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Removal, preconcentration and determination of Ni(II) from different environmental samples using modified magnetite nanoparticles prior to flame atomic absorption spectrometry

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Abstract In this paper, a simple, fast and reliable solid phase extraction (SPE) method to determine Ni(II) using dimethylglyoxim/sodium dodecyl sulfate-immobilized on alumina-coated magnetite nanoparticles (DMG/SDS-ACMNPs) as a new adsorbent prior to its determination by flame atomic absorption spectrometry (FAAS) is described. Under the optimal experimental conditions, the preconcentration factor, detection limit, linear range and relative standard deviation (RSD) of nickel(II) ions were 320 (for 800 mL of sample solution), 4.6 ng mL^{-1}, 10.0–100.0 ng mL^{-1} and 1.9% (for 50.0 ng mL^{-1}, $n = 7$), respectively. This method avoided the time-consuming column-passing process of loading large volume samples in traditional SPE through the rapid isolation of DMG/SDS-ACMNPs with an adscititious magnet. The proposed method was successfully applied to determine the content of Ni(II) in soil, spinach, tomato, black tea, tobacco and different water samples and suitable recoveries were obtained.

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1. Introduction

Important positive and negative roles of trace heavy metal ions such as nickel(II) in human health are known. Ni(II) produces a general toxic effect on the humans and inhalation of nickel and its compounds can lead to serious problems, including nasopharynx, lung and dermatological diseases and malignant tumors (Kristiansen et al., 2000; Kalyakina et al., 2003). It also was long thought to be essential to plants and some domestic animals (Wang, 1991; Zerner, 1991;

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Thauer, 2001; Fay et al., 2005). Thus, separation and determination of toxic Ni(II) in different environmental samples are of great interest to analytical chemists. Flame atomic absorption spectrometry (FAAS) is one of the most widely used instruments for the determination of nickel at trace levels. However, there are some difficulties in direct determination of nickel by FAAS in this quantity levels because of the low sensitivity of instrument (Ngeontae et al., 2007). Therefore, initial preconcentration procedures are often required prior to the determination of Ni(II) by FAAS. Many preconcentration techniques such as ion-exchange (Wang and Hansen, 2000; Kong et al., 2007), cloud point extraction (Sun et al., 2006; Şahin et al., 2010), liquid–liquid extraction (Pan et al., 2007), dispersive liquid–liquid microextraction (Shirkhanloo et al., 2010; Mirzaei et al., 2011) and solid-phase extraction (Silva et al., 1998; Ferreira et al., 1999; Gazda et al., 2004; Praveen et al., 2005; Baytak and Türker, 2006; Ghaedi et al., 2007; Ngeontae et al., 2007; Zhao et al., 2008; Xie et al., 2008; Tuzen and Soylak, 2009; Zhou et al., 2009; Ghaedi et al., 2009; Ciftci et al., 2010; Hosseini et al., 2010; Pourreza et al., 2010; Vellaichamy and Palanivelu, 2011; Topuz and Macit, 2011; Amin et al., 2012; Mohammadi et al., In Press) have been reported for the determination of nickel ions at trace levels in various environmental samples such as plants, soil, food, waste and natural waters.

Many research groups have explored the application of several nanosized solid-phase extraction (SPE) adsorbents such as nanoparticles (NPs), nanotubes and nanocomposites (Li et al., 2008; Zhao et al., 2008; Manzoori et al., 2009; Zhou et al., 2009; Vellaichamy and Palanivelu, 2011). Recently, we also reported the methods for separation and preconcentration of Ag(I) and Pb(II) using magnetite nanoparticles. These methods were based on the solid-phase extraction of trace amounts of silver and lead ions using dithizone/sodium dodecyl sulfate-immobilized on alumina-coated magnetite nanoparticles (Karimi et al., 2011, 2012). In this study, a new method combining nanoparticles adsorption with magnetic separation has been developed and applied for the separation and preconcentration of nickel ions. Our study adopted a doping method to prepare functional magnetic material for separation and preconcentration of nickel(II). Dimethylglyoxim (DMG) was chosen as a doping reagent because of its favorable coordination capacity and selectivity for Ni(II). It is concluded from the extraction data that the new sorbent is a promising material for the SPE of nickel. In this paper, we will explore the possibility of DMG/sodium dodecyl sulfate (SDS) immobilized on alumina-coated magnetite nanoparticles (DMG/SDS-ACMNPs) to act as SPE sorbents for the separation/preconcentration of trace level of nickel ions from environmental samples prior to determination by flame atomic absorption spectrometry (FAAS) technique.

2. Experimental

2.1. Apparatus

A flame atomic absorption spectrophotometer (PG Instruments, England) was used with a nickel hollow-cathode-lamp, an operating current of 8 mA and wavelength and spectral bandwidth of 232.0 and 0.2 nm, respectively. A Fourier transform infrared spectrometer (IR Perresttige-21, Shimadzu) was used to determine the identity of the as-prepared nanoparticles and to characterize the coated Fe_3O_4 nanoparticles. The surface morphology of the powders was observed by the scanning electron microscope (LEO 1455VP SEM). Magnetic properties of the particles were determined by vibrating sample magnetometer (VSM 7400 Model Lake-Shore). pH measurements were made with a Metrohm Model 780 pH meter with a combination glass electrode. Other instruments used were: ultrasonic bath (S60H Elmasonic, Germany), mechanical stirrer (Heidolph, RZR2020), orbital shaker (Ika, KS130 Basic), and an electronic analytical balance (Adam, AA220LA) used for weighting the solid materials. In addition, for magnetic separations a strong neodymium-iron-boron ($Nd_2Fe_{12}B$) magnet (1.2 T, $2.5 \times 5 \times 10$ cm) was used.

2.2. Reagents and solutions

All reagents used were of analytical grade and all solutions were prepared by using triple distilled and deionized water. A stock solution of $1000\ \mu g\ mL^{-1}$ of nickel(II) was prepared by dissolving 0.1238 g of $NiNO_3$ in 2 mL of concentrated nitric acid and was diluted to 100 mL. Working solutions were obtained by further diluting the stock solution to the required concentrations before use. Dimethylglyoxim (DMG), sodium dodecylsulfate (SDS), ferrous chloride ($FeCl_2 \cdot 4H_2O$), ferric chloride ($FeCl_3 \cdot 6H_2O$), aluminum isopropoxide, ethanol, nitric acid, hydrochloric acid and sodium hydroxide were used without further purification processes. The pHs of the solutions were adjusted with phosphate buffer. All of the chemicals were obtained from Merck.

2.3. Preparation of dimethylglyoxim/alumina-coated magnetite nanoparticles (DMG/SDS-ACMNPs)

The alumina-coated magnetite nanoparticles (ACMNPs) were prepared according to Karimi et al., (2011, 2012). A DMG/SDS solution was prepared by dissolving 150.0 mg DMG and 200.0 mg SDS in 100 mL deionized water. 10 mL of DMG/SDS solution was added to 10 mL water containing 0.2 g of ACMNPs. The pH of this suspension was adjusted to 2 by drop-wise addition of HNO_3 ($0.1\ mol\ L^{-1}$) solution. The mixed solution was shaken for 15 min and then separated from the reaction medium under the magnetic field, and rinsed with 10 mL pure water. This product was used as sorbent for nickel ions.

2.4. General procedure

The procedure for the magnetic solid-phase extraction of nickel ion is as follows: 10 mL of nickel ion solution ($5\ \mu g\ mL^{-1}$) was added to DMG/SDS-ACMNPs from section 2.3, subsequently the pH value was adjusted to 8.0–9.0 with phosphate buffer and the solution was shaken for 10 min to facilitate adsorption of the metal ions onto the nanoparticles. Then the magnetite adsorbents were separated easily and quickly using a magnet and decanted directly. Subsequently, 2 mL of $0.1\ mol\ L^{-1}$ HNO_3 solution was added as eluent. Finally, the magnet was used again to settle the magnetic nanoparticles and the eluate was separated for FAAS analysis.

2.5. Sample preparation procedure for soil, spinach, tomato, black tea, tobacco and different water samples

4–5 g of soil samples was collected from four different zones in Sirjan, Iran. The samples were digested with a mixture of 20 mL concentrated HCl and 5 mL of concentrated HNO_3 at room temperature, then they were heated to 100 °C for 5 h. The mixtures were evaporated to dryness and then 10 mL of the above acid mixture was added to the residue and evaporated to dryness again. After this, 20 mL of deionized water was added to the beaker and the insoluble parts were filtered. The pH was adjusted to 8.0 with phosphate buffer and the total volumes were made up to 20 mL with deionized water in four beakers and the solutions were taken for separation/preconcentration procedure and the solution was treated according to the general procedure prior to FAAS analysis.

2.0 g of dried powdered sample of spinach was digested in 20 mL of concentrated nitric acid for 30 min and diluted to 50 mL. After a day, the solution was filtered through a filter paper (Whatman, No. 2) and washed with 20 mL of 3.0 mol L^{-1} HNO_3. The pH of the resultant solution was adjusted to 8.0 with phosphate buffer and the solution was treated according to the general procedure prior to FAAS analysis.

The tomato samples once in the laboratory were washed with deionized water and 40 g of sample was heated in silica crucible for 3 h on a hot plate and the charred material was transferred to furnace for overnight heating at 650 °C. The residue was cooled, treated with 10 mL concentrated nitric acid and 3 mL 30% (w/v) H_2O_2 again kept in furnace for 2 h at the same temperature so that no organic compound traces are left. The final residue was treated with 3 mL concentrated hydrochloric acid and 3 mL 70% (w/v) perchloric acid and evaporated to fumes, so that all the metals change to their respective ions. The dissolved solid residue was filtered and its pH was adjusted to 8.0 and made up to 100 mL. Then SPE procedure and FAAS analysis given above was applied to the solution.

4.0 g of dried powdered sample of black tea was digested in 30 mL of concentrated nitric acid and diluted to 50 mL. After a day, the solution was filtered through a filter paper (Whatman, No. 2) and washed with 20 mL of 3.0 mol L^{-1} HNO_3. The pH of the resultant solution was adjusted to 8.0 with phosphate buffer and the solution was treated according to the general procedure prior to FAAS analysis.

1.0 g of tobacco was digested with 6 mL of concentrated HNO3 and 2 mL of 30% (w/v) H_2O_2 in microwave system. After digestion of the samples, the pH of the digested samples was adjusted to 8.0 with phosphate buffer. Then the volume of the digested sample was made up to 30.0 mL with distilled water. Blanks were prepared in the same way as the sample, but omitting the sample. The separation/preconcentration procedure given above was applied to the solution prior to FAAS analysis.

Water samples (i.e., tap water, spring water, river water and mineral water), were filtered after collection through filter paper (Whatman, No. 4) to remove suspended particulate matter and acidified 5.0 mL of concentrated HNO_3 prior to storage in polyethylene containers for use. The solutions were neutralized with concentrated NH_3 and then pH of solutions was adjusted to 8.0 with phosphate buffer. The SPE procedure was carried out as described in the general procedure.

3. Results and discussion

3.1. Characterization of MNPs, ACMNPs and DMG/SDS-ACMNPs

To enable practical application of ACMNPs, it is most important that the sorbents should possess superparamagnetic properties. Magnetic properties were characterized by measuring the hysteresis and remanence curves by means of a vibrating sample magnetometer (VSM). The magnetization curves show that both MNPs and ACMNPs exhibit typical superparamagnetic behavior due to no hysteresis (Karimi et al., 2012). However, these ACMNPs are sufficient for magnetic separation with a conventional magnet. SEM images of MNPs and ACMNPs also showed the uniform size distribution of the nanoparticles (Karimi et al., 2012).

The XRD pattern for the Fe_3O_4 NPs in Fig. 1a shows six characteristic peaks for Fe_3O_4 (2θ = 30.08, 35.42, 43.08, 53.56, 56.98 and 62.62) marked by their indices (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1) and (4 4 0). These peaks are consistent with the database in D8ADVANCE file (PDF No. 03-0862) and revealed that the resultant nanoparticles were pure Fe_3O_4 with a spinal structure and the immobilized process did not change its crystal phase. Fig. 1b shows the ACMNP XRD pattern, as compared to naked MNPs a series of peaks were added that attributed to alumina according to the software database file. The average crystallite size (D) is calculated to be 5.7 ± 3 nm for MNPs and 18.9 ± 2 nm for ACMNPs (after coating the MNPs with alumina), using the Debye–Sherrer formula $D = K\lambda/(\beta\cos\theta)$, where K is the Sherrer constant (K = 0.89), λ is the X-ray wavelength (λ = 1.5406Å), β is the full peak width at half maximum (FWHM), and the θ, Bragg diffraction angle (Hong et al., 2007). The result is well consistent with that of SEM analysis (Karimi et al., 2012).

The modified ACMNPs were also confirmed by FT-IR analysis, as shown in Fig. 2. As can be seen in Fig. 2a, a broad band exists around 588.182 cm^{-1}, assignable to the Fe–O–Fe of the MNPs. The peak at about 1632.45 cm^{-1} can be assigned
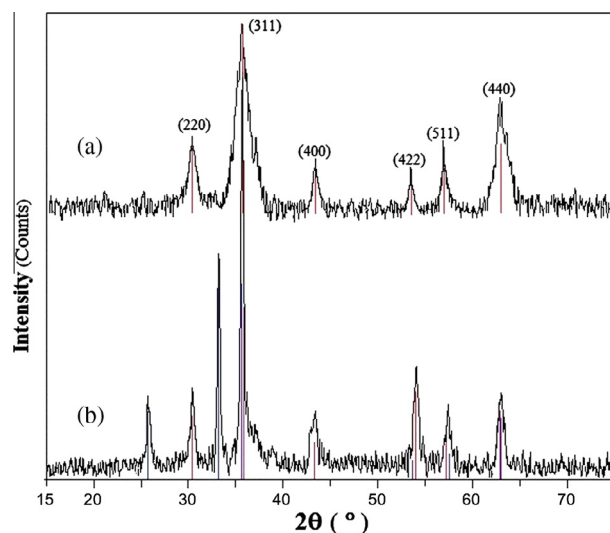

Figure 1 XRD patterns for the naked Fe_3O_4 (a) and alumina coated Fe_3O_4 nanoparticles (b).
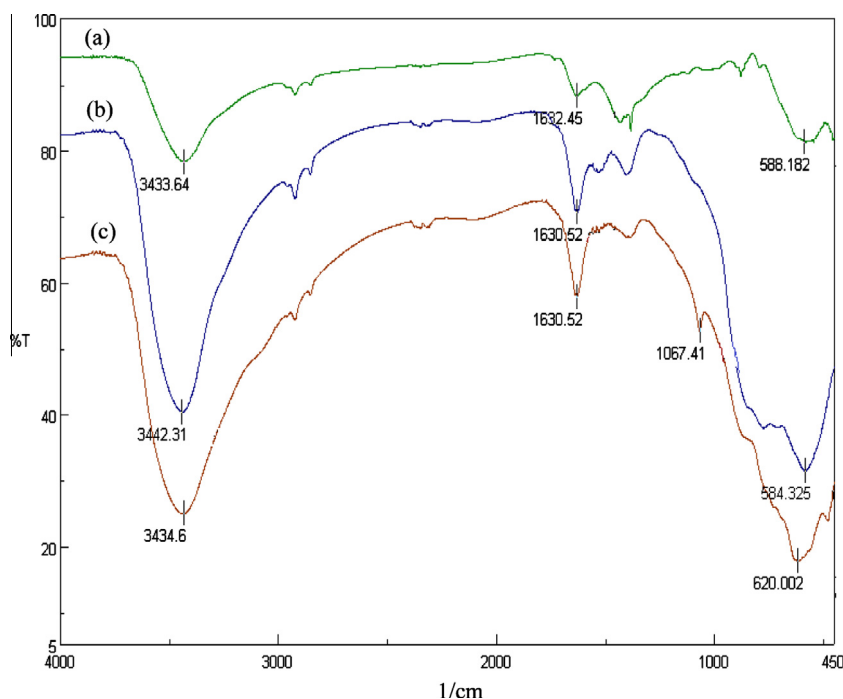
Figure 2 FTIR spectra of the Fe$_3$O$_4$ nanoparticles (a), ACMNPs (b), and DMG/SDS-ACMNPs (c).
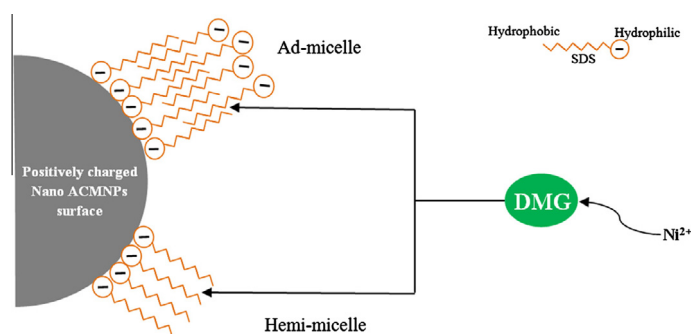

Figure 3 A suggested schematic for adsorption of Ni(II) to the DMG/SDS-ACMNPs.

to the stretching vibration of N$_2$ adsorbed on the surfaces of the nanoparticles. The flexing vibration peak of hydroxyl, resulting from the adsorbed water, can be observed at 3433.64 cm^{-1} (Hong et al., 2008). In the spectrum of ACMNPs (Fig. 2b), compared with the spectrum of MNPs, after binding alumina, and the broadening of the peak at 584.325 cm^{-1} can be assigned to Al–O, that overlapped with Fe–O characteristic peak. Comparison of the FT-IR spectra of ACMNPs and DMG/SDS-ACMNPs (Fig. 2c) also shows a new sharp peak at 1067.41 cm^{-1}, it was due to that the C–N stretching peak of DMG stabilized on ACMNPs. Consequently, the FT-IR data suggest that DMG is successfully immobilized on the ACMNPs' surface.

3.2. Amounts of DMG and SDS

The anionic surfactant of SDS is effectively sorbet on the positively charged alumina surface to form aggregates (Karimi et al., 2012). Therefore, negatively charged SDS surfactant

ions are adsorbed at low pH values due to increased interaction between the alumina and SDS. We tried to coat alumina surfaces with SDS on which DMG could be subsequently trapped (Fig. 3). The SDS would form hemimicelles or admicelles on alumina by strong adsorption and the micelles could trap DMG molecules, homogeneously (Hong et al., 2007). The influence of various amounts of DMG and SDS on the adsorption of nickel ions on ACMNPs was investigated. The results showed that maximum adsorption obtained when 60 and 50 mg of SDS and DMG were used, respectively (Figs. 4 and 5). Thus, these concentrations were selected as the optimum concentrations of SDS and DMG for further studies.

3.3. Effect of pH, standing and magnetic separation time

The effect of pH is the main investigated factor for the extraction studies. The effect of pH on the adsorption of nickel by DMG/SDS-ACMNPs at 25 °C showed that the adsorption of nickel is quantitative (100%) in the pH range of 7.0–10.0
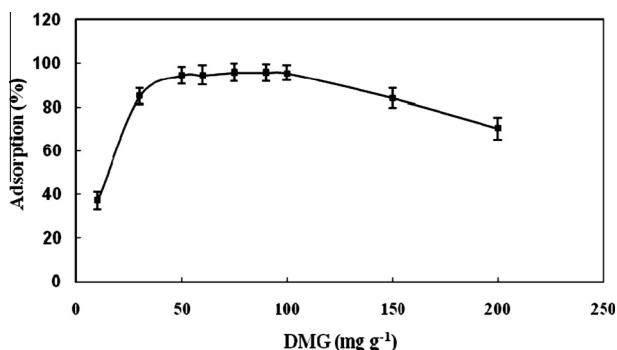
Figure 4   Effect of DMG concentration on adsorption of nickel(II). Conditions: ACMNPs (0.2 g), SDS (10 mL, 100 mg g^{-1}), Ni(II) solution (10 mL, 5 μg mL^{-1}, pH 8).
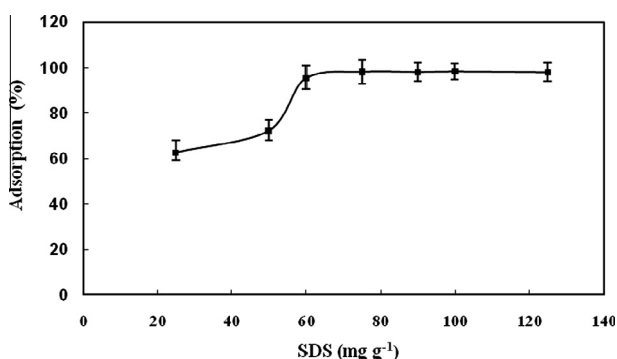

Figure 7   Effect of nanoparticles' amount on adsorption of nickel(II). Conditions as in Fig. 3 except 10 mL DMG (75 mg g^{-1}) was added.

Figure 5   Effect of SDS concentration on adsorption of nickel(II). Conditions as in Fig. 3 except 10 mL DMG (75 mg g^{-1}) was added.
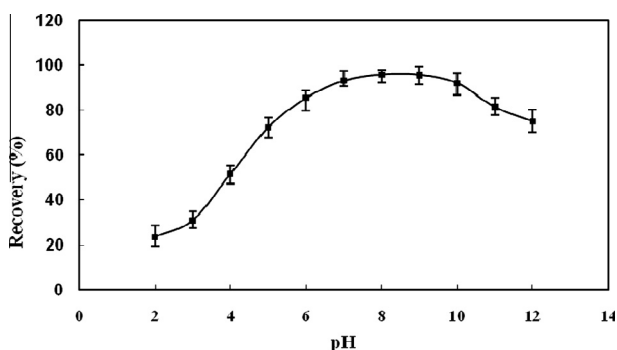

Figure 6   Effect of pH on adsorption of nickel(II). Conditions: Conditions as in Fig. 3 except 10 mL DMG (75 mg g^{-1}) was added.

(Fig. 6). At acidic media the nitrogen atom could be protonated and at basic media the hydroxyl proton dissociates. This reveals that the mechanism of sorption of nickel ion is pH dependent and pH could affect the stability of the complex. Thus, the pH 8.0 was used as optimum pH for further studies.

In order investigation effect of time on adsorption nickel on the DMG/SDS-ACMNPs was studied. In the experiment, DMG/SDS-ACMNPs possessed large saturation magnetiza-
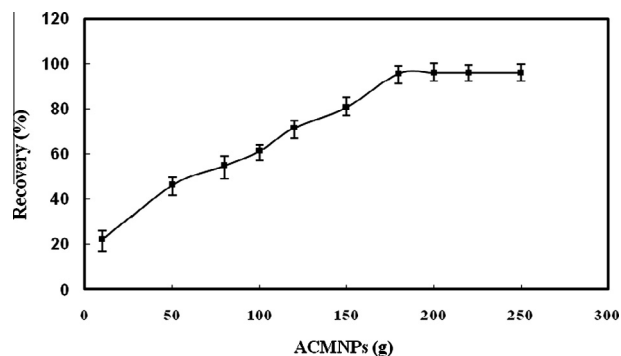
tion and super-paramagnetism properties, which enabled them to be completely isolated at less than 1 min by a strong magnet. When the ACMNPs were isolated immediately without a standing process, the recovery of Ni(II) ions was only 58%. But, when the standing time was adjusted to 5, 10, 20, 30, 40 and 50 min, recoveries were improved to 78, 82, 95.5, 95 and 95%, respectively. Standing time of 20 min was sufficient to achieve satisfactory adsorption and better recovery of nickel ions.

3.4. Effect of sample volume

In order to obtain a preconcentration factor, a larger volume of sample solution is required. To study the effect of sample volume on the recovery of nickel ions, the sample solutions in the range of 50–1000 mL containing 50.0 ng of nickel ions were operated according to the general procedure and eluted using 2.5 mL of nitric acid (1.0 mol L^{-1}). At sample volumes higher than 800 mL, the percent of recovery decreased. Consequently, a preconcentration factor of 320 could be attained for quantitative recovery of 95 ± 2% of Ni(II) when the sample volume was 800 mL.

3.5. Effect of nanoparticles' amount

Fig. 7 shows the effect of nanoparticles' amount for quantitative extraction of Ni(II). Various amounts of ACMNPs (from 10 to 250 mg) were investigated. The extraction was found to be quantitative when the amount was 180 mg or more. Experiments were carried out with 200 mg modified nanoparticles. Thus, 200 mg of ACMNPs was selected as the optimum amount for further studies.

3.6. Desorption conditions

A variety of eluents were tested in order to elute the adsorbed nickel from the sorbent. Different eluents of thiourea, thiosulphate, HNO$_3$, H$_2$SO$_4$ and NaOH at various concentrations were examined so that the most effective eluent for the quantitative recovery of nickel ions could be chosen. It was found that 2.5 mL of nitric acid with a concentration of 1.0 mol L^{-1} was sufficient for quantitative recovery of adsorbed Ni(II).

3.7. Interference study

The study of interference ions was performed by a standard mixture solution containing 50.0 ng mL^{-1} of nickel ion and a certain amount of foreign ions. The following excesses of ions do not interfere (i.e., caused a relative error of less than 5%): more than a 1000-fold (largest amount tested) amount of Na$^+$, I$^-$, F$^-$, Cl$^-$, Br$^-$, NO$_3^-$, SO$_4^{2-}$, ClO$_4^-$, CH$_3$COO$^-$; a 100-fold amount of NH$_4^+$, Mg^{2+}, Fe^{2+}, Zn^{2+}, Co^{2+}, Pb^{2+}, Cr^{3+}; a 50-fold amount of Co^{2+}, Cu^{2+}, Bi^{3+}, Al^{3+}, Fe^{3+} and a 15-fold amount of Pd^{2+}.

3.8. Sorption capacity and sorbent regeneration

Sorption capacity study used here was adapted from the method recommended by Maquieira et al. (1994). The static adsorption capacity of DMG-SDS/ACMNPs was found to be 9.72 mg g^{-1} for nickel ions. Regeneration is one of the key factors for evaluating the performance of the adsorption material. In this work, it was found that the sorbent can be re-used up to 3 times without loss of analytical performance. Considering that 4.0 g of ACMNPs could be prepared in one batch and only 200 mg of ACMNPs was used for one extraction operation, this reusability time is acceptable.
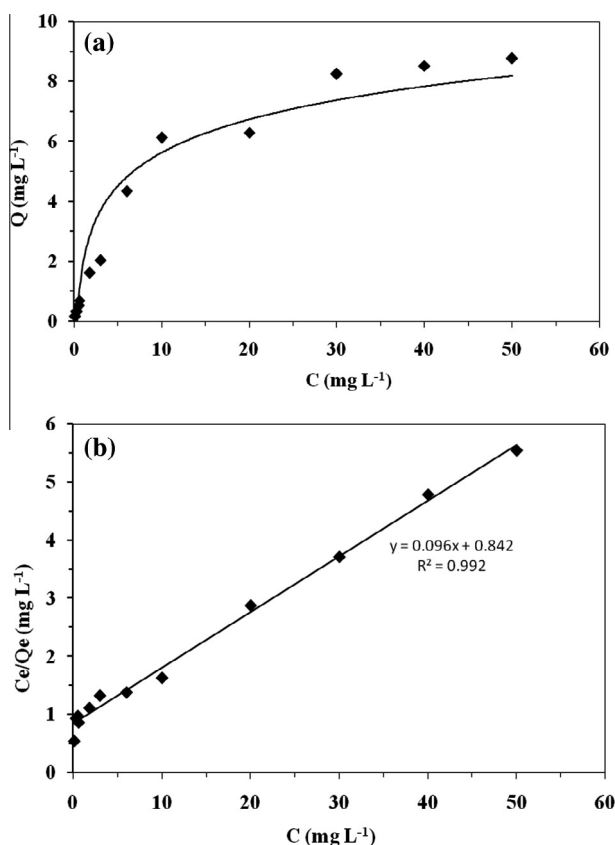
3.9. Adsorption isotherms

The equilibrium adsorption isotherm is principle in depicting the reciprocal behavior between adsorbates and adsorbent and is important for understanding the model of adsorption systems. The analysis of the isotherm data by fitting them to different isotherm models is an important step to find the suitable model that can be used for design purposes (El-Guendi, 1991). The adsorption studies were investigated at fixed adsorbent portion (0.5 g of damped nanoparticles), temperature (25 °C) and varying Ni(II) concentrations (2.0–20.0 μg mL^{-1}). The concentration of Ni(II) in the liquid phase (C_e) was determined by FAAS. Fig. 8a shows the adsorption isotherm, which was fitted to the Langmuir model using the nonlinear regression method. This isotherm relates metal per unit weight of adsorbent (Q_e, mg/g) to (C_e). The linear form of Langmuir isotherm equation is represented by the Eq. (1) (Langmuir, 1918):

$$C_e/Q_e = 1/bQ + C_e/Q \qquad (1)$$

Plotting of C_e/Q_e against C_e will result in a straight line with slope $1/Q$ and intercept $1/bQ$ Fig. 8b. Where Q and b(L/mg) are Langmuir constants related to maximum adsorption capacity (monolayer capacity) and energy of adsorption,

Figure 8 Equilibrium adsorption isotherm of Ni(II) on DMG/SDS-ACMNPs (a) and linearized Langmuir isotherm for Ni(II) by this sorbent (b). Conditions: ACMNPs (0.2 g), DMG (10 mL, 75 mg g^{-1}), SDS (10 mL, 100 mg g^{-1}), Ni(II) solution (10 mL, 2–20 μg mL^{-1}, pH 8), equilibrium time: 10 h, temperature: 25 °C.

Table 1 Recovery results of different samples of water and plants.

Sample	Ni(II)[a]		Recovery (%)
	Added	Found	
Tap water (Sirjan)	0	N.D	–
	5	4.9 ($\pm$0.1)	98.0
	10	10.6 ($\pm$0.3)	106.0
Spring water (Sirjan)	0	1.5 ($\pm$0.2)	–
	5	6.6 ($\pm$0.3)	102.0
	10	11.4 ($\pm$0.3)	99.0
River water (Haji Abad)	0	7.5 ($\pm$0.3)	–
	5	12.7 ($\pm$0.2)	104.0
	10	17.9 ($\pm$0.2)	108.0
Mineral water	0	2.5 ($\pm$0.2)	–
	5	7.5 ($\pm$0.2)	100.0
	10	12.6 ($\pm$0.3)	101.0
Soil	0	25.7 ($\pm$0.3)	–
	5	31.0 ($\pm$0.2)	106.0
	10	36.2 ($\pm$0.3)	110.0
Spinach	0	2.8 ($\pm$0.2)	–
	5	7.5 ($\pm$0.3)	94.0
	10	13.0 ($\pm$0.4)	102.0
Tomato	0	8.5 ($\pm$0.3)	–
	5	13.8 ($\pm$0.2)	106.0
	10	19.0 ($\pm$0.3)	105.0
Black tea	0	1.1 ($\pm$0.2)	–
	5	5.9 ($\pm$0.2)	96.0
	10	10.8 ($\pm$0.4)	97. 0
Tobacco	0	2.7 ($\pm$0.2)	–
	5	7.6 ($\pm$0.2)	98.0
	10	13.0 ($\pm$0.3)	103.0

[a] For liquid sample values are μg mL^{-1} and for solid sample all values are μg g^{-1}.

Table 2 Comparison of the characteristic data between typical published methods and the proposed method for separation/preconcentration and determination of Ni(II).

Sorbent	Detection method	Preconcentration factor	Sorbent capacity (mg g^{-1})	RSD (%)	Linear range (ng mL^{-1})	Detection limit (ng mL^{-1})	Reference
Filter paper/DMG	Diffuse reflectance spectrophotometery	N.R.[a]	N.R.	N.R.	500–5000	470	Gazda et al. (2004)
Styrene-(EGDMA)/DCQ[b]	FAAS	200	7.05	2.25	0–500	2.0	Praveen et al. (2005)
C$_{60}$/DDC[c]	ETAA[d]	99	N.R.	<6.0	N.R.	75.0	Silva et al. (1998)
Amberosorb-572/EDTA[e]	FAAS	50.0	12.2	N.R.	N.R.	1.42	Baytak and Türker (2006)
Amberlite XAD-2/PAN[f]	ICP-AES[g]	N.R.	0.1	3.9	0.0–2.0	16.0	Ferreira et al. (1999)
AC/DTO[h]	FAAS	330	0.50	0.9	17–850	0.75	Ghaedi et al. (2007)
TiO$_2$ nanotubes	FAAS	N.R.	N.R.	2.6	1–150	0.25	Zhao et al. (2008)
Silica gel/gallic acid	FAAS	100	4.62	5.8	1000–5000	0.92	Xie et al. (2008)
Bacillus sphaericus/chromosorb 106	FAAS	250	6.55	N.R	N.R.	1.42	Tuzen and Soylak (2009)
TiO$_2$ nanotubes/8-hydroxyquinoline	FAAS	66.7	N.R.	2.6	1–150	1	Zhou et al. (2009)
SDS-alumina/BHAPN[j]	FAAS	63	11.7	2.1	15–600	2.1	Ghaedi et al. (2009)
Silicagel/aminothioanthraquinone	FAAS	N.R.	8.7	<9.0	N.R.	2.9	Ngeontae et al. (2007)
Amberlite XAD-7/PDAN[k]	FAAS	125	7.2	2.8	200–3000.	0.44	Ciftci et al. (2010)
SDS-alumina/indane-1,2,3-trione 1,2-dioxime	FAAS	444.4	2.28	1.5	5–1500	1.83	Hosseini et al. (2010)
Silica gel/PEG[m]	FAAS	166.6	8.33	3.13	2–100	0.71	Pourreza et al. (2010)
C18/CPAHPD[n]	Spectrophotometry	100	N.R.	1.32	10–370	3	Amin et al. (2011)
MWCNT/D2EHPA[q] and TOPO[r]	FAAS	25	4.78	<10	N.R.	40	Vellaichamy and Palanivelu (2011)
DMG/SDS-ACMNPs	FAAS	320	9.72	1.9	10–100	4.6	This work

[a] Not reported.
[b] Ethylene glycol dimethacrylate/5,7-Dichloroquinoline-8-ol.
[c] Diethyl dithiocarbamate.
[d] Electrothermal atomic absorption spectrometry.
[e] Ethylenediaminetetraacetic acid.
[f] 1-(2-pryidylazo)-2-naphthol.
[g] Inductively coupled plasma-Atomic emission spectrometry.
[h] Activated carbon/dithioxamide.
[j] Bis(2-hydroxyacetophenone)-1,3-propanediimine.
[k] Diamino-4-(4-nitro-phenylazo)-1H-pyrazole.
[m] Polyethylene glycol.
[n] 5-(4′-chlorophenylazo)-6-hydroxypyrimidine-2,4-dione.
[q] Multi-walled nanotubes/Di-(2-ethyl hexyl phosphoric acid).
[r] Tri n-Octyl phosphine oxide.

respectively. Also, the separation factor values (R_L) that describe whether a sorption system is favorable or unfavorable can be expressed as Eq. (2) (Oguz, 2005):

$$R_L = 1/1 + bC_o \qquad (2)$$

The R_L value implies the adsorption to be unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$). Value of R_L was found and approved that prepared DMG/SDS-ACMNPs is favorable for adsorption of Ni(II).

3.10. Analytical performance and method validation

In order to show the validation of the proposed method, under the optimal experimental conditions, the analytical features of the method such as limit of detection (LOD), linear range of the calibration curve and precision of Ni(II) were examined. The LOD of the proposed method based on 3 times the standard deviation of the blank ($3S_b$) was 4.6 ng mL^{-1}. The linear range of calibration curve for Ni(II) was 10.0–100.0 ng mL^{-1} with a correlation coefficient of 0.9985. The regression equation for the line was $A = 0.0894\,C_{Ni} + 0.0184$ ($n = 7$), where C_{Ni} is the concentration of Ni(II) in µg mL^{-1} and A is the absorbance. The relative standard deviation (RSD) for 7 replicate measurements of 50.0 ng mL^{-1} of nickel ion was 1.9%.

3.11. Analytical applications

In order to assess the applicability of the method to real samples, it was applied to the SPE and determination of nickel in different samples of tap water, spring water and plants of tea and spinach Table 1. The reliability was checked by spiking experiments. As the results show, the proposed method is suitable for the separation/preconcentration and determination of Ni(II).

4. Conclusions

It has been demonstrated that the DMG immobilized on modified ACMNPs provides a new and fast route for separation/preconcentration and determination of Ni(II) using FAAS technique in different samples. This sorbent was successfully applied for convenient, fast, simple and efficient enrichment of trace amounts of nickel ions from tap water, spring water and plants of tea and spinach samples. The main benefits of this methodology are: no use of toxic organic solvent(s), simplicity and high capacity of sorbent, preconcentration factor, good stability, fast adsorption and low cost. Magnetic separation greatly shortened the analysis time of the method. Easy regeneration is another property of ACMNPs, and the experiments have proved that these ACMNPs can be reused at least 3 times on average without the obvious decrease of recovery after wash/calcine procedures. Furthermore, it avoids the time-consuming column passing (about 1 h in conventional SPE method) and filtration operation, and no clean-up steps were required. Table 2 shows a comparison of the proposed method with other reported SPE methods. It could be seen that some obtained values for the proposed method such as reliable as sorbent capacity and preconcentration factor are as or better than some of the previously reported methods.

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