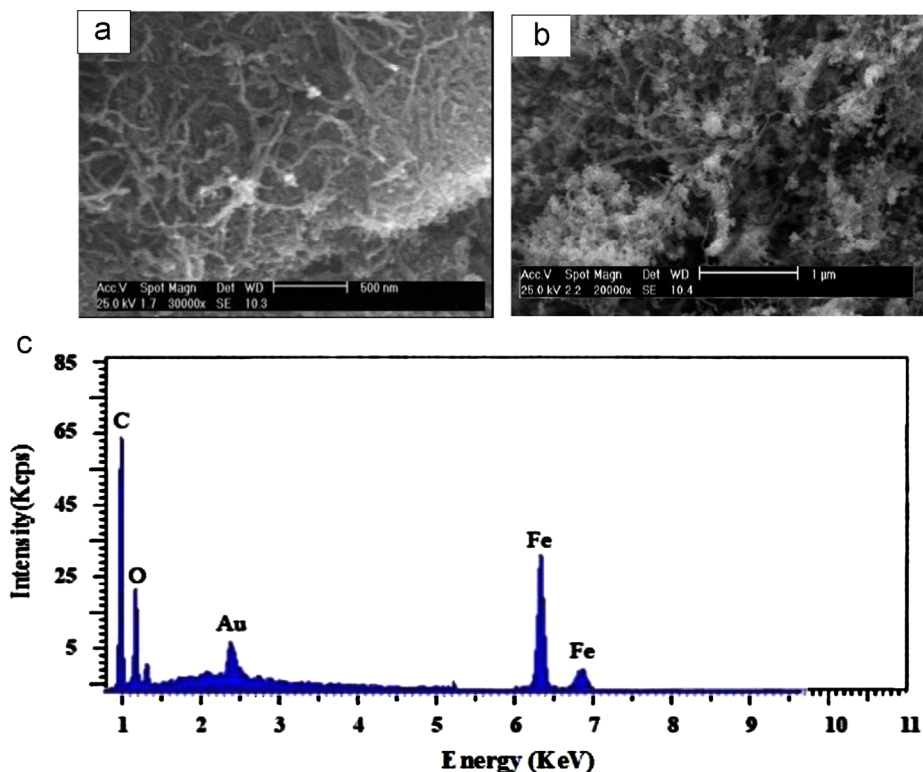

Fig. 1. SEM images of oxidized MWCNT (a) and MMWCNT (b) nanocomposite, EDS spectrum of MMWCNT (c).
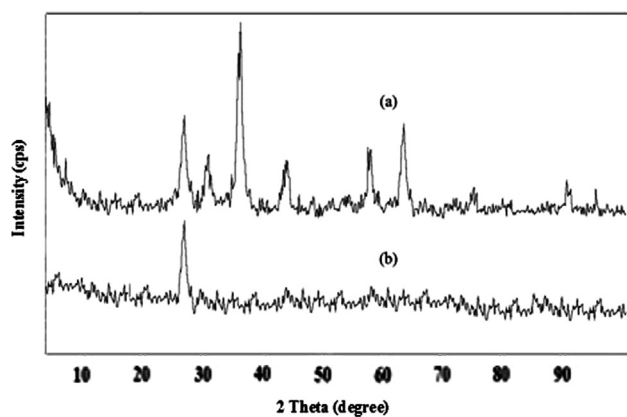
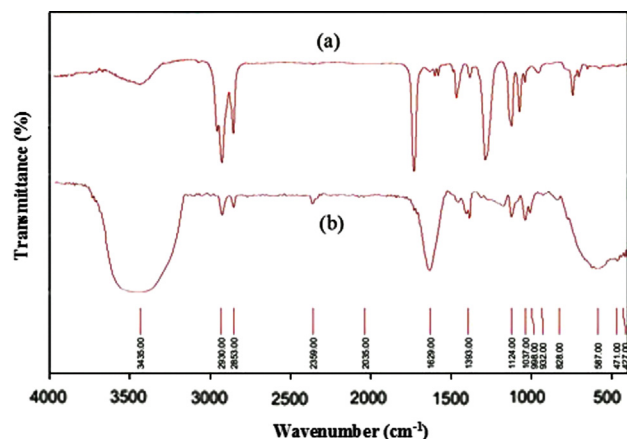**Fig. 2.** XRD patterns of (a) Fe_3O_4–MWCNT nanocomposite and (b) Oxidized MWCNT.

Fig. 3. FT-IR spectra of (a) Oxidized MWCNT and (b) Fe_3O_4–MWCNT nanocomposite.

peaks reveal a cubic iron oxide phase ($2\theta = 30.1°$, $35.0°$, $43.2°$, $53.5°$, $57.3°$ and $62.8°$) which are close to JCPD standards: Fe_3O_4 ($2\theta = 30.014°$, $35.578°$, $43.180°$, $53.652°$, $56.788°$ and $62.757°$) that can be assigned to magnetite or maghemite. Other peaks are also observed at $2\theta = 36.000°$, $43.283°$, $47.680°$, $50.240°$ which may be related to the presence of hematite.

Fig. 3 shows the surface groups on oxidized MWCNT and MMWCNT analyzed by FT-IR. Several significant bands in Fig. 3a are attributed to carboxylic acid groups introduced by acid oxidizing, including the appearance of C=O stretching band at $1723 \, cm^{-1}$, C=C at $1278 \, cm^{-1}$, –CH_2 at $2924 \, cm^{-1}$ and O–H stretching band at $3440 \, cm^{-1}$. The FT-IR spectra of MMWCNTs composites (Fig. 3b) appear at $1629 \, cm^{-1}$ for COO^- asymmetric stretching band, $3435 \, cm^{-1}$ for O–H stretching band and $587 \, cm^{-1}$ for Fe–O characteristic band, indicating the MMWCNT is composed of oxidized MWCNT and Fe_3O_4.

The adsorption characteristics of these nanocomposites were as follows: after dispersion of MMWCNTs in aqueous solution, the MMWCNT nanocomposites were fully mixed with the solution and the color of the solution changed from pink to black. After stirring the mixture, the MMWCNT nanocomposites can be easily separated from the aqueous solution by placing the strong magnet near the tube and the supernatant was colorless.

3.2. Effect of pH

The pH value plays an important role with respect to the adsorption of different ions on CNTs [23–26]. The surface charge depends on the pH of the surrounding electrolyte. The oxidation of CNTs with concentrated acids leads to the surface
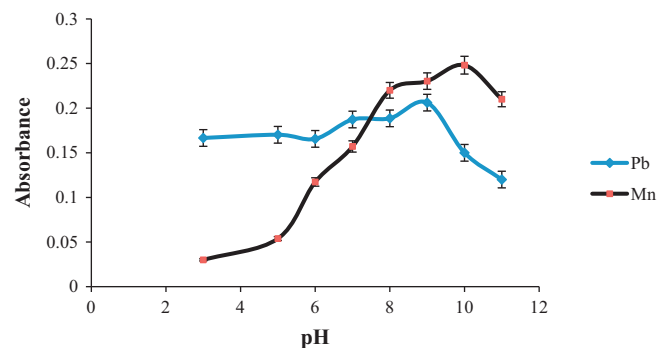

Fig. 4. The effect of sample pH on Absorbance. Concentration of Pb and Mn=50 and 20 µg L^{-1} respectively. 0.5 mL of 100 mg L^{-1} of PAN, 12 mg of the MMWCNT, extraction time=5 min, elution with 200 µL of 2 M HNO_3.

functionalization with oxygen-containing groups, and the iso-electric point (IEP) of MWCNTs shifts to the lower pH values [23]. When the pH of the solution is higher than the IEP of the oxidized CNTs, the negative charge on the surface provides electrostatic attractions that are favorable for adsorbing cations. The decrease of pH leads to the neutralization of surface charge, so the adsorption of cations onto CNTs decreases quickly. In this study, pH not only affects the surface charge of the adsorbent, but also plays an important role in the complexation of the metal ions with PAN.

In order to evaluate the effect of pH on the adsorption of metal ions on CNTs, a series of sample solutions of Pb and Mn were adjusted to different pH values between 3 and 10 by using 0.5 M of NH_3 and 0.5 M of HNO_3 and processed according to the recommended procedure (Section 2.5) (Fig. 4).

Generally, adsorption of tested metal ions increased with the increase of pH. The low adsorption that took place in acidic region can be attributed in part to competition between metal ions and hydrogen on the same site. With the increase of pH, the charge of CNTs surface becomes more negative, which causes electrostatic interactions and thus results in higher retention of metal ions. In addition, optimum pH for complexation of the heavy metal ions with PAN is between 8 and 10 [6]. On the other hand, under these conditions, metal ions can form stable cationic ammonia complexes, which can in turn prevent the metal ion precipitation at alkaline conditions. Formation the cationic ammonia complexes enhances adsorption of the metal ions on the negative surface of the adsorbent at alkaline conditions. However, at pHs higher than 10.0, metal ions can precipitate as hydroxide form [2,6]. Thus pH=9.0 was chosen for further studies.

3.3. Effect of PAN concentration

PAN acts as tridentate ligand and can form very stable complexes with metal ions (as ML or ML_2) through hydroxyl oxygen atom, nitrogen atom of pyridine and one of the azo group nitrogen atoms [27]. PAN complexes of Pb and Mn can be easily interacted with MMWCNT, which increases absorption of them. At 20 µg L^{-1} and 50 µg L^{-1} of Mn and Pb, the effect of PAN concentration on absorbance was studied by changing the molar ratio of PAN to metal ions in the range of 0–20 (results not shown). By increasing the PAN to metal ions ratio up 4 for both ions, absorbance will increase and at higher ratios, absorbance was constant.

3.4. Effect of amount of MMWCNT

In comparison with the traditional adsorbents (microsized sorbents), CNTs offer a significantly higher surface area to volume ratio. Therefore, satisfactory results can be achieved with fewer

amounts of CNTs. In addition, insufficient amount of adsorbent will cause the breakthrough of the analytes whereas higher amounts will increase the cost and time of the analytical procedure. Higher amounts of adsorbent material may also adversely affect the final absorbance if the back extraction (elution) of the analytes from sorbent is not quantitative.

In order to study the effect of the adsorbent, 4–15 mg of the MMWCNT was added to 50 mL of the sample solution. The obtained results showed that by increasing the sorbent amounts from 4 up to 10 mg due to the increasing of accessible sites, absorbance slowly increased then, remained constant. So, a 10 mg of the MMWCNT was selected for all subsequent experiments for both ions.

3.5. Effect of sample volume and extraction time

In SPE, the sample volume is determined by typical concentrations of potential analytes and degree to which they will need to be concentrated from the sample prior to analysis. It also depends upon the detection limits and the linearity range of the instrument used for the analysis. In order to obtain a higher enrichment factor, a larger volume of sample solution is required. Due to the magnetically assisted separation of the adsorbent (MMWCNT), It is possible to collect the adsorbent from larger volumes of the sample solution. Thus, the extraction of $50\ \mu g\ L^{-1}$ of Pb and $20\ \mu g\ L^{-1}$ of Mn from different volumes of water samples ranging from 50 to 150 mL was investigated. Lead (II) ions were quantitatively recovered in the sample volume range of 50–100 mL while the recoveries of manganese (II) ions were quantitative in the sample volume range of 50–150 mL.

For studying effect of extraction time on extraction efficiency of the metal ions, the extraction times were varied in the range of 1–15 min. It was observed that after 5 min, absorbance of the metal ions had no significant variation. Thus, the extraction time of 5 min was selected for further studies.

3.6. Desorption conditions

One of the important factors that affect the preconcentration procedure is the type, volume and concentration of the eluent used for the removal of metal ions from the sorbent [28].

In preliminary studies, volume of the eluent was investigated and was optimized. At higher volumes of the eluent, the FAAS absorption of the metal ions decreased due to dilution effect. On the other hand, at lower volumes of the eluent, separation of the eluent from the adsorbent was difficult, so, 200 μL of the eluent was selected as optimum value.

Adsorption of the analytes onto MMWCNT is highly pH-independent (adsorption of the complexes on the surface of the adsorbent is performed at pH=9.0); hence desorption of the analytes can be accomplished by decreasing the pH of the solution. In order to desorp adsorbed Pb and Mn complexes from MMWCNTs, various eluting solutions with different concentrations were examined on the optimal working conditions with model solutions (Fig. 5). Maximum absorbance was obtained with 50% (v/v) ethanol in 2 M HNO$_3$ for both analytes. Hence, 200 μL of ethanol in 2 M HNO$_3$ was taken as solvent of choice and used in the further studies for extraction purposes.

On the other hand, in order to obtain maximum desorption efficiency, effect of the desorption time was investigated in the range of 1–5 min. Based on the obtained results, a time of 2 min was chosen for further studies.
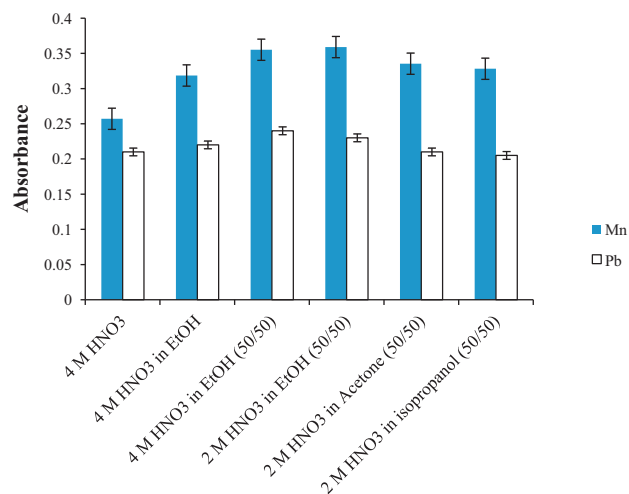

Fig. 5. Selection of type and concentration of eluent. pH=9.0, concentration of Pb and Mn=50 and 20 μg L^{-1} respectively, 120 μg μL of 100 mg L^{-1} of PAN, extraction time=5 min.

Table 1
Effects of interfering ions on preconcentration and determination of 20 μg L^{-1} of Mn and 50 μg L^{-1} of Pb.

Interference	Interference to Pb ratio (w/w)	Recovery (%) (Pb)	Interference to Mn ratio (w/w)	Recovery (%) (Mn)
Na$^+$, K$^+$	1000	100	1000	100
Ca^{+2}	200	104	800	102
Ni^{+2}	100	105	500	94
Cu^{+2}	140	95	500	103
Sr^{+2}	100	90	80	96
As^{+3}	160	110	600	102
Zn^{+2}	160	109	500	95
Cd^{+2}	100	100	200	101
Al^{+3}	100	100	100	97
Pb^{+2}	–	–	700	95
Mn^{+2}	800	100	–	–
Fe^{+3}	100	90	150	90
Mo^{+6}	200	100	400	104
U	100	110	600	104
Th	100	110	500	93

3.7. Interference studies

In view of the high selectivity provided by FAAS, the only interference may be attributed to the preconcentration step, in which the cations may react with PAN, which may lead to decrease in extraction recovery. So, interference of coexisting ions on the preconcentration of Pb and Mn was investigated. To study the effect of interfering counter ions, 50 mL of the solutions containing 20 μg L^{-1} of Mn and 50 μg L^{-1} of Pb and the interfering ions with the weight ratios in the range of 100–1000 respected to Pb and Mn ions were taken and the recommended procedure based on Section 2.5 was followed. The results are shown in the Table 1. It can be seen that a very good selectivity was achieved.

3.8. Regeneration experiments

The regeneration of the adsorbent is a key factor in improving process economics. The repeated availability of MMWCNT through many cycles of sorption/desorption was investigated to evaluate the application potential of this material in the preconcentration and determination of Pb and Mn from aqueous solutions. MMWCNT can be regenerated by acid/ethanol and reused for eight successive SPE processes. At higher cycles, absorbance

decrease may be due to losing or dissolving some amounts of the adsorbent during the successive steps.

extraction, which were about 390 and 697 for Pb ($V=100$ mL) and Mn ($V=150$ mL) respectively.

3.9. Analytical performance

In order to evaluate the applicability of the developed extraction method to analysis of Lead and manganese, repeatability, reproducibility, linearity and limit of detection were investigated utilizing standard solutions in distilled water. Results of analytical parameters are enumerated in Table 2. The calibration curves for studied elements were linear from 0.5–100 µg L^{-1} and 5–200 µg L^{-1} with the same coefficient of determination (R^2) of 0.998 for Mn and Pb respectively. The limit of detection (LOD) for the elements based on $3S_b/m$ definition (where m is the slope of the calibration curve and S_b is the standard deviation for six blank measurements) were 0.6 and 1 µg L^{-1} for Mn and Pb respectively. Relative standard deviations (RSDs%) of the method for determination of the elements were 4.1% and 4.3% (six replicate measurements at 20 µg L^{-1} of Mn and 50 µg L^{-1} of Pb) for Mn and Pb respectively. The enhancement factors were calculated as the ratio between the slopes of the calibration curves after and before

3.10. Application of the proposed method to real samples

In order to evaluate the applicability of the developed extraction method to analysis of Pb and Mn in the real samples with complex matrices, lipstick, rice and urine samples were extracted and analyzed using the proposed method under the optimum conditions. Sample preparation for the real samples was performed according to Section 2.4. The obtained results are given in Table 3. Accuracy was assessed by comparing results with those obtained by direct determination using inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS). According to the paired t-test, no significant difference at 95% confidence level was observed.

Also, in order to establish the validity of this method certified reference material (CRM) namely, Seronorm LOT NO2525 was analyzed. The result found was in good agreement with the certified values of CRM (Table 3).

Table 2
Figures of merit of the proposed method for the extraction and determination of Pb^{+2} and Mn^{+2}.

Metal ion	Enhancement factor (EF)	Detection limit (µg L^{-1}) (LOD)	RSD % ($n=6$)	Linear dynamic range (µg L^{-1}) (LDR)	Calibration equation	R^2
Pb^{+2}	390	1.0	4.3	5–200	$I=0.003$ C–0.002	0.998
Mn^{+2}	697	0.6	4.1	0.5–100	$I=0.009$ C+0.037	0.998

Table 3
Determination of Pb^{+2} and Mn^{+2} in real samples (mean ± SD, $n=3$).

Sample	Proposed Pb^{+2}	Method Mn^{+2}	ICP-MS Pb^{+2}		ICP-OES Mn^{+2}
Rice (µg g^{-1})	0.67 ± 0.04	9.4 ± 0.2	0.75 ± 0.02		8.8 ± 0.1
Lipstick (µg g^{-1})	1.50 ± 0.09	21.4 ± 1.0	1.70 ± 0.02		22.5 ± 0.4
CRM urine (µg L^{-1})			Certified value		
	86.3	10.2	91.1	11.1	
Uncertainty (95%)			84.1–98.1	10.1–12.1	

Table 4
Comparison of the proposed method with some of the methods reported in the literature extraction and determination of lead and manganese using SPE method.

Adsorbent	EF		LOD		RSD (%)		Detection	Ref.
	Pb	Mn	Pb	Mn	Pb	Mn		
Oxidized MWCNT	15.4	20.6	1.0	0.28 µgL^{-1}	4.62	2.64	FAAS	[29]
MWCNT	20	20	8.0	3.5 µgL^{-1}	–	–	FAAS	[30]
Fe$_3$O$_4$@SiO$_2$	–	–	0.26	0.26 ngL^{-1}	7.4	4.6	ICP-MS	[31]
Amberlite XAD-2010/DDTC	–	–	0.26	0.10 µgL^{-1}	2.1	5.1	FAAS	[32]
Diaion SP-850/Alpha-benzoin oxime	50	50	0.5	0.42 µgL^{-1}	< 8.0	< 8.0	FAAS	[33]
Amberlite XAD-2000/8-Hydroxyquinoline	100	100	0.8	2.2 µgL^{-1}	< 6.0	< 6.0	FAAS	[34]
Activated carbon	–	–	187	113 ngL^{-1}	4.2	3.6	FAAS	[35]
MMWCNT 697	390	697	1.0	0.6 µgL^{-1}	4.3	4.1	FAAS	This work

The results of analysis of real samples showed that the development method can be reliably used for the determination of Pb and Mn in different matrices.

3.11. Comparison of the proposed method with other methods

The proposed method was compared with a variety of methods reported recently in the literature for the preconcentration and determination of lead and manganese. The distinct features of the proposed method are summarized in Table 4. As can be seen from Table 4, it is evident that the enhancement factor obtained with the MMWCNT is very high in comparison with other methods. Also, good sensitivity, large dynamic linear range, low detection limits which can be attributed to the large surface area, and rapid dynamics of extraction of MMWCNT are the other significant features of the method which are comparable to or even better than some of them which use very sensitive detection method such as ICP-MS.

4. Conclusion

The magnetic multi-wall carbon nanotube nanocomposite with high magnetism were prepared and used as sorbent for preconcentration and determination of manganese and lead from aqueous solutions. This sorbent was successfully applied for convenient, fast, simple and efficient enrichment of trace amounts of Mn and Pb from lipstick, rice and urine samples. The magnetic separation greatly improved the separation rate while avoided the time-consuming column passing or filtration operation. The main benefits of this methodology are no use of toxic organic solvents, simplicity, low cost, high enhancement factor and good stability. Easy regeneration is another property of MMWCNT, and the experiments have proved that these adsorbents can be reused at least eight times on average without the obvious decrease of recovery after wash/clean procedures.

The methodology proposed has proved to be simple, reliable, sensitive and reproducible. Therefore, the method could be applied to the accurate determination of Mn and Pb in other samples with complex matrices.

Acknowledgment

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