Determination of nickel and cadmium in fish, canned tuna, black tea, and human urine samples after extraction by a novel quinoline thioacetamide functionalized magnetite /graphene oxide nanocomposite

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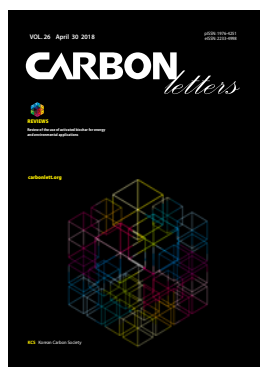
Abstract

In this research, a novel and efficient quinoline thioacetamide functionalized magnetic graphene oxide composite ($GO@Fe_3O_4@QTA$) was synthesized and utilized for dispersive magnetic solid phase preconcentration of *Cd(II) and Ni(II) ions in urine and various food samples*. A number of diverse methods were employed for characterization of the new nanosorbent. The design of experiments approach and response surface methodology were applied to monitor and find the parameters that affect the extraction performance. After sorption and elution steps, the concentrations of target analytes were measured by employing FAAS. The highest extraction performance was achieved under the following experimental conditions: pH, 5.8; sorption time, 6.0 min; $GO@Fe_3O_4@QTA$ amount, 17 mg; 2.4 mL 1.1 mol L^{-1} HNO_3 solution as the eluent and elution time, 13.0 min. The detection limit is *0.02 and 0.2 ng mL^{-1} for Cd(II), and Ni(II) ions, respectively.* The accuracy of the new method was investigated by analyzing two certified reference materials (sea food mix, Seronorm LOT NO 2525 urine powder). The interfering study revealed that there are no interferences from commonly occurring ions on the extractability of target ions. Finally, the new method was satisfactorily employed for rapid extraction and determination of target ions in urine and various food samples.

Key words: magnetic graphene oxide, quinolinethioacetamide, Ni(II) and Cd(II), extraction, separation

1. Introduction

Great attention has been attracted to the utilization of nano-structure sorbents in analytical chemistry, especially carbon-based nanosorbents such as graphene (G), graphene oxide (GO) [1,2], and magnetic nanoparticles (MNPs) [3-5]. G and GO are two widely used carbon-based sorbents in solid phase extraction (SPE) owing to their excellent properties such as very high specific surface area and sorption capacity, a single-layered structure, and excellent physicochemical properties [1,2]. Nevertheless, there are some limitations when G and GO are employed as sorbents such as their poor dispersion in aquatic samples, difficult collection from the extraction media, long sample loading time, and high back pressure when packed into a cartridge. The combination of large specific surface area, nanoscale, and sheet-like configurations of G and GO with the super-paramagnetic property of Fe3O4 are thereby expected to be excellent candidates for high-performance magnetic SPE (MSPE) [2]. The resultant nanocomposite can be simply dispersed and collected from the extraction media and benefit from the excellent extraction properties of G and GO along with super paramagnetic properties of Fe3O4 nanoparticles NPs [1].

Most heavy metals and metalloids are very toxic and environmental pollutants. These

toxic elements tend to coordinate with various biological ligands containing N, S, and O atoms [6]. These coordination interactions can lead to changes in the molecular conformation of proteins, enzyme inhibition, and breaking of hydrogen bonds. In this regard, the toxicity and carcinogenic nature of these pollutants such as the ions influencing the central nervous system (Hg(II), Pb(II), As(III)); the kidneys or liver (Cu(II), Cd(II), Hg(II), Pb(II)); or skin, bones, or teeth (Ni(II), Cu(II), Cd(II), Cr(III)) [7-9] can be illustrated by these interactions. Accordingly, monitoring and quantification of very low concentrations of heavy metals is often a major task for analytical chemists, as it is a good tool for identifying, monitoring, and quantification of these toxic elements in biological and various food samples. Therefore, developing simple, fast, sensitive, and environmentally friendly methods for monitoring and quantification of toxic metals is of particular significance.

Due to the matrix complexity and low concentration of heavy metals in real matrixes, a preconcentration and matrix elimination step is often mandatory before the analysis step [10]. In this regard, diverse extraction and separation methods such as liquid-liquid extraction [11], cloud point extraction [12], ion exchange [13], and SPE have been utilized and developed for the removal\extraction and preconcentration of these analytes in real matrices [14-20].

The most universally employed method for the separation and extraction of toxic elements from various real matrixes is SPE, owing to its simplicity, rapidity, minimal cost, and lower consumption of toxic reagents [21]. In this regard, various solid phases such as modified GO [22,23], modified duolite XAD 761 [24] MNPs [25,26], and modified porous sorbents [27-30] have been used in the SPE protocol. Fast and complete gathering of the sorbents from extraction media is in most cases difficult, time-consuming, and labor-intensive, which can cause additional environmental problems [31]. Therefore, using a nanosorbent with a super-paramagnetic property can solve this difficulty and facilitate the separation of nanosorbents from the solution, by employing an external magnetic field, and hence accelerates the sample preparation process [1,32].

The object of this research is separation and determination of Cd(II) and Ni(II) toxic ions in urine and various food samples by employing a novel quinolinethioacetamide functionalized magnetic graphene oxide composite (GO@Fe_3O_4@QTA). After the synthesis process, the nanocomposite was characterized by employing Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), elemental analysis, and vibrating sample magnetometry (VSM) techniques. The super-paramagnetic property of the nanosorbent along with excellent properties of GO makes the entire method a rapid and facile approach for the separation and extraction of target toxic ions. Functionalization with quinolinethioacetamide promotes the selectivity of the viable sorbent toward the target heavy metals. In this regard, GO acts as a support and spacer and prevents the aggregation of Fe_3O_4 NPs. Furthermore, the SiO_2 layer protects the Fe_3O_4 NPs in strong acidic media, which are often necessary for elution of sorbed ions from the sorbent surface. The design of experiments approach was utilized to characterize the affecting variables and achieve the best extraction performance throughresponse surface methodology (RSM). Ultimately, the new preconcentration method was utilized for the separation and determination of target toxic ions in urine and three various food samples.

2. Experimental

2.1. Reagents and materials

All reagents ($FeCl_3$, $(NH_4)_2Fe(SO_4)_2.6H_2O$, HCl, HNO_3, H_2SO_4, 3-(aminopropyl) triethoxysilane (3-APTS), NaOH, 2-propanol, carbon disulfide (CS_2), toluene, ammonium hydroxide (28% w/v), tetraethyl orthosilicate (TEOS), 8-aminoquinoline (8-AQ), ethanol, and methanol were of analytical grade and purchased from Merck (Darmstadt, Germany) or from Fluka (Seelze, Germany) Companies. Stock solutions (1000 mg L^{-1}) of Cd(II) and Ni(II) were obtained from Merck. Other standards or working solutions were prepared in deionized water.

2.2. Instrumentation

A Shimadzu (Kyoto, Japan) flame atomic absorption spectrometer model AA-680 consisting of an air/acetylene flame was used for the quantification of Ni(II) and Cd(II) ions. Nickel and cadmium hollow cathode lamps were employed as radiation sources (Cd wavelength, 232.0; Ni wavelength 228.8 nm). The pH measurements were conducted at 25ºC±1ºC by using a digital WTW Metrohm ion analyzer model 827 (Herisau, Switzerland) consisting of a combined glass-calomel electrode. FT-IR spectra were obtained by utilizing a Bruker FT-IR spectrophotometer model IFS-66. Elemental analysis was conducted on a ThermoFinnigan Flash EA112 elemental analyzer (Okehampton, UK). SEM images were recorded using a KYKY-3200 instrument (Beijing, China). Measurement of magnetic properties was accomplished utilizing a VSM (AGFM/VSM 117 3886 Kashan, Iran) at room temperature in a magnetic field strength of 1 tesla.

2.3. Preparation of standard and working solutions

Stock solutions (1000 mg L^{-1}) of various ions including K^+, Na^+, Ca(II), Cu(II), Mg(II), Pb(II), Co(II), Zn(II), Hg(II), Sn(II), Al(III), Cr(III), and Fe(III) were prepared in 2% (v/v) HNO_3 solution. The mixed working solutions of ions were prepared by stepwise dilution of a stock solution with deionized water and stored at room temperature before use.

2.4. Synthesis of quinolinethioacetamide functionalized magnetic GO composite

The magnetic graphene oxide@Fe_3O_4(GO@Fe_3O_4) was synthesized according to the literature [1]. Specifically, 0.5 g of GO was suspended in 500 mL of deionized water and ultrasonicated for 3 h to obtain a uniform dispersion. Thereafter, 0.85 g of $(NH_4)_2Fe(SO_4)_2•6H_2O$ and 0.422 g of $FeCl_3$ were added to the mixtureunder N_2 atmosphere protection at 50°C. Afterwards, to dissolve iron salts, the suspension was exposed to sonication for 10 min and then 20 mL of 8 mol L^{-1} NH_4OH aqueous solution was added slowly under sonication, which precipitates the Fe_3O_4NPs on the GO sheets. The reaction was continued at 50°C for 30 min to ensure complete growth of Fe3O4NPs crystals [1]. Afterwards, the mixture was cooled to room temperature and
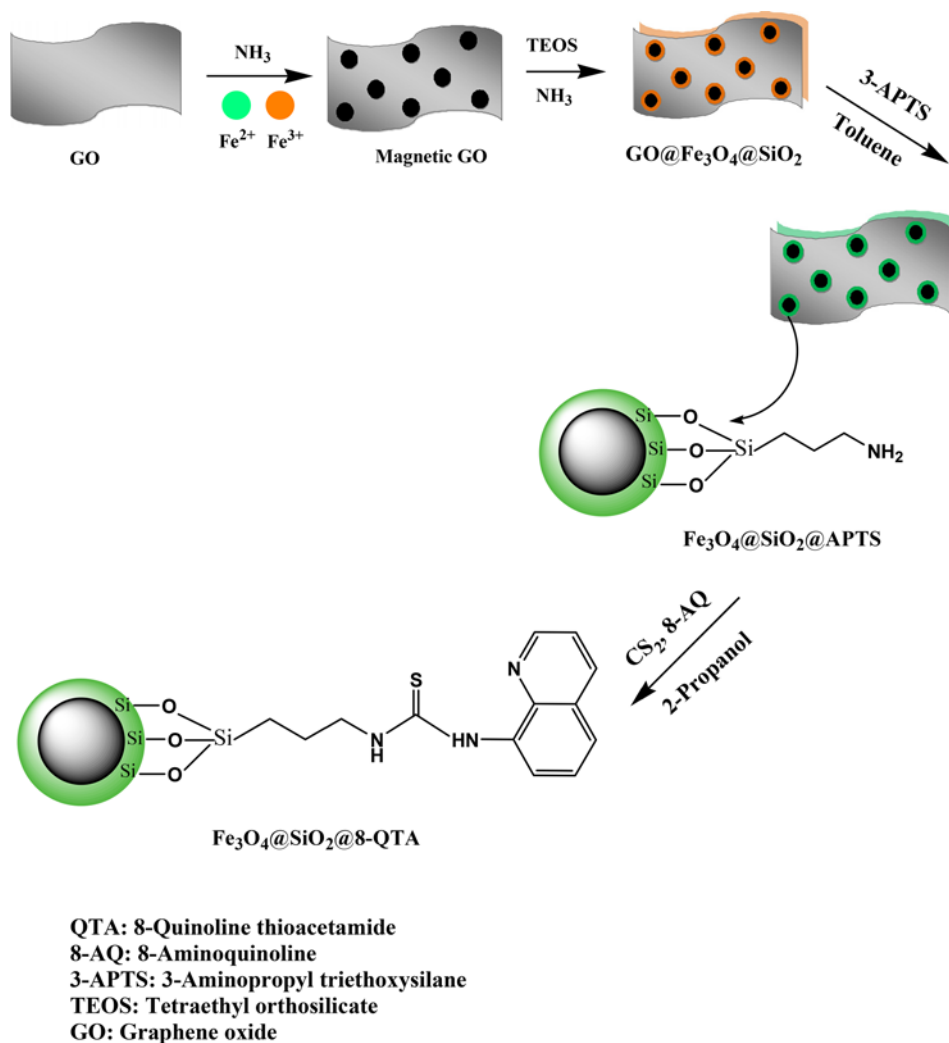
Fig. 1. A schematic representation of the synthesis of GO@Fe₃O₄@QTA nanocomposite.

GO@Fe₃O₄ was separated from the reaction medium using a strong permanent magnet. Separated GO@Fe₃O₄ was washed three times with deionized water followed by washing with ethanol.

To synthesize GO@Fe₃O₄@SiO₂, 1.0 g of GO@Fe₃O₄ was suspended in a solution consisting of 200 mL of deionized water, 100 mL of ethanol, and 10 mL of NH₄OH (25%). Afterwards, 4.5 mL of TEOS was added dropwise to the suspension under vigorous stirring in order to obtain the GO@Fe₃O₄@SiO₂. After stirring for 12 h at 40 °C, the GO@Fe₃O₄@SiO₂ was isolated by a strong magnet (15 cm × 12 cm × 5 cm, 1.4 tesla), washed with ethanol, and then dried at room temperature. Then, 1.0 g GO@Fe₃O₄@SiO₂ was dispersed in 150 mL of dried toluene and 2.0 mL of 3-APTS was added to the mixture and it was refluxed for 24 h. Afterwards, 1.0 g of dried GO@Fe₃O₄@SiO₂@APTS was suspended in 150 mL of 2-propanol and 2.0 g of 8-AQ along with 2 mL of CS₂ were added to the reaction mixture. The nanosorbent was gathered by the strong magnet after reflux for 15 h and dried at 50 °C under a vacuum. The functionalized nanosorbent

(GO@Fe₃O₄@QTA) was characterized by FT-IR spectroscopy, elemental analysis, SEM, and VSM. A schematic representation of the synthesis of this sorbent is depicted in Fig. 1.

2.5. Extraction procedure

First, the pH of the sample solution was fixed at 5.8 by dropwise addition of 0.1 mol L⁻¹ NH₄OH and 0.1 mol L⁻¹ HCl. Thereafter, 17 mg of GO@Fe₃O₄@QTA was dispersed in the solutions. Afterwards, the obtained suspension was stirred for 6.0 min in order to extract the toxic ions completely. In the next step, the samples were exposed to the strong magnet to gather the nanosorbent. The sorbed amount of each ion was measured by FAAS based on the concentration difference before and after the sorption process. Sorption percentage was calculated using the following equation:

$$\text{Sorption\%} = \frac{c_A - c_B}{c_A} \times 100 \qquad \text{(Eq. 1)}$$

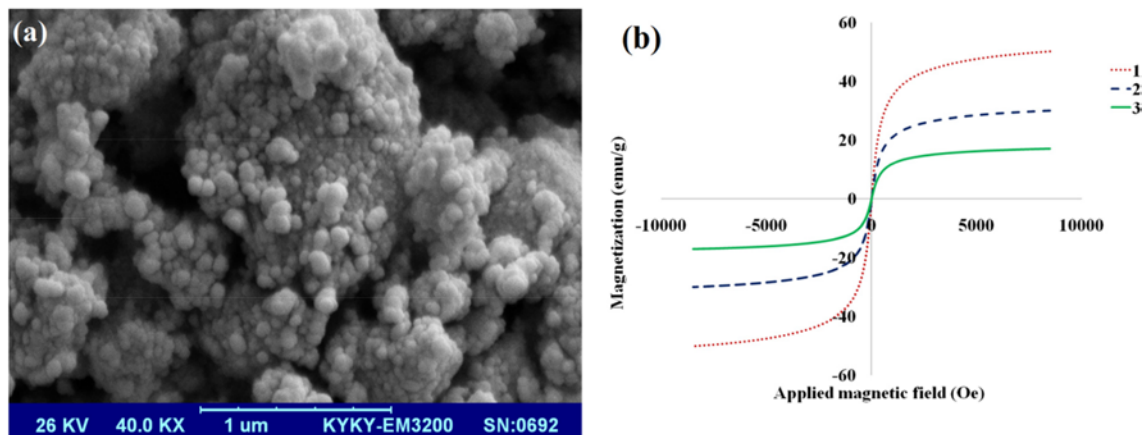where C_A and C_B represent the initial and final concentration (μg

Fig. 2. (a) SEM image of GO@Fe₃O₄@QTA nanocomposite and (b) VSM plots of (1) GO@Fe₃O₄, (2) GO@Fe₃O₄@SiO₂ and (3) GO@Fe₃O₄@QTA nanocomposite.

L^{-1}) of each ion in the solution, respectively. In the elution step, the magnetic nanosorbent was dispersed in 2.4 mL of a 1.1 mol L^{-1} HNO₃ solution and it was stirred for 13.0 min. Afterwards, this mixture was again subjected to the permanent magnet and then the supernatant solution was injected into FAAS in order to quantify the concentration of each ion.

2.6. Real sample pretreatment

The fish, canned tuna, and tea samples were purchased from local markets (Tehran, Iran). In the first step, each sample was washed with distilled water and then dried at 70 °C for 48 h. After chopping the dried samples (spiked or non-spiked), microwave-assisted acid digestion was conducted by addition of 2 mL of distilled water, 4 mL of HNO₃ 65% w/w, and 2 mL of H₂O₂ 33% (w/v) to 0.5 g of the samples. Afterwards, the reactors containing the samples were exposed to the microwave radiation program (2 min at 250 W, no radiation for 2 min, 6 min at 250 W, 5 min at 400 W, 8 min at 550 W, and then venting for 8 min) [33]. Thereafter, the residue was diluted up to 100 mL using double distilled water. The certified reference material (CRM) was digested according to the outlined procedure.

The urine samples were obtained from healthy volunteers and gathered in sterile sample containers and were kept in a refrigerator (4 ºC) before performing the extraction process. Digestion of urine CRM powder (Seronorm LOT NO 2525) was conducted in a mixture of 2 mL of HNO₃ (1% v/v) and 2 mL of H₂O₂ (30% v/v) in a reaction vessel and ultrasonicated for 30 min. The obtained solution was diluted up to 5 mL using deionized water [5, 34]. To determine Ni(II) and Cd(II) ions in the urine samples, 17 mg of the prepared nanosorbent was suspended in the urine sample.

2.7. Experimental design methodology

The experimental design methodology enables the researchers to find the best and most accurate optimum extraction conditions with the minimum number of experiments, experimental cost, and time. Thereby, the main variables affecting the performance of the new MSPE procedure were explored and optimized by means of Box-Behnken design (BBD). Randomization of experiments was performed in order to minimize the effect of uncontrolled parameters. The exact optimum value of a variable can be obtained by utilizing RSM, which graphically exhibits relationships between significant variables and responses [35-37]. Furthermore, the interactions of variables and the curvature among experimental variables were evaluated.

Herein, Design-Expert 7.0.0 trial version(Stat-Ease Minneapolis, USA) was employed in order to analyze the experimental design data and calculate the predicted responses.

3. Results and Discussion

3.1. Characterization studies

3.1.1. FT-IR characterization and elemental analysis
The FT-IR spectrum of the GO@Fe₃O₄@QTA nanocomposite was obtained using the KBr pellet method. The absorption peaks corresponding to Fe-O (576 cm⁻¹), Si-O-Si (1041 cm⁻¹), C-H aliphatic (2986 cm⁻¹), C-N (1307 cm⁻¹), C=N (1603 cm⁻¹), C=C (1565 cm⁻¹), C=S (1229 cm⁻¹), and N-H (792 cm⁻¹) confirmed successful functionalization of GO@Fe₃O₄ with quinoline thioacetamide moieties. A CHNS analysis was conducted to study the elemental contents of the GO@Fe₃O₄@QTA nanocomposite and revealed 38.6% C, 3.1% N, 2.4% S, and 1.8% H in the structure of GO@Fe₃O₄@QTA. The presence of N and S atoms in the structure of the magnetic nanocomposite confirmed the successful synthesis of GO@Fe₃O₄@QTA given that only QTA molecules contain sulfur atoms among the reagents.

3.1.2. SEM analysis
The morphology and dimension of GO@Fe₃O₄@QTA was explored by SEM. The SEM image of nanocomposite (Fig. 2a) depicted that the Fe₃O₄@QTA NPs have an average size of 45 nm and are coated on the GO sheets with a good distribution. Thereby, the aggregation problem of MNPs is almost completely resolved by employing GO as a spacer and support [1,2].

46

3.1.3. Magnetic properties

The magnetic property of GO@Fe$_3$O$_4$, GO@Fe$_3$O$_4$@SiO$_2$, and GO@Fe$_3$O$_4$@QTA nanocomposites were studied at room temperature with a magnetic property measurement system and the obtained VSM plots are illustrated in Fig. 2b. As illustrated in Fig. 2b, the saturation magnetization of GO@Fe$_3$O$_4$, GO@Fe$_3$O$_4$@SiO$_2$, and GO@Fe$_3$O$_4$@QTA was 50.1, 30.1, and 17 emu g^{-1}, respectively, which is sufficient for magnetic separation with a common magnetic field. Moreover, the absence of a hysteresis loop in the curves indicated the superparamagnetic property of the nanocomposites [38].

3.2. Optimization of MSPE parameters

3.2.1. Selection of the sorbent

The sorbent type is a very important factor in the magnetic SPE method. Accordingly, magnetic GO was chosen owing to its excellent properties such as high sorption capacity and the super-paramagnetic property of the magnetite NPs. Furthermore, GO sheets can be easily coated with silane coupling agents such as TEOS, which acts as a protecting layer for magnetite NPs in the strongly acidic medium needed for elution of metal ions [39]. In the last step, the surface of mGO@SiO$_2$ was modified with quinoline thioacetamide groups, which have N and S donor atoms and can enhance the sorption capacity of the sorbent towards the target ions based on soft and hard acid-base theory. Thereby, the extraction capabilities of mGO, mGO@SiO$_2$, mGO@SiO$_2$@8-QTA, and Fe$_3$O$_4$@SiO$_2$@8-QTA nanocomposites were studied and the

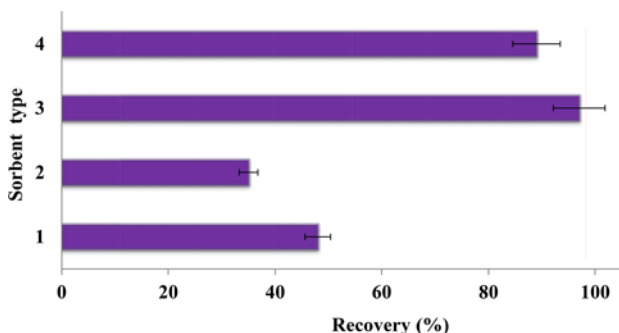**Fig. 3.** Comparison of the capability of various sorbents in MSPE process of target analytes. (1) mGO, (2) mGO@SiO$_2$, (3) mGO@SiO$_2$@QTA, and (4) Fe$_3$O$_4$@SiO$_2$@QTA.

mGO@SiO$_2$@8-QTA nanocomposite exhibited the highest extraction efficiency among the different sorbents (Fig. 3) owing to the high surface area and the presence of quinoline thioacetamide moieties. In comparison to Fe$_3$O$_4$@SiO$_2$@8-QTA, the mGO@SiO$_2$@8-QTA nanocomposite offers a significantly higher surface area to volume ratio owing to the presence of GO sheets and the formation of functional moieties on both sides of these sheets. Therefore, the mGO@SiO$_2$@8-QTA nanocomposite was selected as the most appropriate sorbent for the remaining studies.

3.2.2. Sorption step

In the uptake step, the effects of three factors, pH of the sample, GO@Fe$_3$O$_4$@QTA amount, and uptake time, were explored. A traditional optimization that involves monitoring the effect of one factor at a time on an experimental response suffers from some disadvantages. In the one-variable-at-a-time approach, interaction effects are not included. Additionally, conducting numerous numbers of experiments leads to an increase in time, expense, and consumption of reagents and materials. In response, multivariate statistic approaches have been developed to optimize the analytical procedures. RSM is the most relevant multivariate technique applied for analytical optimization purposes. In RSM, statistical and mathematical techniques based on a polynomial equation are used to fit experimental data, thus evaluating the influence of several variables. Simultaneous optimization of variables with the aim of attaining the best extraction performance is the goal of the RSM approach. In a BBD approach, the number of trials (N) obeys the following expression:

$$N = 2KK - 1 + C_{oo}$$

where K is the variable number and C_o is the center point number [40]. In this regard, K and C_o were set at 3 and 5, respectively, which means that 17 runs should be accomplished. The levels of each factor in BBD are listed in Supplementary Table 1S. The model F-value was 362.73 (P-value<0.0001) and implied that the constructed model is significant and there is only a 0.01 % chance that a model with this large F-value can occur because of noise. The P-value of the lack of fit (LOF) is equal to 0.4906, which indicates that the LOF is not significant relative to the pure error [41]. Based on the design results, the sample pH has a positive and the most

Table 1S. Experimental variables and levels of the Box Behnken design (BBD).

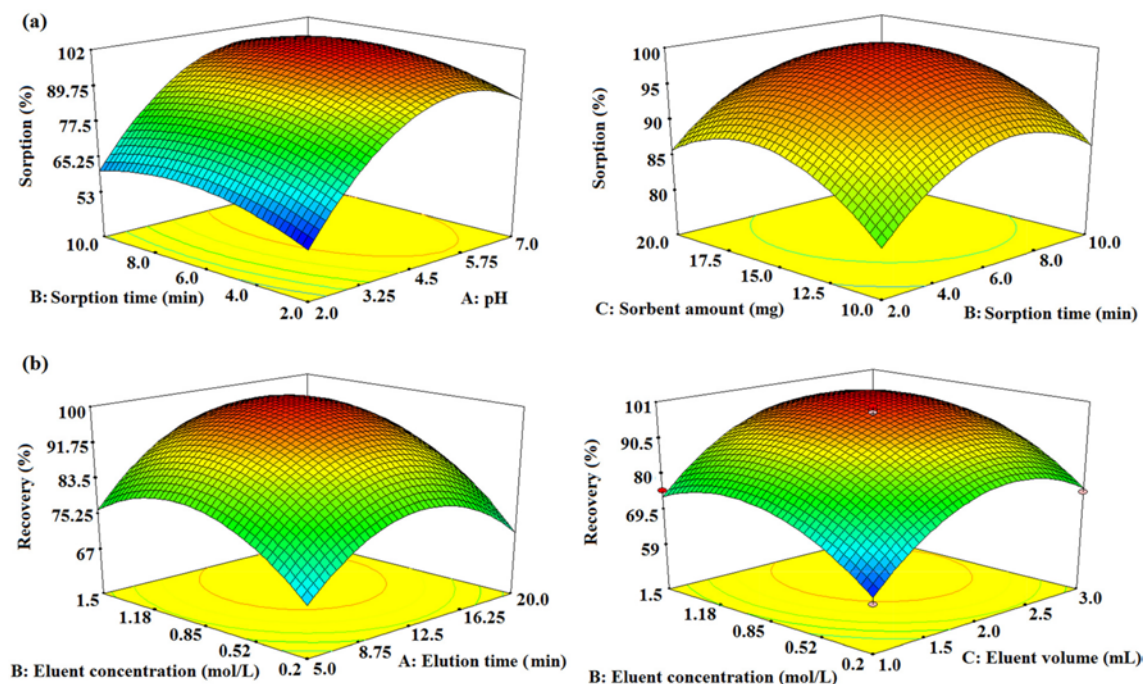|		Level		
		Lower	Central	Upper
Sorption step	A: pH	2.0	4.5	7.0
	B: Sorption time (min)	2.0	6.0	10.0
	C: Sorbent amount (mg)	10.0	15.0	20.0
Elution step	A: Elution time (min)	5.0	12.5	20.0
	B: Eluent concentration (mol/L)	0.2	0.85	1.5
	C: Eluent volume (mL)	1.0	2.0	3.0

Fig. 4. Response surface plots of (a) sorption step and (b) elution step.

significant effect on the sorption efficiency. The sorption of target species increased as the pH value increases. In lower pH values, the sorption is quite low owing to the protonation of N and S atoms of the QTA coating. As the pH increases the protonation of QTA decreases and the condition becomes more suitable for coordination interaction of target ions with the sorbent active sites. Fig. 4a depicts the response surface plots for the analysis of simultaneous effects of the sorption time-sample pH and sorption time-sorbent amount. Based on the design results, the best conditions were selected as pH 5.8; sorption time 6.0 min; and GO@Fe_3O_4@QTA amount 17 mg.

3.2.3. Elution step

First, three acidic eluents including HCl, HNO_3, and H_2SO_4 were tested to recover target ions from the sorbent. Other parameters including pH, uptake time, GO@Fe_3O_4@QTA, eluent volume, and elution time were fixed at 5.8, 6.0 min, 17 mg, 2.0 mL, and 15 min, respectively. The results revealed that HNO_3 acts as the best eluent to recover target ions. Afterwards, the effect of other remaining parameters including elution time, HNO_3 concentration, and eluent volume were optimized using BBD.

BBD was employed owing to the fact that it requires the minimum number of experiments (17 tests). The experimental data exhibited good accordance with the quadratic polynomial model. The model F-value and LOF *P*-value were 98.9 and 0.0509, respectively, which are desirable. Based on the design results, all the aforementioned parameters exhibited a significant positive effect on extraction performance. The obtained R^2, adjusted-R^2, and predicted R^2 values are 0.9872, 0.9772, and 0.8848, respectively, which are quite desirable.

The response surface plots (Fig. 4b) were employed to exhibit simultaneous effects of mentioned variables on the extraction performance. As illustrated in this figure, all the parameters are optimized in the selected range and depicted a curvature. Based on the overall optimization results, the best performance was obtained under the following experimental conditions: eluent concentration, 1.1 mol L^{-1} HNO_3 solution; eluent volume, 2.4 mL; and elution time, 13.0 min.

3.3. Effect of potentially interfering species

Coexisting ions may affect recovery and separation of target analytes, and thus the effect of various metal ions on the extraction performance of Cd(II) and Ni(II) ions was explored under the optimum conditions. The tolerance limit of the potentially interfering ions is listed in Supplementary Table 2S. As illustrated in this table, the presence of coexisting species has no notable effect on the extraction recovery of target analytes, which exhibits the good selectivity of GO@Fe_3O_4@QTA nanosorbent toward Cd(II) and Ni(II) ions under the optimized extraction conditions.

3.4. Effect of sample volume

The effect of sample volume (breakthrough volume) was investigated by employing various solutions containing 0.01 mg of each target ion (50, 100, 200, 300, 400, 500, and 600 mL). Afterwards, the developed MSPE procedure was conducted and the results demonstrated that the dilution effect has no significant effect on the volumes up to 0.5 L. Thus, the new nanosorbent can provide an enrichment factor equal to 208 regarding the sample and eluent volumes.

Table 2S. The recoveries of target ions in the presence of potentially interfering ions.

Potentially interfering ions	Tolerable Concentration Ratio X^c/ Cd, Ni	R^a (%) $\pm$ S^b	
		Cd	Ni
K^+	10000	101 ± 6.6	99.0 ± 4.0
Na^+	10000	99.1 ± 2.8	99.6 ± 2.9
Ca^{2+}	1000	97.8 ± 3.8	96.3 ± 5.8
Al^{3+}	1000	97.0 ± 7.0	95.0 ± 5.6
Co^{2+}	700	96.3 ± 6.1	98.3 ± 5.0
Fe^{3+}	500	98.1 ± 3.0	94.0 ± 5.5
Sn^{2+}	1000	98.5 ± 5.9	99.2 ± 6.7
Mg^{2+}	1000	97.6 ± 4.8	98.0 ± 5.1
Cu^{2+}	300	94.4 ± 4.5	96.2 ± 5.6
Pb^{2+}	200	97.0 ± 3.9	95.6 ± 4.7
Zn^{2+}	150	98.0 ± 5.4	97.1 ± 3.2
Hg^{2+}	100	96.1 ± 4.5	95.7 ± 6.5
Cr^{3+}	400	97.6 ± 6.3	97.6 ± 4.4

[a] Recovery
[b] standard deviation (n = 3)
Conditions: sample pH = 5.8, sample volume = 100 mL, 5 µg of Cd(II) and Ni(II) ions sorption time = 6.0 min; eluent = 2.4 mL, 1.1 mol/L HNO_3 solution, elution time = 13.0 min.
[c] Concentration of potentially interfering ions.

3.5. Maximum sorption capacity measurement

Sorption capacity is the maximum amount of each analyte sorbs per gram of a sorbent. Herein, the sorption capacity of GO@Fe_3O_4@QTA nanosorbent toward the target ions was studied by using 100 mL of the standard solution containing an appropriate concentration of each ion under the optimum extraction conditions. The maximum sorption capacity was expressed as the total amount of each metal ion (mg) sorbed per weight (g). The obtained capacity of the GO@Fe_3O_4@QTA is equal to 233 and 214 mg g^{-1} for Cd(II) and Ni(II), respectively.

3.6. Analytical performance of the MSPE method

Under the optimized MSPE conditions, figures of merit of the new method were achieved. The calibration curve is linear over a 0.07 to 80 ng mL^{-1} range (r^2 = 0.9958) for Cd(II) and 0.7 to 120 ng mL^{-1} (r^2 = 0.9974) for Ni(II) ions. The limit of detection is defined as LOD = $3S_b$/m in which S_b (what exactly?) exhibits a standard deviation of seven replicate blank signals, where m is the calibration curve slope after the extraction process. For a sample volume of 500 mL, the *LOD was 0.02 ng mL^{-1} for Cd(II) and 0.2 ng mL^{-1} for Ni(II) ions.* The precision of the MSPE method was determined as RSD% (relative standard deviation) at a concentration level of 20 ng mL^{-1} for each ion (n = 5) and it was equal to 8.0% for Cd(II) and 6.1% for Ni(II) ions.

3.7. Method validation

The accuracy of the new extraction method was confirmed by analyzing two CRM (sea food mix, Seronorm LOT NO 2525 urine powder) under the optimized MSPE conditions. As tabulated in Table 1, the determined values are in good agreement with the real amount of each metal ion. Thereby, the MSPE method can be used as an authentic technique for fast separation and quantification of target analytes in complex matrices.

3.8. Analytical application of the method in real matrices

The MSPE-FAAS method was employed for separation and quantification of target metal ions in urine, fish, canned tuna, and tea samples utilizing the optimal extraction conditions. The results (Table 2) exhibited the high performance of the GO@Fe_3O_4@QTA nanosorbent for preconcentrative separation of trace levels of target analytes in complicated real samples.

4. Conclusions

Herein, a viable quinolinethioacetamide functionalized magnetic graphene oxideGO nanocomposite has been synthesized and employed as an advanced nanosorbent for magnetic solid phase extractionMSPE of Cd(II) and Ni(II) toxic ions. The new extraction method in combination with FAAS was a facile, fast, precise, accurate, and selective method for separation and determination of target ions. Modification with quinoline thioacetamide moieties improved the selectivity of the method towards the target ions. The magnetic property of the new nanosorbent simplified and accelerated the separation and recovery of the sorbent from the extraction medium. The magnetic sorbent exhibits the benefits of high sorption capacities, low LODs, and a high enrichment factor (208-fold) compared to other methods (Table 3). Also, the RSDs of this method were similar to those of other methods. The analytical performance of the developed method is thus acceptable. Furthermore, this method has other advantages such as low time consumption (20 min) owing to the magnetically-assisted separation and large specific surface area; desirable results therefore can be achieved by utilizing smaller amounts of nanosorbent. The accuracy of the new method was confirmed by analyzing two CRMs (sea food mix, Seronorm LOT NO 2525 urine powder) and, finally, the validated method was applied for the fast determination of target ions in human urine, fish, canned tuna, and tea samples.

Conflict of Interest

No potential conflict of interest relevant to this article was reported.

Acknowledgements

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