Full Length Research Paper

Preconcentration of trace Ni (II) using C_{18} disks modified cyclodextrin–chitosan/nano graphene oxide

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A novel, sensitive and effective method has been developed for preconcentration of Ni on C_{18} disks modified cyclodextrin–chitosan/nano graphene oxide. Simple chemical bonding method to synthesize cyclodextrin–chitosan/nano graphene oxide (CCGO) was reported. The adsorption behaviors of Ni (II) in aqueous solution on CCGO were systematically investigated. The procedure is based on the selective formation of Ni(II) at optimum pH by elution with organic eluents and determination by flame atomic absorption spectrometry. The method is based on complex formation on the surface of the ENVI-18 DISK^{TM} disks modified CCGO followed by stripping of the retained species by minimum amounts of appropriate organic solvents. The elution is efficient and quantitative. The effect of potential interfering ions, pH, CCGO amount, stripping solvent, and sample flow rate were also investigated. Under the optimal experimental conditions, the break-through volume was found to about 1000 ml providing a preconcentration factor of 600. The maximum capacity of the disk modified CCGO was found to be 398±3 μg for Ni^{2+}. The limit of detection of the proposed method is 5 ng per 1000 ml. The method was applied to the extraction and recovery of Ni in different water samples.

Key words: Ni(II), octadecyl slica disk (SPE), flame atomic absorption spectrometric (FAAS), cyclodextrin–chitosan/nano graphene oxide (CCGO).

INTRODUCTION

Ni at trace concentrations acts as both a micronutrient and a toxicant in marine and fresh water systems (Izatt et al., 1985, 1991, 1995; Blake et al., 1996; Arca et al., 2001; Ghoulipour and Husain, 2002; Hashemi et al., 2001; Shcherbinina et al., 1990). This element is needed by plants at only very low levels and is toxic at higher levels. At these levels, Ni can bind to the cell membrane and hinder the transport process through the cell wall. Ni at nearly 40 ng ml^{-1} is required for normal metabolism of many living organisms (Gomes-Gomes, 1995; Unger, 1979). On the other hand, Ni is an important element in many industries. Thus, the development of new methods for selective separation, concentration and determination of it in sub-micro levels in different industrial, medicinal and environmental samples is of continuing interest. The determination of Ni is usually carried out by flame and graphite furnace atomic absorption spectrometry (AAS) (Boudreau and Cooper 1989) as well as spectrometric methods (Bruening et al., 1991; Mahmoud and Soliman, 1997a).

Solid phase extraction (SPE) methods are the best alternatives for traditional classic methods due to selective removal of trace amounts of metal ions from their matrices. Solid phase extraction determinations can
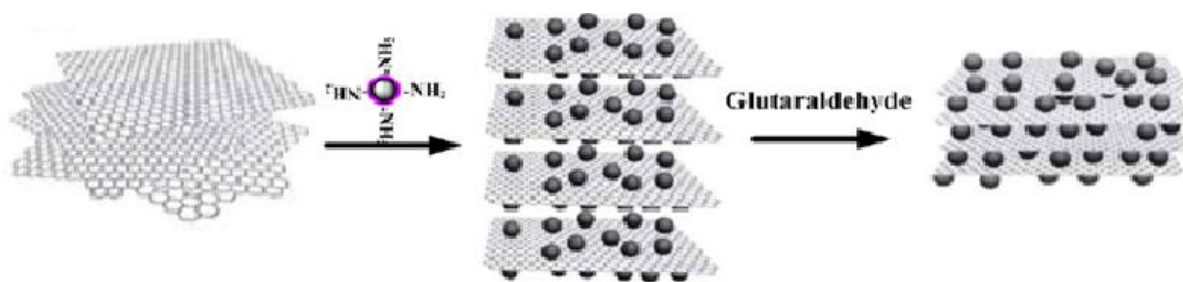
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Figure 1. Schematic of synthesis and structure of CCGO.

be carried out on different efficient ways. One of the most appropriative performation features of SPE is achieved by using octadecyl silica membrane disks. SPE reduce the use of toxic solvent, disposal costs, and extraction time (Mahmoud and Soliman, 1997b; Mahmoud, 1997). The octadecyl silica membrane disks involves shorter sample processing time and decreased plugging due to the large cross-sectional area of the disk and small pressure drop which allows higher flow-rates; reduced channeling resulting from the use of sorbent with smaller particle size and a greater mechanical stability of the sorbent bed (Tong et al., 1990).

In our previous attempts, we modified SPE membrane disks with suitable compounds for selective determination of chromium (Dadler et al., 1987; Moghimi, 2007) and lead (Mahmoud, 1999). Meanwhile, other investigators have successfully utilized these sorbents for quantitative extraction and monitoring trace amounts of lead (Leyden et al., 1976; Moghimi et al., 2009; Liu et al., 1992), copper (Liu et al., 1996; Mishenina et al., 1996; Wang et al., 1999), silver (Wang et al., 1997; Zhang et al.,1982), mercury (Zhou et al., 1983; Zargaran et al., 2008), cadmium (Tabarzadi et al., 2010), palladium (Shin et al., 2004), Ni (Moghimi and Abdouss, 2012) and UO$_2$ (Mahmoud, 1998; Moghimi et al., 2006).

The ß-cyclodextrin–chitosan nanoparticles have attracted attentions due to its many excellent properties such as easy separation and high adsorption capacity (Fang et al., 2007; Guo et al., 2010). In this work, ß-cyclodextrin–chitosan/nano graphene oxide materials were prepared via a step procedure route that the carboxyl group of GO chemically reacts with the amine group of magnetic ß-cyclodextrin–chitosan with consequent formation of chemical bond between GO and chitosan.

In the present report, we wish to describe a proper concentrative method for assessment of trace levels of Ni in different water samples. To the best of our knowledge, octadecyl silica membrane disks modified by cyclodextrin–chitosan/nano graphene oxide (CCGO) have not been used for Ni isolation and preconcentration, previously of this work was the development of a rapid, efficient and highly sensitive method for selective

extraction and concentration of ultra trace amounts of Ni^{2+} ions from aqueous media using octadecyl silica membrane disks modified by CCGO and Flame Atomic Absorption Spectrometric (FAAS) determination.

EXPERIMENTAL

Reagents

All acids were of the highest purity from Merck and were used as received. Methanol and chlorofom were of high-performance liquid chromatography (HPLC) grade from Merck. Analytical grade nitrate salts of litium, sodium, potassium, magnesium, calcium, strontium, barium, zinc, cadmium, lead, nickel, cobalt(II), and Ni(II) were of the highest purity. Ultra pure organic solvents were obtained from E. Merck, Darmstat, Germany, and high purity double distilled deionized water was used throughout the experiments.

The stock standard solution of Ni^{2+} was prepared by dissolving 0.1000 g of the Ni powder in 10 ml concentrated nitric acid and diluted to 1000 ml with water in a calibrated flask. Working solutions were prepared by appropriate dilution of the stock solution. Chitosan with 80 mesh and average molecular weight of 6.36×10^5 was purchased from Qingdao Baicheng Biochemical Corp. Glutaradehyde, 1-ethyl-3-(3-dimethylaminoprophy) carbondiimide hydrochloride (EDC), N-hydroxyl succinimide (NHS), and ß-Cyclodextrin were Aldrich products. All other reagents used in this study were analytical grade. The synthesis of the CCGO is illustrated in Figure 1.

Synthesis of ß-Cyclodextrin–chitosan (CCGO)

ß-Cyclodextrin–chitosan was prepared following the method of Fan et al. (2012) and Leilei et al. (2013). Nano graphene oxide was prepared from purified natural graphite by the modified Hummers method (Ramesh et al., 2004). A GO dispersion was prepared by sonicating GO for 2 h in ultrapure water. 0.1 M EDC and 0.1 M NHS solution was added to the GO dispersion with continuous stirring for 2 h in order to activate the carboxyl groups of GO (Depan et al., 2011). The pH of the resulting solution was maintained at 7.0 using dilute sodium hydroxide. ß - cyclodextrin–chitosan (0.1 g), the activated GO solution and 5 ml glutaraldehyde were added into a flask and dispersed in distilled water by ultrasonic dispersion for 10 min. After ultrasonic dispersion, the mixed solutions were stirred at 65°C for 2 h. The precipitate was washed with 2% (w/v) NaOH and distilled water in turn until pH was about 7.0 (Fan et al., 2012). Then, the obtained product was collected by the aid of an adscititious magnet and dried in a vacuum oven at 50°C. The obtained product was CCGO (Leilei et al., 2013). The application of

Table 1. The operational conditions of flame for determination of Ni.

Slit width	0.7 nm
Operation current of HI-HCL	15 mA
Resonance fine	324.8nm
Type of background correction	Deuterium lamp
Type of flame	Air/acetylene
Air flow	7.0 ml.min^{-1}
Acetylene flow	1.7 ml.min^{-1}

CCGO is shown in Figure 1.

Apparatus

Determination of Ni^{2+} contents in working samples were carried out by a Varian spectra A.200 model atomic absorption spectrometer equipped with a high-intensity hallow cathode lamp (HI-HCl) according to the recommendations of the manufacturers. These characteristics are tabulated in Table 1. CCGO (40 mg) were packed into an SPE ENVI-18 DISK^{TM} disks. Solid phase extractions were carried out by glassy membrane disks, ENVI-18DISK^{TM} 47 mm diameter × 0.6 mm thickness containing octadecyl silica bonded phase (30 μm particles, 70 A° pore size) obtained from Supelco in conjunction with a standard Millipore 47 mm filtration apparatus equipped with a vacuum pump. The pH measurements were carried out by an ATC pH- meter (EDT instruments, GP 353).

Sample extraction

Extraction were performed with glassy membrane disks, ENVI-18 DISK^{TM} 47 mm diameter × 0.6 mm thickness containing octadecyl silica bonded phase (30 μm particles, 70 A° pore size) from Supelco. The disks were used in conjunctions with a standard Millipore 47 mm filtration apparatus connected to water aspirator (Moghimi, 2007).

Sample treatment

The water samples were filtered through 45 μm nylon filters. Sampling vessels were polyethylene bottles soaked in 1 mol.L^{-1} HNO$_3$ overnight and rinsed twice with deionized water. The analysis must be done within 2 days of sample collection to limit the risk of interconversion of Ni(II). Then, 5 ml of methanol was added to a 90 ml portion of each before analysis. The surface of the ENVI-18 DISK^{TM} disks is modified with CCGO and therefore could retain Ni^{2+} ions properly. Instead, 10 mg of CCGO an appropriate volume of an organic solvent (5 ml) miscible with water. The most suitable solvent under the experimental conditions was acetone.

Disk cleaning and conditioning

A disk was placed in the apparatus and was washed with 10 ml of methanol to remove all contaminants arising from the manufacturing process and the environment. Then, the disk was dried by passing air through it for several minutes. In order to insure optimal extraction of the analytes of interest, the disk was again washed with 10 ml of methanol, immediately followed by 10 ml of water, without letting the surface of the disk dry. This step pre-wets
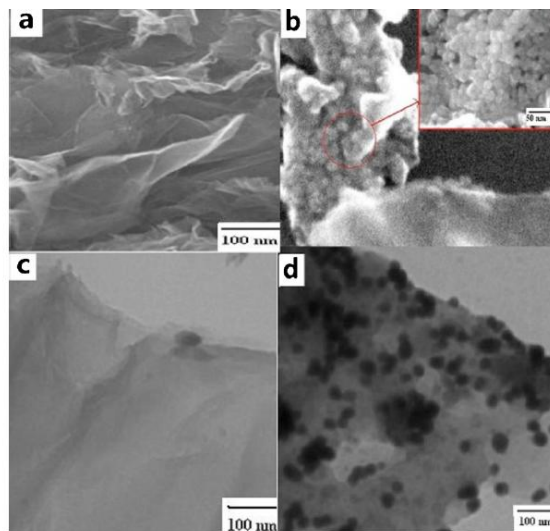

Figure 2. SEM and TEM images of the GO (a, c) and CCGO (b, d).

the disk surface before to extraction. Improper performance of this step causes slow flow – rate and poor analyte recoveries. It is important to avoid any air contact with the surface of the disk before the addition of the sample.

Sample addition

After complete homogenization, accurate volumes of the sample solutions (100 ml portions) were transferred to the top reservoir of the disk apparatus. At the same time, the solution was drawn through the disk by applying a mild vacuum. Application of vacuum was continued until the disk was completely dry (about 5 min).

Analyte elution

In order to elute the analyte selectively, exactly 5 ml of acidified solvents 0.1 M HCl in methanol was passed through the disk and collected into a 5.0 ml volumetric flask under the extraction funnel. It was found that ultra pure alcoholic organic solvents were the best eluting agents. The concentration of Ni(II) in the eluates were then determined by FAAS using an external calibration graph.

RESULTS AND DISCUSSION

Figure 2a, b shows the typical SEM and TEM images of GO. GO present the sheet-like structure with the large thickness, smooth surface, and wrinkled edge. The obtained GO display layered structures and become very thin. After the combination with the ß -cyclodextrin – chitosan, as shown in Figure 2b, d, the ß -cyclodextrin – chitosan spheres are decorated and anchored on the surface of GO layers. Notably, the pleats structure of the GO may favor to hinder the magnetic ß -cyclodextrin – chitosan spheres from agglomeration and enable their good distribution on the GO, while the magnetic ß –
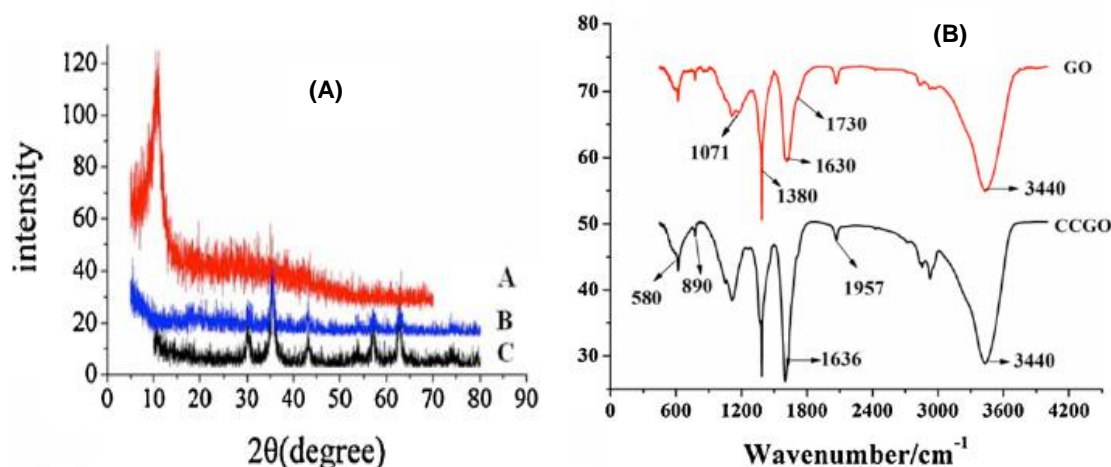
Figure 3. (a) XRD patterns of the GO, (b) IR spectra of pure GO, and CCGO.

cyclodextrin –chitosan serve as a stabilizer separate GO against the aggregation. Figure 3a shows the typical XRD patterns of the GO (A). As shown in Figure 3a, after oxidation, the characteristic graphite peak ($2\Theta = 26°$) disappear and is replaced by a well-defined peak at $2\Theta = 10.8°$ with 0.8 nm d-spacing. The increased d-spacing of GO sheets is due to the presence of abundant oxygen-containing functional groups on both sides of the graphene sheets causing an atomic-scale roughness on the graphene sheets. In Figure 3b, the peaks at 2Θ values of 18.2° (1 1 1), 30.0° (2 2 0), 35.3° (3 1 1), 42.9° (4 0 0), 53.4° (4 2 2), 56.9° (5 1 1), and 62.5° (4 4 0) are consistent with the standard XRD data for the cubic phase Fe_3O_4 (Figure 3a) with a face-centered cubic (f c c) structure (Deng et al., 2005; Vestal and Zhang, 2003).

Thus, the contribution of the nonmagnetic GO layer to the total magnetization may be responsible for the decrease in the saturation magnetization. In addition, SEM and TEM observation suggests that the magnetic ß -cyclodextrin –chitosan are intimately attached to the surface of GO (Rana et al., 2005). The BET surface area and pore volume of CCGO estimated from Barret–Joyner–Halenda (BJH) analysis of the isotherms are determined to be 445.6 m^2/g and 0.4152 cm^3/g, indicating large surface area in CCGO. The FTIR pattern of GO, which is shown in Figure 3b, reveals the presence of the oxygen-containing functional groups. The peaks at 1071, 1380, 1630 correspond to C- O- C stretching vibrations, C-OH stretching, C-C stretching mode of the sp^2 carbon skeletal network, respectively, while peaks located at 1730 and 3440 cm^{-1} correspond to C-O stretching vibrations of the -COOH groups and O-H stretching vibration, respectively (Ai et al., 2007). The major characteristic peaks of CCGO (Figure 3b) can be assigned as follows: 580 cm^{-1} (characteristic peak of Fe_3O_4), 890 cm^{-1} (R-1, 4-bond skeleton vibration of ß - cyclodextrin), and 3440 cm^{-1} (O- H stretching vibration).

In addition, there are two characteristic absorbance bands centered at 1636 and 1597 cm^{-1}, which correspond to the C-O stretching vibration of –NHCO- (amide I) and the N-H bending of -NH_2, respectively. However, in the case of GO grafted derivatives, it can be distinctly observed that the -NH_2 absorbance band has shifted to a lower value and the intensity of acetylated amino group -NHCO- (amide I) has increased, which proves that NH_2 groups on the chitosan chains have been reacted with the- COOH groups of GO and therefore have been converted to -NHCO -graft points. These indicate that the CCGO has been prepared successfully.

Evaluation of the role of the CCGO

Some preliminary experiments were performed for investigation of absence or presence of CCGO on the quantitative extraction of Ni(II). It was concluded that the membrane disk itself does not show any tendency for the retention of Ni(II), but introduction of 100 ml portions of aqueous Ni(II) samples containing 10 µg of Ni(II) and 10 mg of CCGO leads to satisfactory its retention (Table 2). The latter case is most probably attributed to the existence of a considerable interaction between Ni(II) and the CCGO. It should be mentioned that formation of stable complexes between Ni(II) and CCGO at pH=2 is probably due to an ion pair formation mechanism. However, at pH higher than 2 the retention and percentage recovery of Ni(II) are negligible (Table 3).

Choice of eluent

In order to select the most appropriate eluent for the quantitative stripping of the retained Ni(II) on the disks, 5

Table 2. The effect of presence of CCGO on extraction percent of Ni(II)[a].

CCGO	pH	Extraction percent of Ni(II)
Absence	2-6	0.03(7.3)[b]
Presence	2-6	98.9(2.5) to 63(2.2)

[a] Initial samples contained 10 μg of Ni (II) in 100 ml of water. [b] Values in parentheses are RSD_S based on five individual replicate analyses.

Table 3. Effect of different eluting solvents on percentage recovery of Ni(II) adsorbed on the disk [a].

Stripping solution	% Recovery		
	2 ml	5 ml	10 ml
Methanol	82.3(2.6)[b]	92.5(2.7)	98.7(2.0)
Acidified methanol [c]	54.5(2.3)	83.5(2.6)	83.8(2.9)
Ammoniacal methanol[d]	53.4 (2.5)	87.5(2.6)	86.3(2.8)
Ethanol	82.5(1.3)	99.61.5)	99.0(2.3)
Acetonitril	36.6(4.3)	46.5(5.5)	69.5(2.9)
Formic acid(1M)10% $V.V^{-1}$ methanol	55.2(1.2)	68.3(2.0)	71.5(2.8)
Hydrochloric acid(1M)10% V.V-1 methanol	54.3(1.9)	92.0(2.6)	91.6(2.0)
Hydrochloric acid(1M)10% $V.V^{-1}$ methanol	55.6(2.5)	65.3 (2.5)	97.7(1.6)
Nitric acid(2M)10% $V.V^{-1}$ methanol	59.8(1.9)	85.9(2.3)	85.4(2.0)
Nitric acid(1M)10% $V.V^{-1}$ methanol	64.0(2.5)	85.8(2.1)	87.7(1.6)
Ethanol	85.1(2.8)	95.7(2.0)	97.7(2.2)

[a] Initial samples contained 10 μg of each Ni in 100 ml water. [b] Values in parentheses are RSDs based on five individual replicate analysis. [c] Acidified solvents obtained by addition of $0.1M$ HCl. [d] Ammoniacal solvents obtained by addition of 0.1 M NH_3.

ml of various non organic (each containing 10% $V.V^{-1}$ methanol) and different organic solvents were tested. The results are tabulated in Table 2. As can be seen, the best eluting solvents were found to be 5 ml of methanol or ethanol, resulting in quantitative elution of Ni(II) from the disk. It should be emphasized that presence of methanol in any kind of employed solvents helps to better the contact of eluent with hydrophobic surface of the disk.

The effect of the pH

The pH of the sample solutions were adjusted to different values between 2-9 by addition of hydrochloric acid or a suitable buffer such as sodium acetate-acetic acid or sodium dihydrogen phosphate- disodium hydrogen phosphate, and then solutions passed through the disks. Eventually, the metal ions were stripped by pure methanol or ethanol solutions followed by flame atomic absorption determination of the eluted Ni(II). Then, percentage recovery at various pH values was determined (Figure 4). According to the results shown in Figure 4 up to pH 4.0 to 4.5, complete recoveries are obtained. However, at higher pH values, percentage recovery decays. This is due to fact that in an acidic solution the protonation of CCGO occurs and there is a weak tendency for retention between Ni(II) and CCGO,

whereas at higher values (pH>5), Ni(II) reacts with hydroxide ions to produce Ni $(OH)_2$. Therefore, sodium acetate-acetic acid buffer with pH=4.5 was used for the preconcentration step. Other solvents used for dissolving CCGO were methanol and ethanol. The influences of these solvents on the recoveries as a function of pH are compared and shown in Figure 3. Mean while, other organic solvents were not tested because of their restricted solubility and formation of two phases with aqueous solutions and incompatibility with flame higher pH values (>7) were not tested because of the possibility of the hydrolysis of octadecyl silica in the disks (Moghimi, 2007). Ni(II) ions can be retained quantitatively by the modified membrane disk through the pH range from 4.0 to 4.5, however, at lower pH (< 4.0), nitrogen atoms of the CCGO could be protonated and the stability of complex is reduced.

Effect amount of counter anion

In order to investigate the effect of counter ion on the recovery Ni^{2+} ions by the modified disks, different counter anions were tested (Table 4), it is immediately obvious that the nature of the counter anion strongly influences the retention of Ni ions by the disk. The results revealed that the CCGO behaves in pH range 4.0 to 4.5 (Leilei et
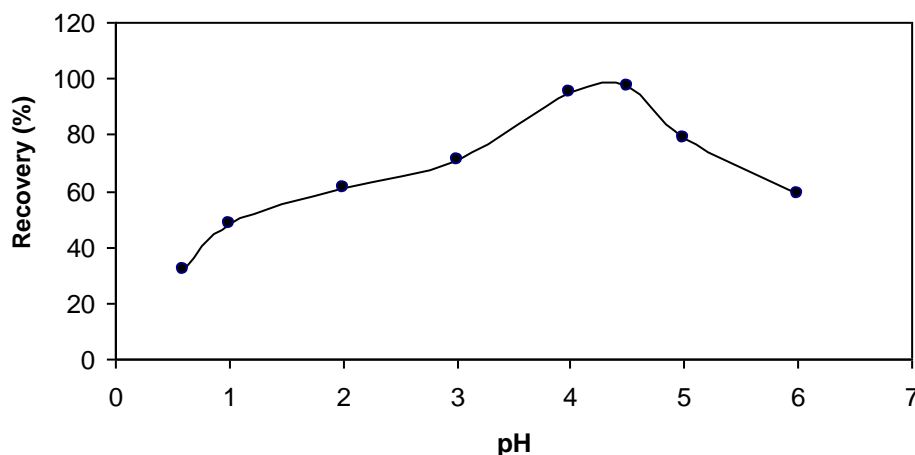
Figure 4. Influence of sample pH on the percentage recovery of Ni(II).

Table 4. Percent recovery of Ni from the modified membrane disk in the presence of 0.01 M of different counter anions [a].

Counter anion	% Recovery
Cl^-	13.8
Br^-	23.9
ClO_4^-	35.0
SCN^-	45.8
Picrate	76.9
Acetate	98.7

[a] Initial samples contained 10 µg of Ni(II) in 100 ml of water.

al., 2013) so that the Ni ions are retained as ion pair complexes by the membrane disks. As seen, acetate ion is the most efficient counter anion for the SPE of Ni(II) ions. The influence of the concentration of sodium acetate ion on Ni recovery was investigated, and the results are shown in Table 4. As seen, the percent recovery of Ni^{2+} increased with the acetate concentration until a reagent concentration of about 0.1 M is reached, beyond which the recovery remained quantitative. Moreover, acetate ion acts as a suitable buffering agent, while it effectively contributes to the ions- pair formation; thus, in the SPE experiments, there was no need for the addition of any buffer solution.

The influence of flow-rate

One of the most important parameters affecting solid phase extraction is the speed of the process. Hence, the effect of flow-rates on extraction efficiencies was investigated. It was found that in the range of 10-100 ml.min^{-1}, the retention of Ni(II).was not considerably affected by the sample solutions flow-rates and leads to reproducible and satisfactory results (Figure 5). Thus, the flow-rate was maintained at 89 ml.min^{-1} throughout the experiment.

Quantity of the CCGO

The optimum amount of CCGO for the quantitative extraction of Ni(II) was also investigated by adding various amounts of it to solution (between 2-20 mg), the results are listed in Table 5. The experimental results revealed that the extraction of Ni(II) was quantitative using a sample solution containing more than 10 mg CCGO. Hence, subsequent extractions were performed with 15 mg of CCGO.

Disk efficiency
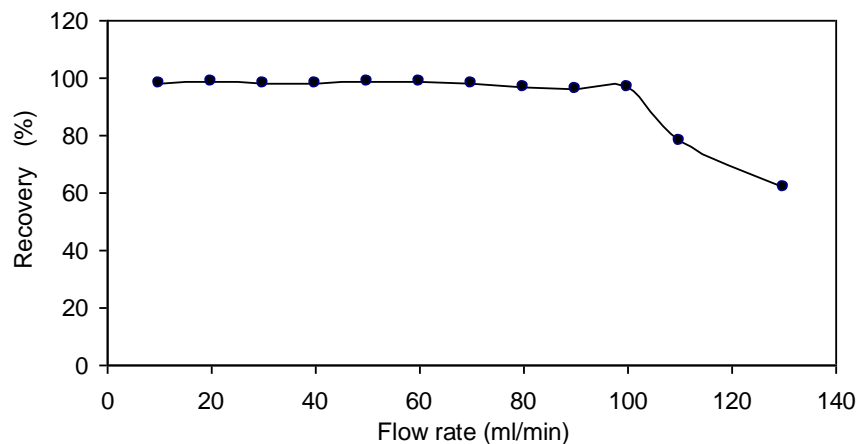
Undoubtedly, one of the major parameters affecting in the

Figure 5. The effect of the flow-rate on extraction percent of Ni(II).

Table 5. Influence of the CCGO amount on the recovery of Ni (II) ions [a].

CCGO amount (mg)	Recovery(%) of Ni (II)
2	34.25(2.6)[b]
5	44.46(2.0)
8	83.20(2.6)
10	95.5(2.5)
15	98.5(2.5)
20	98.6(2.8)

[a] Initial samples contained 10 µg of each Ni in 100 ml water.
[b] Values in parentheses are RSDs based on five individual replicate analysis.
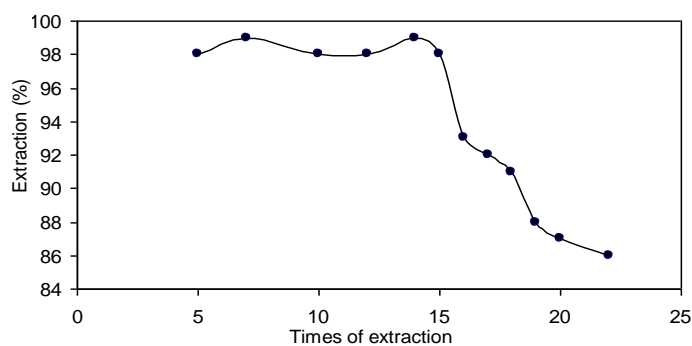

Figure 6. Influence of eluent (5 ml of methanol) type on disk efficiency.

SPE determinations is the efficiency of the used membrane disks. However, to the best of our knowledge this case has not been discussed elsewhere in similar reports. Under the optimum experimental conditions, it was found out that each ENV-18 DISK[TM] disk could perform at least 14 replicate analyses if organic eluting solvents are used. On the other hand, acidic, eluents practically decrease the number of time a disk could be used to 10 replicates. These observations are represented in Figure 6.

Table 6. Separation of Ni from binary mixtures[a].

Diverse ion	Amounts taken (mg)	% Found	% Recovery of Ni^{2+} ion
Na$^+$	92.4	1.15(2.4)[b]	98.5(2.7)
K$^+$	92.5	1.36(2.3)	98.0(2.2)
Mg^{2+}	24.5	0.70(2.6)	98.5(1.7)
Ca^{2+}	26.3	2.65(3.0)	98.5(1.8)
Sr^{2+}	2.45	2.85(2.1)	98.4(2.0)
Ba^{2+}	3.66	3.16(2.1)	98.7(2.3)
Mn^{2+}	2.66	1.75(2.2)	96.3(2.3)
Co^{2+}	2.17	6.44(2.3)	93.0(1.9)
Cu^{2+}	1.64	2.43(2.4)	93.7(2.4)
Zn^{2+}	2.76	4.97(2.1)	97.6(2.4)
Cd^{2+}	2.77	2.96(2.4)	97.2(2.7)
Pb^{2+}	1.74	2.74(1.9)	97.7(2.7)
Hg^{2+}	1.67	2.71(2.1)	97.7(2.7)
Ag$^+$	2.6i	3.47(2.9)	97.6(2.3)
UO^{2+}	2.76	2.74(2.1)	98.3(2.7)

[a]Initial samples contained 10µg Ni $^{2+}$ and different amounts of various ions in 100 ml water(0.1 M acetate ion). [b] Values in parentheses are RSDs based on five individual replicate analysis.

Analytical performance

When solutions of 10 µg Ni in 10, 50, 100, 600, 1000, 2000, 2500 and 3000 ml solutions under optimal experimental conditions were passed through the disks, the Ni(II) was quantitatively retained in all cases. Thus, the breakthrough volume for the method must be greater than 2500 ml, providing a concentration factor of >600. The limit of detection (LOD) of the method for the determination of Ni(II) was studied under the optimal experimental conditions. The LOD based on 3σ of the blank (5 ml of methanol) is 5 ng per 1000 ml. The capacity of modified disks (5 mg CCGO) was determined by passing 50 mL portions of sample solutions containing 8 mg of Ni and 0.1 M sodium acetate-acetic acid buffer with pH 4.0-4.5, followed by the determination of the retained metal ions in the eluting solution using AAS. The maximal capacity of the disk obtained from three replicate measurements was 398±3 µg of Ni^{2+} on the disk.

In order to investigate the selective separation and determination of Ni^{2+} ions from its binary mixtures with various metal ions, an aliquot of aqueous solutions(50 ml) containing 10 µg Ni^{2+} and mg amounts of other cations was taken and the recommended procedure was followed. The results are summarized in Table 6. The results show that the Ni(II) ions in binary mixtures are retained almost completely by the modified disk, even in the presence of up to about 100 mg of various ions. Meanwhile, retention of other cations by the disk is very low and they can separated effectively from the Ni^{2+} ion. Its is interesting to note that, in other experiments, we found that in the presence of high enough concentrations NH$_2$OH.HCl as a suitable reducing agent (> 0.5 M)

(Moghimi, 2007).

Analysis of water samples

In order to assess the applicability of the method to real samples, it was applied to the extraction and determination of Ni from different water samples. Tap water (Tehran, taken after 10 min operation of the tap), rain water (Tehran, 20 January, 2013), Snow water (Tehran, 16 February, 2013) and Sea water (taken from Caspian Sea, near the Mahmoud-Abad shore) samples were analyzed (Table 7). As can be seen from Table 4 the added Ni ions can be quantitatively recovered from the water samples used. As is seen, the recovered Ni ion reveals that the results are quite reliable and are in satisfactory agreement with those obtained by inductively coupled plasma atomic emission spectroscopy (ICPAES).

Conclusion

Results presented in this work demonstrate well the tremendous possibilities offered by the solid phase extraction of trace amounts of Ni(II) in water samples using Octadecyl Silica membrane disks modified by CCGO and its determination by FAAS. The developed method was simple, reliable, and precise for determining Ni in water. In addition, the proposed method was free of interference compared to conventional procedures to determine Ni (Moghimi et al., 2012; Zargaran et al., 2008). The method can be successfully applied to the separation and determination of Ni in binary mixtures.

Table 7. Recovery of Ni added to 1000 ml of different water samples (containing 0.1 M acetate at pH= 4.0-4.5).

Sample	Ni^{2+} added (µg)	Ni^{2+} determined (ng.ml^{-1})	ICP-AES
Tap water	0.0	1.72(2.8)[a]	ND
	10.0	11.93(2.0)	11.8
Snow water	0.0	4.85(2.5)	ND
	10.0	14.94(2.6)	14.5
Rain water	0.0	2.65(2.3)	ND
	10.0	12.85(2.4)	12.9
Sea Water	0.0	12.96(2.3)	12.8
	10.0	22.50(2.5)	23.0

[a] Values in parentheses are %RSDs based on five individual replicate analysis, [b] Not detected.

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