Iranian Journal of Analytical Chemistry
Volume 4, Issue 2, March 2017 (1-9)

مجله ایرانی شیمی تجزیه
دوره ۴، شماره ۲، مهرماه ماه ۱۳۹۶ (۹-۱)

استخراج فاز جامد مغناطیسی مقادیر ناچیز نیکل در نمونه‌های مواد غذایی با نانوذرات اکسید آهن پوشش داده شده با پلی دوپامین

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تاریخ دریافت: ۲۳ بهمن ۱۳۹۵ تاریخ پذیرش: ۳ خرداد ۱۳۹۶

Magnetic Solid – Phase Extraction of Trace Amounts of Nickel in Food Samples Using Polydopamine Coated Fe_3O_4 Nanoparticles

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Received: 11 February 2017 **Accepted:** 24 May 2017

چکیده

یک روش ساده و سبز برای پیش تغلیظ Ni^{2+} بر اساس جذب سطحی کمپلکس دی متیل گلی اکسیمات آن بر روی نانوذرات اکسید آهن پوشش داده شده با پلی دوپامین توسعه یافت. کمپلکس جذب‌شده به آسانی با ۱ میلی لیتر کلروفرم واجذب و غلظت نیکل با اسپکتروفتومتری مرئی- ماورا بنفش تعیین شد. اثر pH، میزان جاذب و زمان استخراج بر روی جذب کمپلکس نیکل دی متیل گلی اکسیمات بوسیله روش طراحی آزمایش باکس- بنکن مورد بررسی قرار گرفت. در شرایط بهینه، محدوده وسیع خطی از ۶۰۰/۰ -۵/۰ میلی گرم بر لیتر با حد تشخیص ۱/۴۹ میلی گرم بر لیتر بدست آمد. روش پیشنهادی برای استخراج و پیش تغلیظ نیکل در نمونه‌های مختلف مواد غذایی بکار برده شد و نتایج آن با روش رسمی AOAC مقایسه گردید.

واژه‌های کلیدی

نیکل؛ پلی دوپامین؛ استخراج فاز جامد مغناطیسی؛ نانو جاذب؛ دی متیل گلی اکسیم.

Abstract

A simple and a green methodology has been developed for the preconcentration of Ni^{2+} based on the adsorption of its dimethylglyoximate complex on polydopamine coated Fe_3O_4 nanoparticles. The adsorbed complex was easily desorbed using 1.0 mL of $CHCl_3$ and the concentration of nickel was determined by UV-Vis spectrophotometry. The effects of pH, sorbent mass, extraction time on the sorption of nickel dimethylglyoximate complex were investigated using Box–Behnken design. In optimal experimental conditions, a wide linear range of 5.0-600.0 µg/L with detection limit of 1.49 µg/L was obtained. The proposed method was applied for extraction and preconcentration of Ni^{2+} in various food samples and the results were compared with the official AOAC method.

Keywords

Nickel; Polydopamine; Magnetic Solid–Phase Extraction; Nanosorbents; Dimethylglyoxime.

1. INTRODUCTION

Magnetic solid–phase extraction (MSPE), is a novel type of solid–phase extraction based on magnetic sorbents with high extraction efficiency, rapid extraction kinetics and convenient operation, which has received significant attention in recent years [1-2]. In this procedure, the magnetic sorbent is exposed to a sample containing the analyte of interest. After the sorption of the analyte from solution, the sorbent is easily separated by the application of an external magnet. Then, the analyte is eluted from the sorbent by the appropriate solvent and is determined through the analytical instrument [3]. Magnetic nanoparticles (MNPs), as an important class of nanoscale materials, have lately been the

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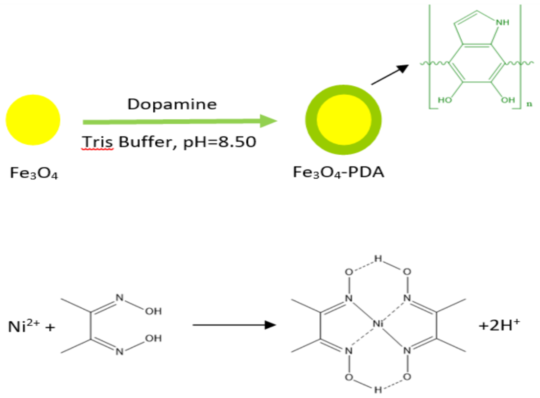
*Corresponding Author: m_nekoeinia@pnu.ac.ir; mohsen.nnia@gmail.com focus of continued research as the adsorbent for MSPE thanks to their high surface area, great extraction capacity, diverse functionalized possibilities and facile separation ability as well [4].

Among the MNPs sorbents used, magnetic iron oxide nanoparticles (Fe_3O_4 and Fe_2O_3) are the most popular due to their low price, low toxicity and unique magnetic properties [1, 4]. Although bare Fe_3O_4 MNPs were used as a sorbent for the extraction of organic analytes from complex matrices [5], but extraction efficiency and selectivity of bare MNPs could be improved by surface modification [6].

Dopamine (DA) is the most abundant catecholamine in the brain that contains both catechol and amine functional groups [7]. Polydopamine (PDA) films as multifunctional coatings can be easily grown and adhered onto a large variety of organic and inorganic materials through self-polymerization of DA in alkaline solution [6, 8]. Due to the simplicity and versatility of the polymerization process, PDA has been applied for surface modification of solid materials such as organic polymer, ceramic and/or inorganic metal oxides materials [9]. The use of PDA as affinity material for the construction of multifunctional (amino and catechol groups) nanocomposites has several advantages, including biocompatibility, dispersibility in water, and providing π– π stacking interaction to the targets [10]. Several studies indicated that dopamine has the potential to modify iron oxide nanoparticles directly and the PDA-modified nanoparticles can be used as adsorbents. Wang et al. [10] have synthesized core-shell structured Fe_3O_4@PDA nanoparticles and developed as a MSPE adsorbent in dispersion mode for the determination of trace polycyclic aromatic hydrocarbons in environmental samples. Their study indicated that only 20 mg of Fe_3O_4@PDA adsorbents are required to extract PAHs from 500 mL water samples. McCullum et al. [11] have described MSPE−HPLC−MS/MS to quantification of aflatoxins from liquid foodstuff samples using Fe_3O_4@PDA as the adsorbent. The use of PDA as a modifier of the Fe_3O_4 nanoparticles serves not only for sample clean-up and eliminating any potential matrix, but also for aflatoxins enrichment, allowing the quantification at very low levels. Recently, Chai et al. [12] introduced Fe_3O_4@PDA as the adsorbent for the extraction and enrichment of four synthetic colorants prior to high performance liquid chromatography analysis. The results indicated that the high extraction performances for colorants were obtained owing to the large specific surface area of the nanoparticles and the multiple interactions between PDA and analytes.

In this study, a simple method has been developed for the solid–phase extraction of nickel based on the adsorption of its dimethylglyoximate complex on polydopamine coated Fe_3O_4 nanoparticles (Scheme 1). The adsorbed complex could be desorbed using $CHCl_3$ and the concentration of Ni^{2+} was determined using UV-Visible spectrophotometry. The sorbent was characterized by Fourier transform infrared spectroscopy and transmission electron microscopy. The effect of parameters affecting the extraction step including pH, extraction time and sorbent mass were investigated and optimized by Box–Behnken design.



Scheme 1. (a) Schematic illustration for synthesis of Fe_3O_4-PDA. (b) The reaction of Ni^{2+} with DMG.

2. EXPERIMENTAL

2.1. Reagents

Dopamine was supplied by Caspian Tamin Pharmaceutical Company (Iran). $FeCl_3.6H_2O$, $FeCl_2.4H_2O$, $NiCl_2.6H_2O$, tris-(hydroxymethyl) aminomethane (Tris), sodium hydroxide, hydrochloric acid, dimethylgolyoxime (DMG), ethanolandchloroform were purchased from Merck. A 100 mg/L stock solution of Ni^{2+} was prepared by dissolving 0.0405 g of $NiCl_2.6H_2O$ in a 100 mL volumetric flask and was diluted to the mark with doubly distilled water. A 0.5 % solution of DMG was prepared by dissolving 0.5 g of DMG in 100 mL ethanol (95% V/V). Tris buffer solution (pH=8.5, 0.1 mol/L) was prepared by dissolving appropriate amount of tris-(hydroxymethyl) aminomethane in doubly distilled water and pH was adjusted by addition of the appropriate amounts of 0.1 mol /L HCl solution.

2.2. Apparatus

The UV-Vis absorbance spectra were recorded using double beam UV-Visible spectrophotometer (PG Instrument, T80+), equipped with 10 mm glass cuvettes. The pH measurements were performed with a Milwaukee model MI-180 pH-meter using a combined glass electrode. FT-IR spectra were recorded using a Perkin-Elmer spectrometer (Spectrum 65). Transmission electron micrographs were obtained by a Zeiss - EM10C TEM.

2.3. Synthesis of the magnetic Fe_3O_4–PDA nanoparticles

The magnetic Fe_3O_4 nanoparticles were prepared by the chemical co-precipitation method [10]. 10.4 g of FeCl3.6H2O, 4.0 g of FeCl2.4H2O and 1.7 mL of concentrated HCl were mixed in 50 mL water. The mixture was added dropwise to 500.0 mL NaOH (1.5 mol/L) solution under vigorous stirring. The precipitate was heated to 80 °C for 30 min and washed with 200 mL doubly distillated water four times.

For synthesis of the Fe_3O_4–PDA nanoparticles, 0.2 g of Fe_3O_4 was added to100 mL of Tris buffer (pH 8.5, 0.1 mol/L) and the mixture was sonicated for three minutes. A vial of dopamine (Each 5.0 ml vial contains 200 mg of dopamine) was added dropwise to the suspension and then shaked at 300 rpm for 24 h at room temperature. The Fe_3O_4-PDA was separated by external magnet, washed with ethanol–water mixture (1:1 v/v) several times. Finally the product was dried at 85 ºC for 6 h.

2.4. Procedure of SPE

An aliquot of a solution containing 5-600 μg/L of Ni^{2+} was mixed with 1.0 mL of DMG solution (0.5 %), followed by the addition of 20.0 mL of Tris buffer (pH 6.6, 0.1 mol/L). The solution was diluted up to the mark with doubly distilled water and incubated for 5.0 minutes at room temperature. Then, 0.059 g of sorbent was added to the solution and the mixture was stirred for 23 min. The sorbent was isolated by an external magnet and the supernatant was decanted. The adsorbed complex could be desorbed using 1.0 mL $CHCl_3$ and the absorbance of $Ni(DMG)_2$ was measured at 328 nm.

2.5. Preparation of food samples

Several agricultural products including tomato, lettuce, onion, potato, and carrot were collected from local markets. Thirty gram of each sample was washed thoroughly with distilled water, grounded, homogenized, and dried at 80 °C for 4 h. An amount of 6.0 g of dried sample was dissolved in 10 mL of 3 mol/L HNO_3 solution and was filtered [13]. The digested solution was quantitatively transferred to a 100 mL volumetric flask and diluted with deionized water to the mark and mixed well. A volume of 10 mL of this solution was transferred into a 250 mL volumetric flask, mixed with 25.0 mL of Tris buffer (pH 8.5, 0.1 mol/L), and followed by the addition of 5.0 mL of DMG solution (0.5 %). The solution was diluted up to the mark with doubly distilled water and was treated according to the recommended procedure.

For the determination of nickel in tea, 0.6 g of the dry black tea leaves (Chakosh-sabz, one of the Iranian brands) was decomposed at 500 °C for 60 min in a muffle furnace. The resulting ash was dissolved in few drops of concentrated HNO3 and heated for 45 min at 80 °C [14]. After cooling at room temperature, the mixture was filtrated and quantitatively transferred to a 100 mL volumetric flask and diluted with distilled water. A volume of 10 mL of this solution was transferred into a 250 mL volumetric flask and mixed with 25.0 mL of Tris buffer (pH 8.5, 0.1 mol/L), followed by the addition of 5.0 mL of DMG solution (0.5 %). The solution was diluted up to the mark with doubly distilled water and was treated according to the recommended procedure.

2.6. Box–Behnken design

A three-factor, three levels Box–Behnken design was employed in order to achieve the highest amount of the adsorption of $Ni(DMG)_2$ by the Fe_3O_4–PDA. Sorbent mass, pH and the extraction time were investigated as independent variables and absorbance of the complex at 327 nm was considered as the dependent variable. The experiments were done in random order, and each experiment was replicated twice. The Levels of these factors were founded from sufficient preliminary experiments. The variables and levels of the Box–Behnken design model are given in Table 1. The polynomial equation generated by this experimental design is as follows:

$$y = \beta_0 + \sum_{i=1}^{n} \beta_i x_i + \sum_{i=1}^{n} \beta_{ii} x_i^2 + \sum_{1\le i\le j}^{n} \beta_{ij} x_i x_j + \varepsilon \qquad (1)$$

where y is the estimated response (dependent variable); x_i and x_j are coded variables of the independent variables; β_0 is the constant, the β_i is the linear coefficient, β_{ii} is the quadratic coefficient, β_{ij} is the interactive coefficient and ε is a random error. The coded value of variables can be calculated using the following equation:

$$x = \frac{\mathrm{X} - \left|\frac{\mathrm{X_{max}} + \mathrm{X_{min}}}{2}\right|}{\left|\frac{\mathrm{X_{max}} - \mathrm{X_{min}}}{2}\right|}$$

where x is the coded value of a variables; X is the real value of an independent variables and X_{max} and X_{min} are the maximum and minimum values of the real variable [15].

Table 1. The experimental variables and levels of the Box–Behnken design.

Variables	Symbols		Levels		
	Uncoded	Coded	Low	Middle	High
pH	X_1	x_1	0.02	0.05	0.08
Sorbent mass (g)	X_2	x_2	5	20	35
Extraction time (min)	X_3	x_3	6.0	8.0	10.0

3. RESULT AND DISCUSSION

In neutral or slightly basic medium, Ni2+ forms a water insoluble complex with the DMG [16]. The Ni(DMG)2 complex is soluble in CHCl3 and other non-polar organic solvents [17]. Fig. 1 indicates the absorption spectra of the reagent blank and extracted Ni(DMG)2 complex in CHCl3, which exhibits two maximum peaks at 328 and 375nm.

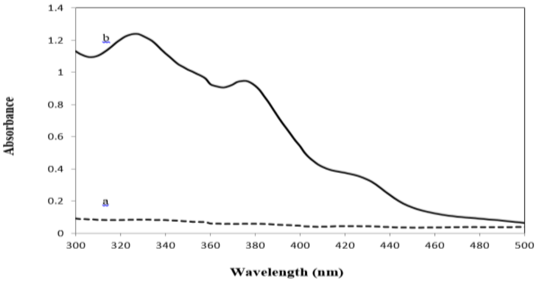


Fig. 1. Absorption spectra of (a) DMG and (b) its complex with Ni^{2+} after MSPE. Conditions: C_{DMG}= 0.5 %,$C_{Ni^{2+}}$= 500.0 µg/L, sorbent mass= 0.059 g, sample volume: 100.0 mL, volume of $CHCl_3$= 1.0 mL, pH=6.6, Extraction time= 23.0 min.

3.1. Characterization studies

The morphology and size of Fe_3O_4–PDA were studied by transmission electron microscopy (TEM). Fig. 2 shows the TEM images of the Fe_3O_4–PDA composite. As can be seen in the TEM image, the prepared nanoparticles have spherical shape with a grain size around 10 nm.

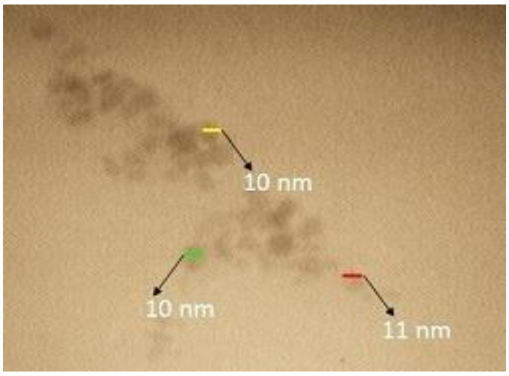


Fig. 2. TEM image of Fe_3O_4-PDA.

The formation of PDA layer on Fe_3O_4 surface was confirmed by FT-IR spectroscopy. As shown in Fig. 3, the peaks at 1602 cm^{-1} and 1288 cm^{-1} are related to the aromatic rings in the PDA polymer. In addition, the broad peak spanning at 3100–3500 cm^{-1} is derived from the overlap of hydroxyls, water adsorbed in PDA polymer and amines of PDA [18]. All of the features described above indicate that the PDA polymer has been successfully immobilized on the surface of Fe_3O_4 nanoparticles.

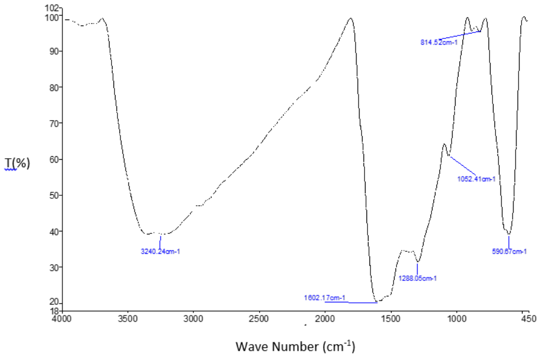


Fig. 3. FTIR spectrum of Fe_3O_4-PDA.

3.2. Optimization conditions for the solid–phase extraction of Ni^{2+}

Comparison of the preliminary results (Fig. 4) on the extraction of 100.0 mL of Ni^{2+} solution (500 µg/L) by 0.02 g unmodified and modified Fe_3O_4 showed that the modified magnetic nanparticles extract nickel complex more efficiently than the unmodified form (at least 2.3 times). Thus, bonded PDA on the surface of Fe_3O_4 had an effective role in increasing sorption and desorption of $Ni(DMG)_2$.

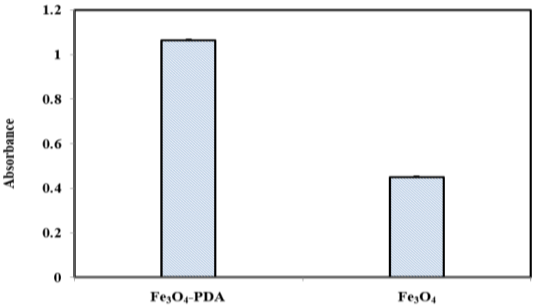


Fig. 4. Comparison of the extraction efficiency of $Ni(DMG)_2$ complex using Fe_3O_4 and Fe_3O_4-PDA. Conditions: C_{DMG}= 0.5 %, $C_{Ni^{2+}}$= 500.0 µg/L, sorbent mass= 0.020 g, sample volume: 100.0 mL, volume of $CHCl_3$= 1.0 mL, pH=8.0, Extraction time= 15.0 min.

The best extraction conditions of $Ni(DMG)_2$ complex with Fe_3O_4–PDA were carried out using the Box–Behnken design. According to the results of preliminary experiments, several variables that could potentially affect the extraction efficiency were chosen: extraction time; sorbent mass and pH. To reduce the number of experiments, the other parameters such as concentration of Ni^{2+} (500 µg/L) and incubation time for complex formation of Ni(DMG)2 (5 min) were kept constant according to the data from previous experiments [19].

A total of 30 experiments (15 experiments were repeated two times) have been utilized to evaluate the effects of the three main independent parameters (sorbent mass, extraction time and pH) on $Ni(DMG)_2$ extraction efficiency. The Box–Behnken design matrix and the corresponding results of these designed experiments (absorbance) are presented in Table 2.

Table 2. Utilized Box-Behnken Design matrix, observed and predicted values by the developed multi-parameter model.

Standard run order	X_1	X_2	X_3	Absorbance	
				Observed	Predicted
20	6.0	0.05	5	1.02	1.04
30	8.0	0.05	20	1.21	1.21
17	10.0	0.02	20	0.69	0.71
22	6.0	0.05	35	1.26	1.17
13	8.0	0.05	20	1.20	1.21
24	8.0	0.02	5	0.85	0.77
18	6.0	0.08	20	1.26	1.25
19	10.0	0.08	20	0.92	0.85
15	8.0	0.05	20	1.21	1.21
14	8.0	0.05	20	1.23	1.21
2	10.0	0.02	20	0.71	0.71
21	10.0	0.05	5	0.48	0.57
29	8.0	0.05	20	1.21	1.21
25	8.0	0.08	5	0.99	0.97
6	10.0	0.05	5	0.50	0.57
7	6.0	0.05	35	1.24	1.17
16	6.0	0.02	20	1.08	1.14
11	8.0	0.02	35	1.04	1.04
3	6.0	0.08	20	1.25	1.25
23	10.0	0.05	35	0.84	0.82
4	10.0	0.08	20	0.90	0.85
27	8.0	0.08	35	1.01	1.09
28	8.0	0.05	20	1.22	1.21
10	8.0	0.08	5	1.00	0.97
5	6.0	0.05	5	1.00	1.04
8	10.0	0.05	35	0.85	0.82
26	8.0	0.02	35	1.00	1.04
9	8.0	0.02	5	0.86	0.77
12	8.0	0.08	35	1.00	1.09
1	6.0	0.02	20	1.10	1.14

An analysis of variance (ANOVA) was carried out in order to evaluate the significance of the model and of their parameters (Table 3). The values of probability (P-values) were used as a tool to check the significance of each parameter. The P-values less than 0.05 imply that the model and model terms are statistically significant. Results of analysis of variance shows that the proposed regression model is significant with a model F-value of 39.73. Also, it can be seen from Table 3 that three main effect coefficients (X_1, X_2 and X_3) and three quadratic term coefficients (X_1^2, X_2^2 and X_3^2) are significant, while the other term coefficients are not significant. In addition, the goodness of fit of the model was evaluated by the determination coefficient (R^2) and adjusted determination coefficient(R^2_{adj}). The R^2 and R^2_{adj} values were obtained 0.9468 and 0.9229, respectively. The value of determination coefficient shows that only 5.32% of the total variations are not explained by the regression model. Based on Box-Behnken design, empirical relationships between the absorbance of $Ni(DMG)_2$ (Y) and significant independent variables were expressed by the following equation:

$$Y=1.2140-0.2076\,x_1+0.0654\,x_2+0.0931\,x_3-0.1444\,x_1^2-0.0809\,x_2^2-0.1693\,x_3^2$$

where as it is noted in Table 1, x_1, x_2 and x_3 denotes coded values of the pH of experiment, utilized sorbent mass and extraction time respectively.

Table 3. Analysis of variance (ANOVA) for the proposed model based on Box-Benken design.

Source of variation	Df ^{a}	SS ^{b}	MS ^{c}	F value	P value †
Model	9	1.27742	0.141935	39.56	0.000
X_1	1	0.68932	0.689315	192.15	0.000
X_2	1	0.06851	0.068513	19.1	0.000
X_3	1	0.13876	0.138756	38.68	0.000
X_1^2	1	0.15406	0.154059	42.94	0.000
X_2^2	1	0.04838	0.048376	13.48	0.002
X_3^2	1	0.21169	0.211693	59.01	0.000
$X_1 X_2$	1	0.00086	0.000861	0.24	0.630
X_1X_3	1	0.00673	0.006728	1.88	0.186
$X_2 X_3$	1	0.00769	0.007688	2.14	0.159
Error	20	0.07175	0.003587		
Total	29	1.34917			

S = 0.05988, R^2_{adj}= 92.32%, R^2= 94.70%.

^{a} degree of freedom, ^{b} Sum of square, ^{c} Mean square

†p values < 0.05 were considered to be significant.

Fig. 5 demonstrates response surface plots for the relationship between sorbent mass, pH and extraction time on the absorbance of $Ni(DMG)_2$. In these plots, the response is mapped against two experimental factors while the third is fixed at its central level. The curvatures of these plots indicate the non-linear relation between the response and the three variables. Fig. 5a represents the effect of sorbent mass and extraction time on the response at constant pH. This plot shows that both sorbent mass and extraction time have positive mutual impact on response. Fig. 5b exhibits the surface plot of the absorbance of $Ni(DMG)_2$ complex as a function of pH and extraction time. As can be seen, at any pH, the response increased with an increase in time up to 23 min and then declined with further increase in extraction time. At the extraction times longer than 23 min, the extraction recoveries decreased probably due to saturation of surface adsorption sites and desorbing of $Ni(DMG)_2$ complex from adsorbent surface by stirring hydrodynamic forces [20]. Also, as shown in Fig. 5c, at any fixed extraction time, the response increased with an increase in pH up to 6.6 and then declined with further increase in pH. According to the overall result of the optimization process, pH 6.6, 0.059 g sorbent mass and 23 min extraction time were chosen as the optimal conditions.

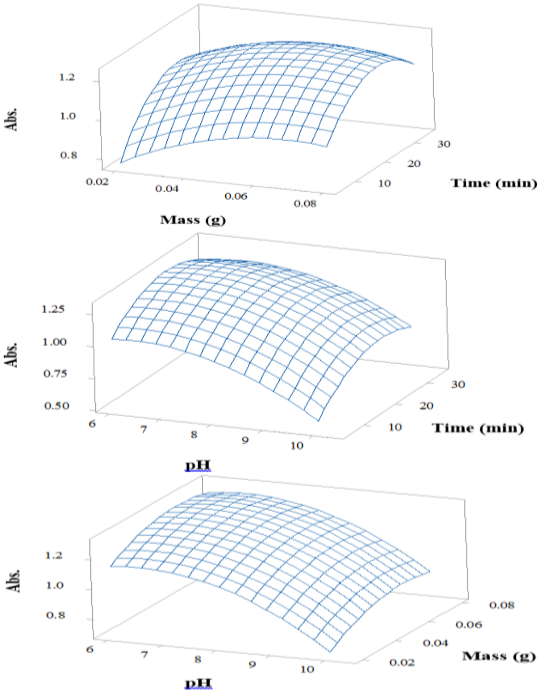


Fig. 5. Response surface obtained from Box–Behnken design for sorption efficiency of $Ni(DMG)_2$ complex .

In order to find the highest enrichment factor, the effect of changes in the volume of sample solution was investigated. Experiments were performed using different sample volumes (50.0, 100.0, 150.0, 200.0, 300.0 and 400.0 mL) with the same concentration of Ni^{2+} at pH 6.6 with 0.059 g of Fe_3O_4–PDA. The results (Fig. 6) show that the absorbance of complex was increased up to 200.0 mL and then declined with further increase in volume of sample solution. At lower volumes of sample solution, the magnetic nanoparticles are not dispersed well in the solution, resulting in a decrease in the extraction efficiency. Also, at higher volumes complex $Ni(DMG)_2$ is not effectively adsorbed, which is probably due to the lower interaction between the complex and magnetic nanoparticles. By looking at the final elution volume (1.0 mL) and the sample solution volume (200.0 mL), a preconcentration factor of 200 was obtained.

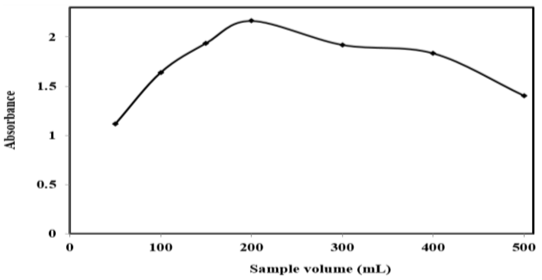


Fig. 6. Effect of sample volume on the sorption percentage of 500µg/L of Ni2+. Conditions: C DMG= 0.5 %, CNi2+= 500.0 µg/L, sorbent mass= 0.059 g, volume of CHCl3= 1.0 mL, pH=6.6, Extraction time = 23.0 min.

The influences of various eluents on desorption of $Ni(DMG)_2$ from Fe_3O_4–PDA were also studied. A series of common organic solvents such as CH_3OH, C_2H_5OH, CH_3CN, CH_2Cl_2, $CHCl_3$ and CCl_4 were utilized in order to find the best eluent for desorption of the complex from the sorbent surface. The adsorbed $Ni(DMG)_2$ complex was eluted by passing 1.5 ml of each of above solvents. The results indicated that the highest absorbance value was achieved when $CHCl_3$ was used as the eluent (See Fig.7). Consequently, $CHCl_3$ has been used as an eluent in further studies. According to the literature, separation of nickel as its DMG complex form has been accomplished by chloroform [17, 19, 21] .

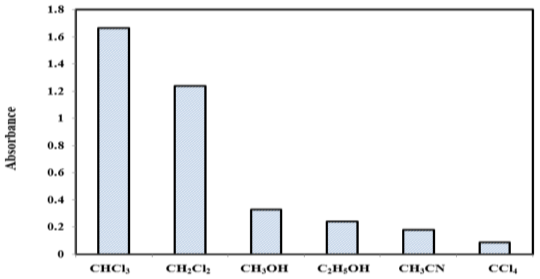


Fig. 7. The desorption efficiency of different eluent solvent. Conditions: C DMG= 0.5 %, CNi^{2+}= 500.0 µg/L, sorbent mass= 0.059 g, sample volume: 200.0 mL, desorption solvent volume = 1.0 mL, pH=6.6, Extraction time= 23.0 min.

To choose the proper volume of eluent, the retained Ni(DMG)$_2$ complex on the sorbent were stripped with varying volumes (0.5–2.0 mL) of $CHCl_3$. Although elution with 0.5 mL of $CHCl_3$ gave highest absorbance value, use of 1.0 mL of $CHCl_3$ provided more precise results than smaller volumes. So, an eluent volume of 1.0 mL was chosen for further studies in order to achieve high levels of precision and preconcentration factor.

3.3. Recycle testing of the adsorbent

Stability and regeneration is one of the most important properties for considering the performance of the adsorbent. The stability and reusability of the nanosorbent was tested at optimum experimental conditions by five repeating the adsorption-desorption cycle using the same sorbent. After each adsorption–desorption cycle, the adsorbent was washed thoroughly with doubly distillated water and dried at room temperature. According to which is represented in Fig. 8, the sorbent is stable up to 5 adsorption–elution cycles without obvious decrease in the absorbance of the Ni(DMG)$_2$ and can be reused properly.

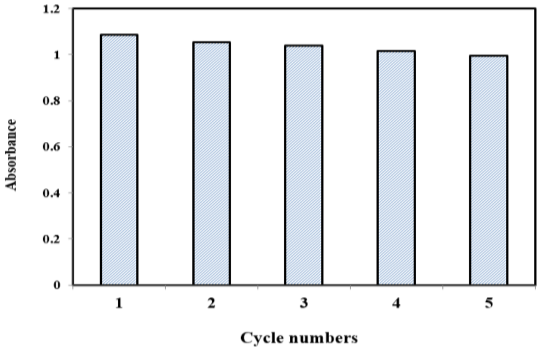


Fig. 8. Regeneration of Fe^3O^4-PDA over 5 cycles. Conditions: C DMG= 0.5 %, CNi^{2+}= 500.0 μg/ L, sorbent mass= 0.059 g, sample volume: 100.0 mL, volume of CHCl3= 1.0 mL, pH=6.6, Extraction time= 23.0 min.

3.4. Analytical figures of merit

Under the optimum conditions described, the calibration curve was linear over the concentration range of 5–600 μg/L. The linear regression equation for this range was $A=4\times10^{-3}C+0.001$ (r = 0.999), where A is the absorbance, C is the concentration of Ni^{2+}, μg/ L. The limit of detection (LOD) and limit of quantification (LOQ) based on 3Sd/m and 10Sd/m (where Sd and m are standard deviation of the blank and slope of calibration graph) were 1.49 μg/L and 4.96 μg/L, respectively. Relative standard deviation (RSD%) for analysis of Ni^{2+} was 0.22 % for ten replicate measurements.

3.5. Interference study

Selectivity of the developed method was examined by studying the effect of foreign species on the determination of 100 μg/L Ni^{2+}. Tolerable limit was defined as the highest amount of foreign species that produced an error less than ± 3% relative error in Ni^{2+} determination. The tolerance limits for different foreign species are listed in Table 4. The results show that excess amounts of common cations and anions do not interfere with the determination of trace quantities of Ni^{2+}.

Table 4. Effect of foreign species on the determination of 100 μg/L of Ni^{2+}.

Foreign species	Tolerance limit(μg/L)
Na^+	100[a]
K^+	100
Ca^{2+}	100
Ba^{2+}	100
Mn^{2+}	100
Fe^{2+}	100
Fe^{3+}	100
Zn^{2+}	100
Pb^{2+}	100
Hg^{2+}	100
Ag^+	100
Co^{2+}	50
Cu^{2+}	50
Cl^-	100
Br^-	100
I^-	100
F^-	100
SO_3^{2-}	100
SO_4^{2-}	100
NO_3^-	100
PO_4^{3-}	100
CO_3^{2-}	100

[a] Largest amount tested.

3.6. Analysis of food samples

The proposed method has been successfully applied for nickel content determination in food samples. The results are represented as μg/gr dry matter in Table 5. The concentrations of Ni^{2+} were also determined in all food samples by official AOAC methods [22]. The analytical results obtained by the proposed and official AOAC methods were in good agreement and were not significantly different (according to the *t*-test at the 95% confident level), thus verifying the high accuracy of the developed method.

Table 5. Analytical results for the determination of trace nickel in different food samples with the proposed and AOAC methods.

Sample	Found [a] (μg/g)	
	Proposed method	AOAC method
Lettuce	6.84 ± 0.14	6.87 ± 0.02
Potato	6.19 ± 0.22	6.20 ± 0.03
Carrot	5.37 ± 0.13	5.39 ± 0.02
Tomato	6.93+0.13	6.92+0.03
Onion	10.10±0.22	10.09±.02
Black tea leaves	149.38±2.01	149.08±0.22

[a] Mean± standard deviation (*n* = 3)

4. CONCLUSIONS

In this work, Fe_3O_4–PDA nanosorbent was prepared and used as an effective adsorbent for the preconcentration of Ni^{2+} in aqueous solution prior to UV-Vis spectrometry. The polydopamine was directly grafted onto the surface of Fe_3O_4 nanoparticles by self-polymerization of dopamine in air under a basic condition. These modified magnetic nanoparticles are environmental friendly and no poisonous substances are released into water samples during extraction and cleanup process. Polydopamine layer, due to presence of amino and catechol groups, provides a high extraction efficiency of the adsorbent to $Ni(DMG)_2$ complex. The proposed method is highly selective and sensitive and has been applied to the determination of trace amount Ni^{2+} at μg/L levels in food samples.

ACKNOWLEDGMENTS

The authors are grateful to the PNU Research Council for financial support of this research.

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