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Application of modified multiwalled carbon nanotubes as solid sorbent for separation and preconcentration of trace amounts of manganese ions

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Abstract In this work, the potential of modified multiwalled carbon nanotubes for separation and preconcentration of trace amounts of manganese ion is studied. Multiwalled carbon nanotubes were oxidized with concentrated HNO_3 and then modified with loading 1-(2-pyridylazo)-2-naphtol. Mn(II) ions could be quantitatively retained by modified multiwalled carbon nanotubes in the pH range of 8–9.5. Elution of the adsorbed manganese was carried out with 5.0 mL of 0.1 mol L^{-1} HNO_3. Detection limit is 0.058 ng mL^{-1} and analytical curve is linear in the range of 0.1 ng mL^{-1}–5.0 μg mL^{-1} in the initial solution with a correlation coefficient 0.9977 and the preconcentration factor is 100. Relative standard deviation for eight replicate determination of 0.5 μg mL^{-1} of manganese in the final solution is 0.41%. The effects of the experimental parameters, including

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the sample pH, flow rates of sample and eluent solution, eluent type, breakthrough volume and interference ions, were studied for preconcentration of Mn(II) ions in detail to optimize the conditions. The method was successfully applied for separation, preconcentration and determination of manganese in different samples.

1. Introduction

Carbon nanotubes (CNTs) are an allotrope of carbon. A carbon nanotube is a one atom thick sheet of graphite rolled up into a seamless cylinder with diameter of the order of a nanometer. Such cylindrical carbon molecules have novel properties that make them potentially useful in a wide variety of applications in nanotechnology, electronics, optics and other fields of materials science. They exhibit extraordinary strength and unique electrical properties and are efficient conductors of heat (Meyyappan, 2005). The name Carbon nanotubes is derived from their size, since the diameter of a nanotube is on the order of a few nanometers, while they can be up to several millimeters in length. There are two main types of carbon nanotubes: single walled carbon nanotubes (SWCNTs) and multiwalled carbon nanotubes (MWNTs) depending on the carbon atom layers in the wall of the nanotubes (Iijima and Ichihashi, 1993). Since carbon nanotubes were first prepared in 1991 (Popov, 2004), they have become attractive materials for their novel structural characteristics (Liang et al., 2004). CNTs have high surface area, mechanical strength, thermal and chemical stability. Due to their unique characteristic and strong adsorption ability (Saridara et al., 2005) , they have been successfully used to remove many kinds of pollutants such as dioxin from air (Long and Yang, 2001), lead (Li et al., 2006), cadmium (Li et al., 2003a,b), zinc (Lu and Chiu, 2007), fluoride (Li et al., 2003a,b), 1,2-dichlorobenzene (Peng et al., 2003) and trihalomethanes (Lu et al., 2005) from different media.

A large number of industries discharge metal-containing effluents into water resources without adequate treatment. Contamination of the environment by manganese is currently an area of concern. Although, manganese is an essential micronutrient, over-exposure causes poisonous effects such as memory impairment, disorientation, hallucinations, speech disturbance, compulsive behavior and acute anxiety (Seiler and Sigle, 1998; Wang and Lu, 1995). Manganese is present in many alloys and is found in a number of pharmaceutical, biological and environmental samples. The World Health Organization study group suggested occupational limits of manganese are 0.2 mg m^{-3} and 0.03 μg mL^{-1} in air and water, respectively (Seiler and Sigle, 1998). Very low concentrations of manganese are present in various complex samples. Therefore, it is from the analytical point of view to develop a sensitive, selective and economical method for determination of the trace amounts of manganese (Miyazaki and Tao, 1991). Flame atomic absorption spectrometry (FAAS) is a simple and easily available technique for determination of manganese in real samples. However its main problem is the low sensitivity for trace manganese at ng mL^{-1} level. This limitation can be overcome by the use of preconcentration. For this purpose, various preconcentration/separation sorbents including Amberlyst 36 (Kenduzler et al., 2006), XAD-2 resin (Dogutan et al., 2003), polyvinylpyrrolidine (Tokman et al., 2004), anion exchanger resin (Sarzanini et al., 2001), activated carbon (Xingguang et al., 2003) and modified kaolinite (Afzali et al., 2005) are used.

The goal of this study is to modify MWCNTs by 1-(2-pyridylazo)-2-naphtol (PAN). Moreover, the performances of modified multiwalled carbon nanotubes (MMWCNTs) are tested as a new sorbent for the preconcentration of trace Mn(II). Separation and preconcentration of Mn(II) were carried out in a glass column filled with MMWCNTs and the Mn(II) is determined by AAS. Applications of the proposed method for the analysis of different samples are also described.

2. Experimental

2.1. Apparatus

A Varian model SpectrAA 220 flame atomic absorption spectrometer (Varian Inc., Palo Alto, CA) was used in the following conditions: wavelength, 279.5 nm; lamp current, 5.0 mA; slit width, 0.2 nm; acetylene flow, 1.5 L min^{-1}; air flow as oxidant, 3.5 L min^{-1}. The measurement pH was carried out using a Metrohm pH meter (Model 713) with a combined pH glass electrode calibrated against two standard buffer solutions at pH 4.0 and 7.0. The column dimensions were 10×80 mm with a sintered glass plate located at the bottom of the column.

2.2. Reagents and materials

All chemical materials were of analytical reagent grade. Manganese(II) sulfate monohydrate from Merck (Merck, Darmstadt, Germany) was dissolved in double distilled water, diluted to 1000.0 mL in a standard volumetric flask, and standardized by a known method (Vogel, 2000). Buffer solution with pH 8.0–9.5 was prepared by mixing an appropriate ratio 0.5 mol L^{-1} ammonia and ammonium acetate. A 0.05% solution of 1-(2-pyridylazo)-2-naphtol (Merck) was prepared by dissolving it in ethanol. MWCNTs with an average outer diameter of 3–20 nm, length of 1–10 μm, number of walls 3–15 and surface area of 350 m^2 g^{-1} were obtained from Plasma Chem. GmbH (Berlin, Germany).

2.3. Preparation of MMWCNTs

Raw MWCNTs were heated at 300 °C for 40 min to remove amorphous carbon. Prior to use, MWCNTs were oxidized with concentrated HNO_3 according to the literature, in order to create binding sites onto the surface of MWCNTs (Xu et al., 2003). The treatment was carried out by the dispersion of 5 mL of 6 mol L^{-1} HNO_3 to 1.0 g of MWCNTs, and then refluxing for 6 h at 100 °C. Afterward, the oxidized MWCNTs were washed with distilled water until the removal of any excess nitric acid (neutral pH of solution), then a 0.05% solution of 1-(2-pyridylazo)-2-naphtol was added to MWCNTs, and refluxed for 3 h at 75 °C that produced MMWCNTs which were dried at 100 °C and stored for use.

2.4. Preparation of column

MMWCNTs (20 mg) were dispersed in water, and then poured into a funnel-tipped glass tube plugged with a small piece of glass wool at the ends. A glass column packed with 0.02 g of MMWCNTs sorbent (height of packing being about 15 mm) were used as the operational column. The column could be used repeatedly 50 times after washing with distilled water.

2.5. Recommended procedure

An aliquot of the solution containing 0.05–50.0 μg of manganese was taken in a 100 mL beaker and it was added to 5 mL of buffer solution with pH ~8.5, then diluted to ~50 mL with distilled water. This solution was passed through the column at a flow rate of 2 mL min^{-1}. After passing this solution, the column was washed with 5 mL of distilled water. The adsorbed manganese on the column was eluted with 5.0 mL of 0.1 mol L^{-1} nitric acid, at a flow rate 1 mL min^{-1}. The eluent was collected in a 5.0 mL volumetric flask and manganese was determined by flame atomic absorption spectrometry.

3. Results and discussion

Preliminary experiments showed that MWCNTs have a low tendency for the retention of Mn(II) (less than 62%) but were not selective. Recent work (Afzali and Mostafavi, 2008) indicates that the MWCNTs can adsorb organic material, so 1-(2-pyridylazo)-2-naphtol was added to MWCNTs, since 1-(2-pyridylazo)-2-naphtol is a good reagent complexing with Mn(II). MMWCNTs were capable of retaining Mn(II) in the sample solution (98.7 adsorption of Mn(II) when the test solution contained 2.5 μg of Mn(II) in 50 mL water). So, the adsorption of PAN on the surface of MWCNTs had an effective role in sorption of Mn(II). In other words the sorbent was selective and sensitive for separation and preconcentration of trace amounts of manganese in the sample solution. In order to achieve the best performance, the separation/preconcentration procedure was optimized for various analytical parameters, such as, the nature and concentration of eluent, pH of the sample solution, volume and type of the eluent solution, the flow rate of the eluent and the sample solutions and volume of the sample solution. Various ions interferences effects were also investigated.

3.1. Effect of the sample pH

Due to pH, one of the important analytical factors in the solid phase extraction of metal ions (Mester and Sturgeon, 2003), the influences of pH of the aqueous solution on the recovery of Mn(II) ions on MMWCNTs were investigated. The percentage of sorption of Mn(II) on the sorbent surface as a function of the pH of the sample solution is shown in Fig. 1. The percentage of sorption of Mn(II) depends on the pH of the sample solution. The optimum pH range was around 8.0–9.5. In subsequent studies, the pH was maintained at approximately 8.5.

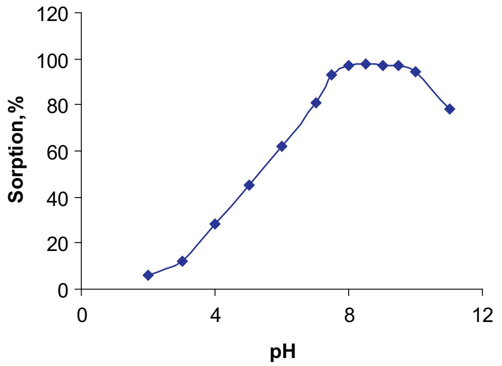

Figure 1 Effect of the sample pH on the percent sorption of Mn(II). Conditions: Mn, 2.5 μg; flow rate of sample, 2 mL min^{-1}; eluent solution, 5.0 mL HNO_3, 0.1 mol L^{-1} with flow rate 1 mL min^{-1}; wavelength, 279.5 nm; lamp current, 5.0 mA; slit width, 0.2 nm; acetylene flow, 1.5 L min^{-1}; air flow as oxidant, 3.5 L min^{-1}.

3.2. Effect of flow rate of sample

Flow rate of the sample solution is a measure of the contact time between the sample solution and the sorbent. The flow rate of the sample solution was studied within the range 0.2–5 mL min^{-1}. Results showed that the flow rate variation in the range of 0.2–3 mL min^{-1} did not have a significant effect on the sorption of the Mn(II). It was found that the adsorption of Mn(II) on MMWCNTs is relatively rapid. In order to achieve better precision, a flow rate of 2 mL min^{-1} was chosen for further studies.

3.3. Selection of eluent

A series of selected eluents such as, HCl, HNO_3, H_2SO_4 and sodium thiosulfate were used in order to find the best eluent for desorption of manganese ion from the sorbent surface. An aliquot of 0.5 μg mL^{-1} Mn(II) solution was passed at a flow rate of 2 mL min^{-1}, through a series of columns containing 0.02 g sorbent at pH 8.5. The adsorbed manganese ion was eluted by passing through the above selected eluents by means of 5.0 mL of 0.1 mol L^{-1}. The amount of manganese ion hence extracted into the liquid phase by each eluent was measured using FAAS and the percentage of recoveries of Mn(II) were calculated in each case. The results showed that the best recovery was achieved when HNO_3 was used as the eluent.

3.4. Effect of eluent flow rate

The effect of flow rate of the eluent solution on desorption of 2.5 μg Mn(II), from the sorbent surface (0.02 g) was studied in range of 0.5–5 mL min^{-1}. The manganese ion was desorbed completely at an eluent flow rate of less than 2 mL min^{-1}, for effective and quantitative elution. However a flow rate of 1 mL min^{-1} was chosen for future studies.

3.5. Breakthrough volume

When solutions containing 2.5 μg of Mn(II) in 100, 200, 300, 400 and 500 mL water were passed through the columns, the

Table 1 Analysis of manganese in standard alloy.

Sample	Composition (%)	Found[a]	Recovery (%)
NKK No. 920 Aluminum alloy	Cr, 0.27; Si, 0.78; Bi, 0.06; Ti, 0.15; Sn, 0.20; Ga, 0.05; Pb, 0.10; Fe, 0.72; Zn, 0.80; Ca, 0.03; Mg, 0.46; Sb, 0.10; Co, 0.10; Ni, 0.29; V, 0.15; Cu, 0.71; Mn, 0.20	0.195 ± 0.004	97.5

Conditions and instrumental setting were the same as in Fig. 1.

[a] Mean of four determination ± standard deviation.

Mn(II) was quantitatively retained in all cases. Therefore we conclude that the breakthrough volume of the method under optimum conditions should be greater than 500 mL. Consequently, by considering the final elution volume of 5.0 mL of 0.1 mol L^{-1} HNO_3 and a breakthrough volume of 500 mL, a preconcentration factor of 100 was easily achievable.

3.6. *Evaluation of sorbent capacity*

The sorption capacity of MMWCNTs was determined by passing different volumes of 50.0 μg mL^{-1} Mn(II), followed by the determination of retained Mn(II) using FAAS. The maximum capacity of the sorbent was 1180 μg of Mn(II) per gram of sorbent. The MMWCNTs sorbent was subject to several loadings with the sample solution and the subsequent elution. It was found that adsorption properties of the adsorbent remained constant after 50 cycles of sorption and desorption.

3.7. *Interferences*

The interferences of coexisting ions in binary mixtures of Mn(II) with foreign ions were studied on the percentage of recovery of manganese (0.5 μg mL^{-1}). After introducing the binary solution into a column, the adsorbed manganese ion was eluted by 5.0 mL of 0.1 mol L^{-1} nitric acid. The content of manganese in effluents was determined by using FAAS, and the recoveries were calculated. Considering the selectivity provided by the solid phase extraction and flame atomic absorption spectrometry, many anions and cations were evaluated. An ion was considered to interfere when its presence produced a variation of 4% error. The effect of foreign ions on the preconcentration and determination of manganese was investigated. Among the tested ions; I^-, SCN^-, Cl^-, Br^-, NH_4^+, CH_3COO^-, $S_2O_3^{2-}$, Na^+, K^+, Al^{3+} did not show any interference at a concentration of 1000 times higher than manganese concentration. However Fe^{3+}, Cu^{2+}, Mg^{2+}, Ca^{2+} showed interferences at a concentration of 250 times higher than manganese concentration and Co^{2+}, Cr^{3+}, Zn^{2+}, Pb^{2+}, Cd^{2+}, Ni^{2+} showed interference at a 20 times higher than manganese concentration.

3.8. *Analytical curve and sensitivity*

Analytical figures of merit were evaluated for the determination of manganese according to the recommended procedure under the optimize conditions. Under optimum conditions, the calibration curve was linear from 0.1 ng mL^{-1}–5.0 μg mL^{-1} in initial solution. The recommended procedure was repeated eight times to find the relative standard deviation in the determination of 0.5 μg mL^{-1} of Mn(III) ion and RSD was found to be ±0.41% in final solution. The obtained limit of detection 0.058 ng mL^{-1} was based on three times the standard deviation of the blank solution measurements (n = 8) in

Table 2 Analysis of manganese in water samples (mean ± standard deviation, n = 4).

Sample	Mn(II) spiked (ng mL^{-1})	Mn(II) detected (ng mL^{-1})	Recovery (%)
River water (Shahdad)	0.0	8.31 ± 0.17	–
	5.0	13.39 ± 0.26	101.6
Tap water (Kerman)	0	24.32 ± 0.44	–
	10	34.11 ± 0.57	97.9
Well water (Kerman)	0	18.36 ± 0.32	–
	10	28.42 ± 0.51	100.6

Conditions and instrumental setting were the same as in Fig. 1.

Table 3 Comparison the MMWCNTs sorbent with other sorbents for preconcentration Mn(II).

Sorbent	Eluent	Analysis methods	Recovery (%)	Preconcentration factor	D.L.[a] (ng/ml)	Refs.
Amberlyst 36	HNO_3	FAAS	95	200	0.245	Kenduzler et al. (2006)
XAD-2	HCl	Spectrophotometry	95	60	17	Dogutan et al. (2003)
Polyvinylpyrrolidine	–	GFAAS	98	–	4.1	Tokman et al. (2004)
Anion exchange resin	HCl	ET-AAS	92	40	–	Sarzanini et al. (2001)
Activated carbon	HNO_3	GFAAS	98	26	4.7	Xingguang et al. (2003)
Kaolinite	H_2SO_4	FAAS	98	160	4.3	Afzali et al. (2005)
MMWCNTs	HNO_3	FAAS	96	100	0.058	Present study

[a] D.L. = detection limit.

original solution. The sensitivity for 1% absorbance was 9.1 ng mL^{-1}. It is possible to retain 0.05 μg of manganese from 500 mL of the solution by passing it through the column where the concentration is 0.1 ng mL^{-1} in aqueous solution.

3.9. Analysis of manganese in standard alloys

The method was applied to the determination of manganese in Nippon Keikinzoku Kogyo (NKK) CRM No. 920 Aluminum alloy. A 100.0 mg sample of the standard alloy was decomposed with 10 mL of a mixture which contained concentrated HNO_3 and HCl (1:1 ratio) and the solution was evaporated to dryness by heating in a water-bath. The solution was filtered and diluted to 100.0 mL with distilled water in a standard flask. An aliquot of this sample was taken and the procedure was applied. The results obtained are given in Table 1. These results are in agreement with the certified values.

3.10. Analysis of manganese in water samples

Before the analysis of water samples, the samples were filtered through a cellulose membrane filter of 45 μm pore size. For preconcentration, the pH of 60 mL of the water sample was adjusted to 8.5 with a buffer solution and the preconcentration procedure was applied to the final solution. The proposed method was used for the determination of manganese in various waters from the Kerman region in Iran. The results are given in Table 2.

4. Conclusion

Many sorbents have been reported for preconcentration and determination of manganese. This paper demonstrates the use of a sorbent based on the MMWCNTs as a new sorbent. In this paper, a new method for the application of MWCNTs is proposed. By using this new sorbent, a simple, rapid, precise, accurate and reliable method is developed for the preconcentration of trace amounts of manganese in different samples. Moreover, the preconcentration factor of the sorbent is found to be high. Table 3 compares the proposed method with those which were reported previously for the preconcentration of manganese. It shows that the proposed method has a low detection limit compared with previous studies (Kenduzler et al., 2006; Dogutan et al., 2003; Tokman et al., 2004; Sarzanini et al., 2001; Xingguang et al., 2003; Afzali et al., 2005) and it allows the determination of ng mL^{-1} levels of manganese. The method is economical due to the possibility of multiple uses of the sorbent. The procedure used for the measurement of manganese in standard alloy shows a good accuracy. The proposed procedure was applied for the determination of manganese in complex samples. The PAN is fairly sensitive and selective for manganese but with the preconcentration step and the use of atomic absorption spectrometry, its sensitivity and selectivity were further improved.

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