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Ionic liquid-modified Fe_3O_4 nanoparticle combined with central composite design for rapid preconcentration and determination of palladium ions

Mehrnoosh Bayat, Farzaneh Shemirani*, Mostafa Hossein Beyki, Malihe Davudabadi Farahani

Department of Analytical Chemistry, University College of Science, University of Tehran, P.O. Box 14155-6455, Tehran, Iran, Tel. +98 21 61112481; Fax: +98 21 66405141; email: shemiran@khayam.ut.ac.ir (F. Shemirani)

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ABSTRACT

In this work, magnetic Fe_3O_4 nanoparticles (NPs) were synthesized by ultrasonic chemical co-precipitation method. Then hydrophobic ionic liquid (IL), as a green coating agent, was deposited on the surface of synthesized NPs in order to improve their extraction capability toward Pd(II) ions as diethyldithiocarbamate (DDTC) complex. Scanning electron microscopy, thermogravimetric analysis, X-ray diffraction (XRD), vibrating sample magnetometer (VSM), and Fourier transformed infrared (FTIR) techniques were used for characterization of the adsorbent. The adsorption rate was fast and the equilibrium time was achieved within 4 min due to the strong interaction of Pd–DDTC complex with the IL and the absence of internal diffusion resistance. The separation of the adsorbent from aqueous bulk was achieved after about 2 min by a magnet, so no centrifugation or filtration was required. The effective parameters such as pH, concentration of ligand, amount of adsorbent, and the extraction time were inspected by using a central composite design in order to identify the most important parameters and their interactions. Under optimum conditions, the detection limit was 0.82 ng mL^{-1} and the relative standard deviation ($n = 10$) was 2.8% for 100 ng mL^{-1} of Pd(II). The proposed method was applied for the preconcentration of Pd(II) from road dust, liver, and water samples, and it was found that the amounts of palladium ions in dust and liver samples were 104 and 8.7 ng mL^{-1}, respectively.

Keywords: Central composite design; Fe_3O_4 nanoparticles; Ionic liquid; Palladium

1. Introduction

Palladium is a valuable metal, which possesses attractive physical and chemical properties such as high melting point, corrosion resistance, electrical conductivity, and extraordinary catalytic properties [1]. Therefore, it has found an extensive range of applications in metallurgy, petrochemistry, electronics, telephone circuits, dental and medicinal prostheses, jewelry, and coating agents [2–5]. Catalytic converters of modern vehicles are considered to be the main sources of Pd(II) pollution, because particles deposited on the roadside can be transported to water, leading to the contamination of plants and food [6]. Palladium also bioaccumulates in the living organisms, causing health risks to humans such as asthma, allergy, rhino conjunctivitis, and other serious health problems [7]. Thus, due to the high economical value of palladium

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*Corresponding author.

and toxicity of its compound, the selective separation and sensitive determination of palladium is of special interest to analytical sciences.

Several determination techniques such as flame atomic absorption spectroscopy (FAAS) [8], graphite furnace atomic absorption spectrometry [9], and inductively coupled plasma atomic emission spectrometry [10] have been used for the determination of trace amounts of palladium ions. In spite of high sensitivity and good selectivity of the modern instruments, interference effect of matrix cannot be always eliminated and direct analysis of real samples is considerably restricted [11]. In this respect, preconcentration of Pd (II) from dilute or complex samples for increasing sensitivity is needed [12].

Liquid–liquid extraction (LLE) and solid-phase extraction (SPE) are two techniques that have found widespread applications on the determination of Pd (II). In the viewpoint of simplicity, cleanness, low reagent, and organic consumption, SPE is most widely applied and is preferred to LLE [13]. Over the past few years, several adsorbents, such as activated carbon [14], silicagel [15], exfoliated graphite [16], carbon nanotubes [17], ion-imprinted polymers [18,19], modified organo-nanoclay [20,21], hydrogel [22], activated alumina [23], modified silica [24,25], and modified nanoalumina [26], have been used for the preconcentration of metal ions. Fe_3O_4 nanoparticles (NPs) as an efficient class of adsorbent, are receiving increasing interest in recent years. They have large surface area-to-volume ratio that promises much greater extraction capacity and makes extraction of target compounds with lower amounts of the adsorbent possible. Moreover, the easy separation of metals loaded on the magnetic adsorbent from the solution can be achieved by using an external magnetic field, and no centrifugation or filtration is needed for sample separation. However, naked Fe_3O_4 NPs have high chemical activity, and are easily oxidized in air [27]. Also, there is no selectivity for quantitative extraction and preconcentration of an interesting species with naked iron oxide from complicated matrix. Therefore, modification and providing proper surface coating for analytical application is necessary. In this case, ionic liquids (ILs) as a class of nonmolecular ionic and green compounds, which are chemically inert, stable, and nonflammable, can be employed [28,29]. As a consequence of the immobilization, ILs lose their liquid nature but they maintain their exceptional physical (thermal stability) and chemical (extraction capacity) properties. They present a great extraction capability toward different analytes which they can interact by electrostatic, hydrophobic, and – interactions. So, our research group efforts have been intensified and focused on the beneficial utilization of ILs as a green coating agent.

In this study, synthesized Fe_3O_4 was modified with hydrophobic IL of 1-hexyl-3-methyl-imidazolium hexafluorophosphate, [HMIM][PF_6], in order to change the surface of Fe_3O_4 to achieve extraction of Pd(II) ions as diethyldithiocarbamate (DDTC) complex prior to determination by flame atomic absorption spectrometry. The optimization step was performed by central composite full factorial design (CCD) in order to identify the most important parameters and their interactions. In comparison with one factor at a time design, by means of CCD, the experimental procedure can be simplified and the overall costs associated with the experiment decreased. The feasibility of adsorbent was investigated for the preconcentration of Pd(II) in road dust, liver, and water samples.

2. Experimental

2.1. Apparatus

The determination of Pd(II) was carried out using the Varian Spectra AA-400 atomic absorption spectrometer equipped with a deuterium background correction and an air–acetylene burner. A Pd(II) hollow-cathode lamp that operated at 5 mA was used as the radiation source. All measurements were carried out in the peak height mode at 244.8 nm, using a spectral bandwidth of 0.2 nm. A Metrohm digital pH-meter (model 692, Herisau, Metrohm, Switzerland) equipped with a glass combination electrode was used for the adjustment of pH. For magnetic separations, a strong neodymium-iron-boron ($Nd_2Fe_{12}B$) magnet (1.31 T) was used. Thermogravimetric analysis (TGA) measurement was performed from room temperature to 600˚C with Q600. FTIR was recorded with one ABB Bomem MB 100 IR spectrometer using KBr discs over the wavelength range of 400–4,000 cm^{-1}. A Field emission scanning electron microscope, model S-4160, was used for the preparation of scanning electron microscopy (SEM) images. X-ray powder diffraction (XRD) measurements were performed using a STADI-MP from the STOE company (Germany) with monochromatized Cu Kα radiation. Magnetization measurement was performed using a vibration sample magnetometer (VSM) (Lake Shore Model 7400, Japan).

2.2. Reagents and solutions

All chemicals used in this work were of analytical grade. $Fe(NO_3)_3.9H_2O$, $FeSO_4$, the standard solutions of Pd(II) (1,000 mg L^{-1}), sodium DDTC, acetylacetone, and 1-hexyl-3-methyl-imidazolium hexafluorophosphate,[HMIM][PF_6] were purchased from Merck (Darmstadt, Germany). A solution of 10^{-3} mol L^{-1} chelating agent, DDTC, was prepared by dissolving its appropriate amount in ethanol. A buffer solution (pH 7.6) was prepared by mixing 50 mL of potassium hydrogen phosphate (1 mol L^{-1}) and 42.4 mL NaOH (1 mol L^{-1}), and diluted with 100 mL by distilled water. Pipettes and vessels in the experiments were kept in 10% nitric acid for at least 24 h and subsequently washed several times with double distilled water.

2.3. Preparation of adsorbent

Magnetic Fe_3O_4 particles were obtained by ultrasonic chemical co-precipitation according to the previously reported methods with some modification [30]. Briefly, 7 g of $Fe(NO_3)_3.9H_2O$ and 1 g of $FeSO_4$ with the molar ratio of 2.5:1 were dissolved in deionized water. Under ultrasonic agitation, ammonia was added to the solution and immediately a black precipitate was produced. Then, obtained Fe_3O_4 precipitate was aged at 65°C for 30 min in ultrasonic water bath. After the reaction, the black precipitates (Fe_3O_4 NPs) were separated using a magnet and washed repeatedly with deionized water and ethanol until a pH level of 7 was reached. Particles were then dried at 75°C. Fig. 1 shows the SEM image of synthesized Fe_3O_4 NPs.

In order to achieve the modification of MNPs, 1.5 g of Fe_3O_4 was added gently to a stirred solution of [HMIM][PF6] (0.5 g) in acetone (15 mL). After stirring for 1 h at room temperature, the solvent was evaporated and the precipitate was washed with methylene chloride and distilled water; dried in an oven at 60°C for 2 h and stored until being used.

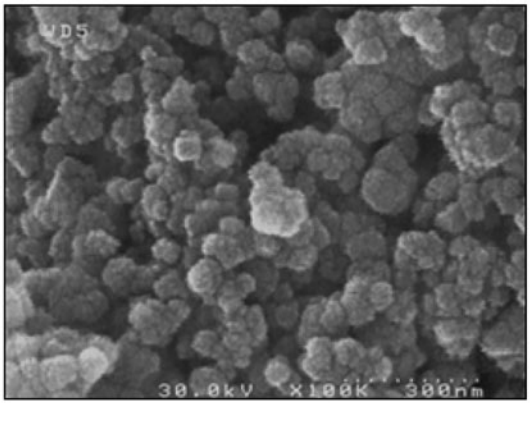

Fig. 1. SEM image of Fe_3O_4 NPs prepared by ultrasonic chemical co-precipitation.

2.4. Procedure of extraction

For separation and preconcentration of Pd(II) with modified Fe_3O_4 NPs, vessel containing 50 mL solution of Pd(II) (3–150 ng mL^{-1}) was prepared and the pH was adjusted to 7.6 by adding 1 mL of the mentioned buffer. Then, according to optimum conditions, 5.5×10^{-6} mol L^{-1} (275 µL) of DDTC was added to the solution. After shaking for 1 min, 28.0 mg of the modified Fe_3O_4 NPs was added, and then it was shaken for 4 min in order to suspend the NPs thoroughly and allowed to complete the extraction process. Subsequently, a strong magnet was placed at the bottom of the tube, after 2 min, the magnetic adsorbent carrying the target ions was assembled and the isolated NPs were eluted with 1 mL of acetylacetone/ethanol (1:1) solution to desorb the Pd(II) ions. Finally, the obtained mixture was shaken and exposed on the magnet, and the eluted phase was injected to FAAS. The same procedure was applied to the blank solution.

2.5. Real sample preparation

To demonstrate the efficiency of the proposed method, it was applied to the analysis of various real samples, such as road dust (collected from busy streets of Tehran), bovine liver (purchased from local supermarkets in Tehran), and different water samples including: spring water, river water (collected from Tajan river located in the north of Iran) and tap water (collected from our laboratory).

2.5.1. Preparation of Water samples

For the preparation of water samples, the nitric acid was added to a 500 mL of river and spring water samples after their collection, in order to prevent adsorption of the ions on the flask walls and filtered through 0.45 µm pore size membrane filters to remove any suspended particles and analyzed by the described method.

2.5.2. Preparation of road dust and liver samples

0.5 g of homogenized dust sample was weighed accurately and digested with 3:1 HCl–HNO_3 in a 200 mL beaker by refluxing the mixture for 5 h [31]. The solution of sample was filtered, cooled to room temperature, and after pH adjustment, it was made up to 100 mL. For the preparation of bovine liver

Table 1
Factors and levels used in the CCD

Variables	Symbols	Levels				
		−α	−1	0	+1	+α
pH	A	5	6	7	8	9
Volume of ligand (μL)	B	50	125	200	275	350
Amount of sorbent (mg)	C	5	15	25	35	45
Time (min)	D	2	3	4	5	6

sample, 5 g of it was transferred into a 250 mL beaker, and 5 mL of 0.5 mol L^{-1} nitric acid was added to moisten the sample thoroughly. Then, 10 mL of concentrated nitric acid was added and heated on a hot plate (130℃) for 3 h. After cooling it to the room temperature, 5 mL of concentrated perchloric acid was added drop wise. After adding hydrogen peroxide, the beaker was heated gently until the sample solution became clear. This was left to cool down and after pH adjustments it was diluted with distillated water up to 100 mL [32]. Finally, the proposed method was applied to determine Pd(II) in 50 mL of this solution. In addition, accuracy of the method was evaluated by spiking Pd(II) in 50 mL of the sample's volume.

2.6. Optimization strategy

The optimization step was carried out using a central composite full factorial design. The CCD is a five-level design which is widely used as response surface methodology. CCD allows a great number of levels without performing experiments at every combination of factor levels. It covers the factor space near the center with more points at the periphery. So, compared with one factor at a time design, the number of experiments and the overall costs associated with the experiment decreases [33,34].

For preconcentration procedure with respect to proposed design, variables chosen for optimization were: pH, volume of the ligand, the amount of the adsorbent, and the time of extraction. Table 1 presents maximum and minimum levels of each factor. The total number of experiments required running the CCD was equal to 30. They were divided into three blocks and carried out in three sequential days, since it was impossible to carry out the experiments during a working day and also, by dividing the experiments, we were enabled to remove the expected variations caused by some changes during the course of the experiments. All experiments were carried out using 50 mL of the sample solution containing 100 ng mL^{-1} of Pd(II). The design matrix with recovery as an analytical response is shown in Table 2.

3. Results and discussion

3.1. Selection of the adsorbent

To evaluate the competitive selectivity of different modified Fe_3O_4 NPs, different adsorbents according to works described in literature and previous papers, such as Fe_3O_4, (Fe_3O_4/SDS), (Fe_3O_4 /SiO_2), and (Fe_3O_4/SiO_2/SDS), were prepared. They were compared with Fe_3O_4 NPs with different ILs such as: (Fe_3O_4/[BMIM][PF_6]), (Fe_3O_4/[,HMIM][PF_6]), and

Table 2
Design matrix and responses for CCD

Run	Block	A	B	C	D	Recovery
1	1	−1	1	−1	−1	36.51
2	1	1	−1	1	1	40.73
3	1	1	1	−1	1	49.21
4	1	−1	−1	−1	1	47.38
5	1	0	0	0	0	54.42
6	1	1	−1	−1	−1	46.36
7	1	0	0	0	0	61.23
8	1	1	1	1	−1	56.41
9	1	−1	−1	1	−1	68.27
10	1	−1	1	1	1	89.49
11	2	1	1	1	1	93.26
12	2	0	0	0	0	90.23
13	2	1	−1	−1	1	87.71
14	2	1	1	−1	−1	37.73
15	2	0	0	0	0	60.24
16	2	−1	1	−1	1	42.11
17	2	1	−1	1	−1	79.24
18	2	−1	1	1	−1	61.39
19	2	−1	−1	−1	−1	77.56
20	2	−1	−1	1	1	83.57
21	3	0	2	0	0	89.68
22	3	0	0	−2	0	47.89
23	3	0	−2	0	0	67.37
24	3	0	0	0	0	58.16
25	3	2	0	0	0	74.63
26	3	0	0	0	0	56.27
27	3	0	0	0	−2	77.31
28	3	−2	0	0	0	65.59
29	3	0	0	0	2	84.29
30	3	0	0	0	0	81.91

(Fe_3O_4/[HMIM][TF_2N]). According to the results reported in Fig. 2, modified Fe_3O_4 NPs with IL had better selectivity for palladium separation from complex matrix in comparison with a naked adsorbent. The interaction of ILs with different analytes are based on electrostatic hydrophobic and π–π interactions. Hence, it presents a greater extraction capability toward palladium complex. Moreover, IL is a green coating agent, therefore IL modified Fe_3O_4 NPs can be used as the preferred adsorbents. In interaction between IL and Fe_3O_4, the anion is the species responsible for attachment to the substrate and the imidazolium ring is responsible for interactions with analytes. So, among the mentioned ILs, [HMIM][PF_6] with more reactive anions and longer hydrophobic chains which cause the stronger interaction with the substrate and Pd–DDTC, was selected for further studies.

3.2. Characterization of the adsorbent

The magnetization curve as a function of the applied magnetic field (VSM) at room temperature for the synthesized Fe_3O_4 NPs is shown in Fig. 3(A). The result indicates that the saturation magnetization (Ms) value is 73.6 emu/g, which is high enough to be used in environmental solution.

Fig. 3(B) shows the FTIR spectra of (a) Fe_3O_4 NPs before modification and (b) [HMIM][PF6] modified Fe_3O_4 NPs. The new absorption peaks at the position of about 1,500–1,600 cm^{-1} appeared after Fe_3O_4 NPs being treated with [HMIM][PF6], could be attributed to the C–C vibration of imidazole ring. The peaks at the position of 2,960 and 3,410 cm^{-1} could be attributed to C–H vibration of saturated hydrocarbon and C–H vibration of an aromatic cycle, respectively. Therefore, our attempt to prepare Fe_3O_4 NPs-IL in this work has been achieved.

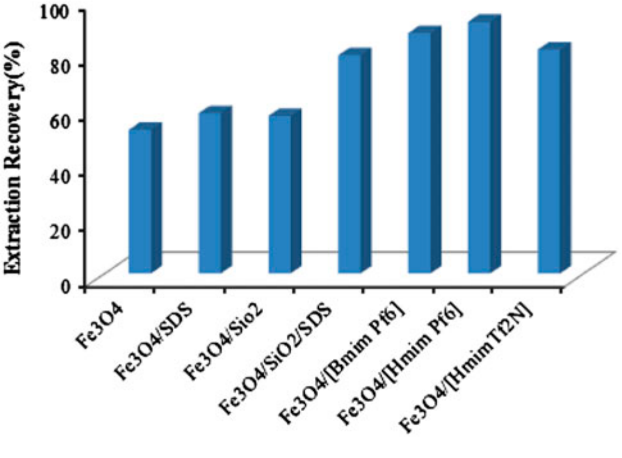

Fig. 2. Effect of different adsorbents on the extraction recovery of Pd(II). Condition: sample volume, 50 mL; Pd(II), 100 ng mL^{-1}; concentration of DDTC, 5.5×10^{-6} mol L^{-1}; pH 7.6; amount of adsorbent, 28 mg; and eluent volume (acetylacetone/ethanol (1:1)), 1 mL.

To determine the amount of IL on the Fe_3O_4 NPs, the sample was investigated by TGA. As illustrated in Fig. 3(C), the thermal analysis of this sorbent displays two weight losses: one at 40–110°C with a 4% loss which is attributed to the removal of the adsorbed water and solvents on the Fe_3O_4 NPs-IL, and another at 220–320°C with a 10% loss in composite mass. From this TGA, it can be observed that the amount of IL immobilized onto Fe_3O_4 NPs was about 10 wt%.

Fig. 3(D) (a) shows XRD patterns of the Fe_3O_4 samples prepared by ultrasonic chemical co-precipitation. Six obvious diffraction peaks at $2\theta = 31$, 36, 43, 54, 57, and 63 can be attributed to the diffraction of crystal faces of (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1), and (4 4 0). XRD peaks are found to be sharp and distinct indicating good crystallinity and homogeneity of the sample. No impurity peak from other iron oxides is observed, implying the good purity of prepared Fe_3O_4 magnetic NPs. In order to prove attachment of palladium ions to the sorbent, the XRD patterns of the modified sorbent was equilibrated with excess amounts of palladium ions solution (50 mL, 20 mg L^{-1}) are shown in Fig. 3(D) (b). The characteristic diffraction peaks for Pd at $2\theta = 40$, 46, and 68 corresponding to diffraction of (1 1 1), (2 0 0), and (2 2 0) palladium crystalline planes were observed.

The naked Fe_3O_4 NPs have low adsorption affinity for Pd–DDTC adsorption; however, when it is treated with IL, Fe_3O_4 acquires high affinity toward palladium complex. The modification method was based on the adsorption of hydrophobic IL, on the surface of Fe_3O_4 NPs and merely resulted in the formation of multiple layers on the carrier (Fig. 4(a)). According to Fig. 4(b), only weak interactions between the imidazolium ring and the substrate surface are expected, while the anion is the species responsible for the attachment with the substrate. The moderate reactions involve H-bonding and dipole–dipole interaction with active sites on the Fe_3O_4 surface [35]. Nevertheless, chemisorptions of the IL on the surface of substrate cannot be ruled out completely and the creation of new covalent bonds between oxygen and phosphor, which release HF into the solution (Fig. 4(c)), can be expected [36]. This implies that the anions of the IL are more strongly attached to the substrate compared to the cations. This configuration can be a favor for the uptake of Pd–DDTC complex because, there will be strong interactions (hydrophobic and π–π interactions) between palladium complex and IL. Moreover, due to

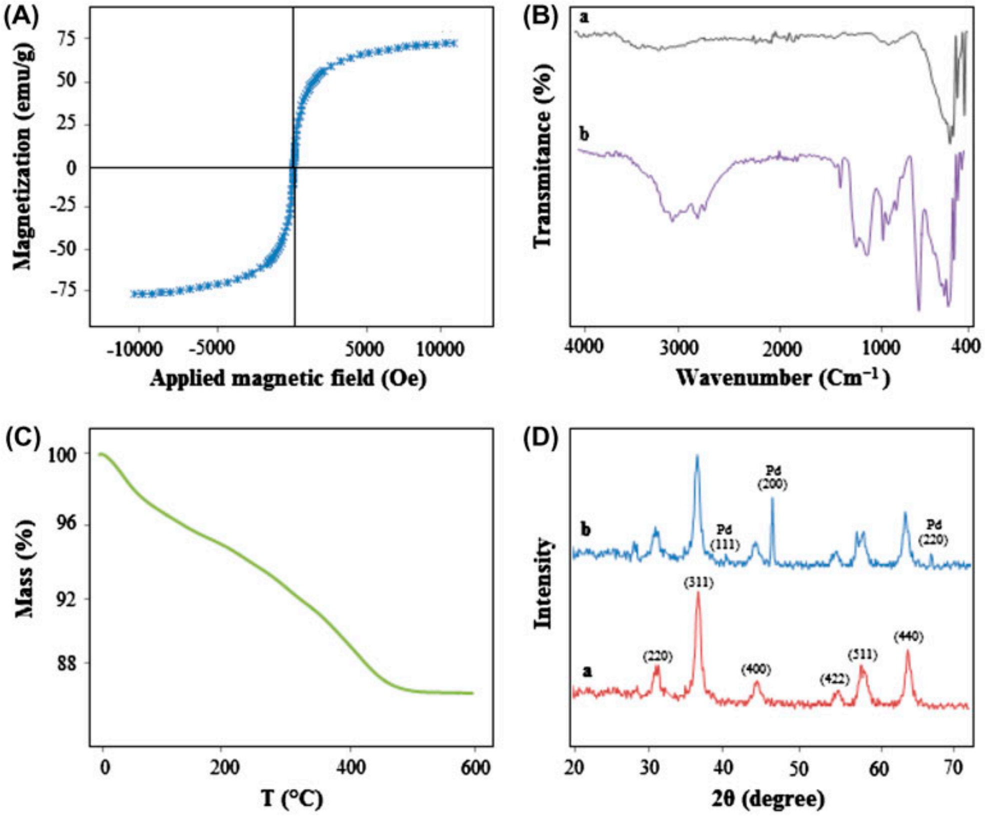

Fig. 3. (A) Magnetic hysteresis loops of Fe_3O_4 NPs synthesized room temperature. (B) FTIR spectra of (a) Fe_3O_4 NPs before modification and (b) IL-modified Fe_3O_4 NPs. (C) The TGA curves for IL-modified Fe_3O_4 NPs. (D) The XRD pattern for (a) synthesized Fe_3O_4 NPs (b) IL-modified Fe_3O_4 NPs equilibrated with palladium ions.

the absence of internal diffusion resistance, a low equilibrium time can be obtained.

3.3. Optimization of the preconcentration procedure using factorial design

The ANOVA results (Table 3) of the quadratic model suggest that the model was highly significant, as it is evident to the *F*-value (23.72) with a low-probability value ($p < 0.0001$). The adequacy of the model was determined by reasonable agreement with R^2 value of 0.9631 and R^2 adjusted value of 0.9233. A fairly high R^2 predicted value of 0.7272 implies that the regression model was statistically significant. As mentioned, R^2, R^2 adjusted, and R^2 predicted can be used to evaluate model fitness, and in a good model these parameters should not be too different from each other [37]. Based on *p*-values of each model term, all the independent variables studied (A, B, C, D) and four quadratic terms (A^2, B^2, C^2, and D^2) significantly affected the preconcentration of Pd(II). However, the interactions between two arbitrary parameters were not significant. By applying multiple regression analysis on the experimental data, the response variable and the test variables were related by the following second-order polynomial Eq. (1):

$$y = +88.41 + 6.83\mathrm{A} + 5.67\mathrm{B} + 4.50\mathrm{C} + 8.25\mathrm{D} - 9.94\mathrm{A}^2 - 6.94\mathrm{B}^2 - 4.8\mathrm{C}^2 - 7.44\mathrm{D}^2 \quad (1)$$

Since there was no significant interaction among four variables, the interaction factors were eliminated from the model equation. The optimal conditions were calculated based on the fitted model and the desirability function. To evaluate the accuracy of the results obtained by the surface model, under optimum condition (condition: pH, 7.6; amount of adsorbent, 28 mg; ligand concentration, 5.5×10^{-6} mol L^{-1}; and extraction time, 4 min), three experiments were carried out. The

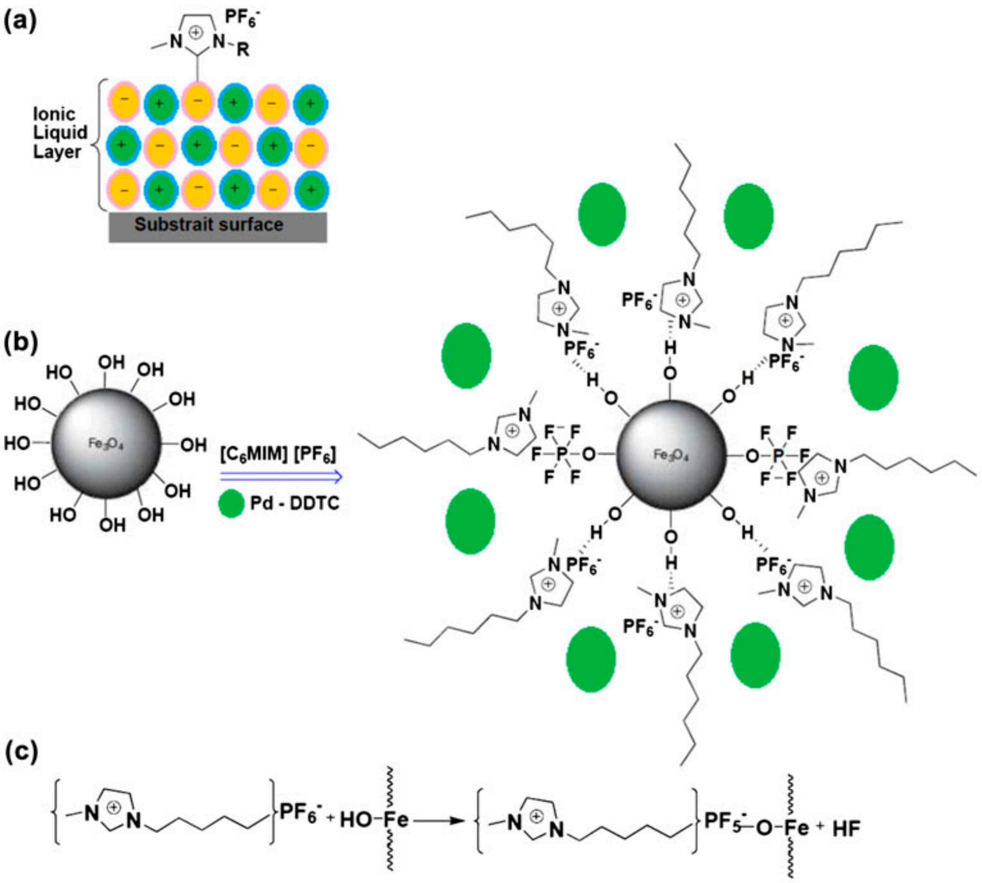

Fig. 4. The synthetic approach to prepare Fe_3O_4 NPs-based supported IL.

results showed a good agreement between the optimum-calculated response (93%) and experimental response (91%).

The three-dimensional (3-D) CCD plots of the response are shown in Fig. 5. These plots are mapped against two experimental factors while the others are held constant at their central level. pH plays a unique role on the metal–DDTC chelate formation and its subsequent extraction because, the existing form of metal ions and DDTC is pH dependent. The effect of sample pH on the extraction efficiency of target metal ions was evaluated in the pH range of 5.0–9.0. When pH of the sample was too acidic, DDTC may decompose and if the pH was too alkaline, precipitation may occur. As it can be seen, the recovery of Pd(II) was improved with the increase in pH up to 7.6 and then decreased. According to Fig. 5(a), pH of 7.6 was selected for the following experiments.

The effect of DDTC concentration in the range of $1–7.5 \times 10^{-6}$ mol L^{-1} was examined,. The recovery was increased by increasing the concentration of DDTC, as expected. Because of some other ions that could be present in real samples and probably react with DDTC, we used a concentration of 5.5×10^{-6} mol L^{-1} (275 μL) in our experiments.

For optimization of the amount of adsorbent, the amount of adsorbent in the range of 15–35 mg was investigated. By increasing the amount of modified Fe_3O_4 NPs due to the increase in the active surface area and accessible sites to the adsorption of the analytes, the extraction efficiency increased. Moreover, NPs offer a significantly higher surface area-to-volume ratio, short diffusion route, and rapid extraction dynamics. Therefore, satisfactory results can be obtained with lesser amounts of these adsorbents. As shown in Fig. 5(b), quantitative extraction of Pd(II) was achieved by using only 28 mg of the modified NPs. At higher amounts of the adsorbent, the extraction efficiency was almost constant.

In order to investigate the effect of shaking time on the extraction efficiency, extraction experiments were carried out at the range of 4–6 min. According to

Table 3
Analysis of variance (ANOVA) for the CCD

Source	Sum of square	d.f.[a]	Mean square	F-value[b]	P-value prob>F[c]	
Block	139.08	2	69.54			
Model	8,505.43	14	607.53	24.22	<0.0001	Significant
A	1,106.50	1	1,106.50	44.11	<0.0001	
B	782.50	1	782.50	31.19	<0.0001	
C	488.52	1	488.52	19.48	0.0007	
D	1,605.57	1	1,605.57	64.01	<0.0001	
AB	6.00	1	6.00	0.24	0.6329	
AC	14.06	1	14.06	0.56	0.4673	
AD	69.89	1	69.89	2.79	0.1190	
BC	1.00	1	1.00	0.040	0.8448	
BD	1.49	1	1.49	0.059	0.8114	
CD	1.64	1	1.64	0.065	0.8023	
A^2	2,682.93	1	2,682.93	106.96	<0.0001	
B^2	1,337.10	1	1,337.10	53.30	<0.0001	
C^2	630.06	1	630.06	25.12	0.0002	
D^2	1,530.88	1	1,530.88	61.03	<0.0001	
Residual	326.10	13	25.08			
Lack of Fit	299.45	10	29.95	3.37	0.1729	Not significant
Pure Error	26.65	3	8.88			
Cor Total[d]	8,970.61	29				

[a] Degrees of freedom.

[b] Test for comparing model variance with residual (error) variance.

[c] Probability of seeing the observed F-value if the null hypothesis is true.

[d] Totals of all information corrected for the mean.

the results in Fig. 5(b), an equilibration time of about 4 min was adequate for the quantitative extraction of the analytes from solution into solid phase.

3.4. Condition of desorption and stability of sorbent

A series of different eluent solutions, were used for desorption of the Pd(II) ions from the modified Fe_3O_4 NPs. From the data given in Fig. 6, acetylacetone/ethanol (1:1) is the best desorbing eluent. As it can be seen, it is well known that, chelation has not been proposed for the desorption of Pd (II) ions with eluent because extraction recovery with thio-urea was not high enough. But, with organic eluent such as ethanol and acetylacetone high extraction recovery was obtained; so attraction between Pd–DDTC complex and acetylacetone/ethanol caused desorption of complex from the sorbent.

The effect of the eluent volume on the recovery of Pd(II) was also evaluated when acetylacetone/ethanol (1:1) was selected. As we know, the volume of eluent is an important parameter because it acquires the best preconcentration factor. The eluent volumes must be kept as low as possible to obtain a higher preconcentration factor. So, 1 mL of mentioned eluent with the best recovery was the optimum eluent volume for desorption of palladium ions from this modified Fe_3O_4 NPs. Desorption times were evaluated in the range of 2–10 min, as well. The results showed that the time of 5 min is sufficient for quantitative desorption of the Pd(II) ions by 1 mL of acetylacetone/ethanol (1:1) solution.

The stability and potential regeneration of the sorbent was investigated. The sorbent can be reused and be stable up to, at least, 3 adsorption–elution cycles without significant decrease in the recovery of Pd(II) ions.

3.5. Sorption capacity

In order to study the sorption capacity of the adsorbent, batch sorption procedures were applied. 28 mg of the adsorbent was stirred with 50 mL of solution containing 0.1–2.5 mg of palladium ions. After 4 min, the remaining palladium ions in the aqueous phase was determined by FAAS. The sorption capacity (q_e, mg g^{-1}) was calculated as Eq. (2):

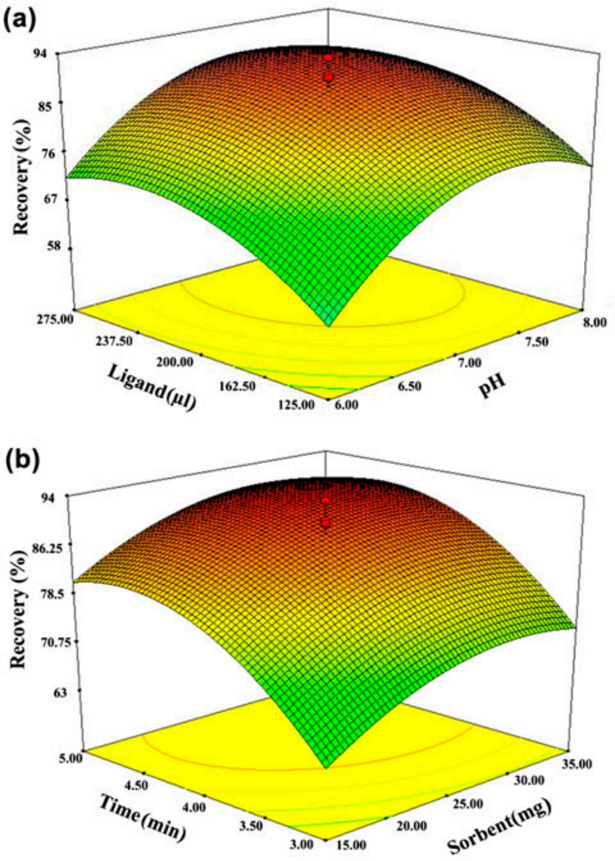

Fig. 5. (a) Three-dimensional response surface plot for the effect of pH and volume of ligand on the response (extraction recovery), in which the values of amount of adsorbent and time were fixed at 28 mg and 4 min, respectively. (b) Three-dimensional response surface plot for the effect of amount of adsorbent and time on the response (extraction eecovery), in which pH and concentration of ligand were fixed at 7.6 and 5.5×10^{-6} mol L^{-1} respectively.

$$q_e = (C_0 - C_e)V\,m^{-1} \tag{2}$$

where C_0 and C_e are the initial and equilibrium concentrations (mg L^{-1}) of analyte ions in the solution, respectively, V is the sample volume (L), and m is amount of adsorbent (g). The maximum capacity of the adsorbent for palladium was found to be 18.4 mg per gram of the adsorbent.

3.6. Analytical features

Under the optimal experimental conditions, the procedure showed a good linear behavior in the concentration range of 3–150 ng mL^{-1} with correlation coefficients (R^2) of 0.995. The limit of detection, defined as LOD = 3 sb/m, where sb is the standard deviation of five replicates of blank signals and m is the slope of the calibration curve after preconcentration, was found to be 0.82 ng mL^{-1}. The relative standard deviation (RSD) of 2.8% was achieved by five replicating measurements of 100 ng mL^{-1} Pd(II). A concentration factor (CF) of about 150 was obtained as a ratio between the volume of the sample solution (150) and the final volume obtained after the elution step (1 mL).

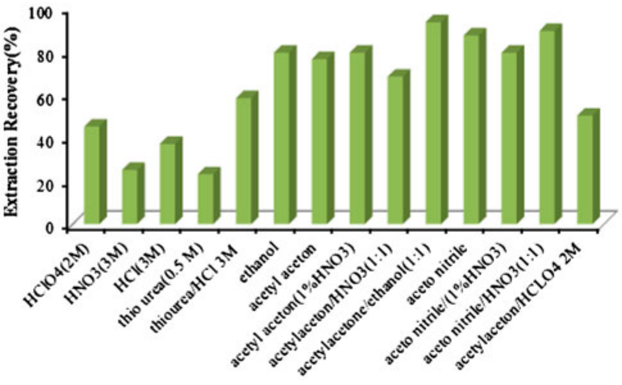

Fig. 6. Effect of different eluents on the extraction recovery of Pd(II). Condition: sample volume, 50 mL; Pd(II), 100 ng mL^{-1}; concentration of DDTC, 5.5×10^{-6} mol L^{-1}; pH 7.6; amount of adsorbent, 28 mg; and eluent volume, 1 mL.

3.7. Effects of interfering ions

To evaluate the selectivity of the proposed method for the determination of trace level of the Pd(II), the interference of coexisting ions on the recovery of the Pd(II) was investigated. The choice of cations and anions is according to their abundance in real samples. The interference can be due to the formation of ion pair between anions and palladium ions or competition of other metal ions for the chelating agent and their subsequent co-extraction with Pd(II). For this purpose, binary mixture (50 mL) between 5 µg of Pd (II) and each interfering cations, in different concentration levels, was extracted by IL-modified Fe_3O_4 NPs. The results are shown in Table 4 and indicated that many studied interfering ions did not affect the extraction efficiency of Pd(II). However, some of the species such as Al^{3+} and Hg^{2+} interfered with the determination of ions. Hence, higher amounts of DDTC were used in the experiments.

Table 4
Effect of interfering ions on the recovery of Pd(II)[a]

Interference	Interference to analyte ratio(w/w)	Recovery (%)
Na^+	1,000	96.23
K^+	1,000	96.75
NO_3^-	1,000	98.32
Cl^-	1,000	97.57
Mg^{2+}	500	98.42
Ni^{2+}	500	96.97
Zn^{2+}	150	94.33
Cr^{3+}	150	96.12
Fe^{3+}	150	98.93
Cd^{2+}	150	96.56
Cu^{2+}	100	97.19
Pb^{2+}	100	95.93
Co^{2+}	100	98.34
AL^{3+}	50	93.86
Hg^{2+}	50	95.26

[a]Condition: sample volume, 50 mL; Pd(II), 100 ng mL^{-1}; concentration of DDTC, 5.5×10^{-6} mol L^{-1}; pH 7.6; Amount of adsorbent, 28 mg; eluent, 1 mL. acetylacetone/ethanol (1:1).

Table 5
Analytical results for the determination of Pd(II) in real samples (Condition: sample volume, 50 mL; amount of DDTC, 5.5×10^{-6} mol L^{-1}; pH 7.6; Amount of adsorbent, 28 mg; eluent, 1 mL acetylacetone/ethanol (1:1)

Sample	Spiked (ng mL^{-1})	Found[a] (ng mL^{-1})	Recovery (%)
Tap water	0	ND[b]	–
	20	19.7 ± 0.8	98.5
	40	40.1 ± 1.8	100.2
River water	0	ND	–
	20	19.1 ± 0.9	95.5
	40	38.4 ± 2.1	96.2
Spring water	0	ND	–
	20	20.1 ± 1.1	100.3
	40	39.8 ± 2.3	99.5
Dust[c]	0	104 ± 8 ng g^{-1}	–
	20	198 ± 16 ng g^{-1}	93.8
Bovine liver[d]	0	8.7 ± 0.9 ng g^{-1}	–
	20	29.5 ± 3 ng g^{-1}	102.8

[a]Mean ± SD, (n = 5).

[b]Not Detected.

[c]μg g^{-1}: Fe^{3+}: 0.94; Ni^{2+}: 0.11; Pb^{2+}: 0.45; Cu^{2+}: 0.32; Zn^{2+}: 0.72; Cr^{3+}:0.22.

[d]μg g^{-1}: Pb^{2+}:0.18; Cd^{2+}: 0.62; Cu^{2+}: 0.68; Zn^{2+}: 2.44; Fe^{3+}: 4.62.

3.8. Determination of Pd(II) in real samples

The proposed procedure has been applied to the determination of Pd(II) in road dust, liver, and water samples. It was found that, the results for palladium ions tested in dust and liver samples were 104 and 8.7 ng mL^{-1}, respectively. Furthermore, the accuracy of the proposed method was checked by spiking samples and a good correlation was obtained between the added and measured amounts. The recoveries were also reasonable, in a range of 93–101%. The results in Table 5 indicate that the proposed method can be reliably used for the determination of Pd(II) in different matrices.

Table 6
Comparison of this method with other methods for determination of Pd(II)

Method	Process time (min)	PF[a]	RSD[b]	LOD[c]	LDR[d]	SC[e]	Ref
Silica gel—FAAS	12.5	75	1.7	1.2	–	4.06	[15]
Exfoliated graphite—FAAS	1	60	2.4	1.0	Upto 0.2	–	[16]
Ion imprinting polymer particles—FAAS	20	–	2.12	2.5	2.5–100	–	[19]
Modified organo- nanoclay—FAAS	–	140	2.3	0.1	0.45–10	2.4	[21]
Silica-Poly ethylene glycol—FAAS	25	125	< 4	0.54	2–80	–	[25]
Modified nano-alumina—FAAS	5	60	0.8	0.6	–	37	[26]
Modified MNPs—FAAS	4	150	2.80	0.82	3–150	18.4	Present work

[a] Preconcentration factor.

[b] Relative standard deviation (%), (n = 5).

[c] Limit of detection (ng mL^{-1}).

[d] Linear dynamic range (ng mL^{-1}).

[e] Sorption capacity (mg g^{-1}).

4 Conclusions

We have developed an efficient SPE system, Fe_3O_4 NPs coated with hydrophobic IL as a green coating agent, and combined with central composite full factorial design in order to decrease the time and the number of experiments, and save material resources. In Table 6, this method has been compared with previous methods that were reported for the determination of palladium. This method has the advantage of treating large-volume samples avoiding time consumption by the fact that no centrifugation or filtration was required for phase separation, and the separation of adsorbent from aqueous bulk was achieved after about 2 min by a magnet. The other advantages of the present method such as good preconcentration factor, wide linear range, and low equilibrium time confirmed the desirability of this method for preconcentration and determination of Pd(II). The feasibility of the adsorbent based on the modification with IL was investigated for the preconcentration of Pd(II) from different real samples. Therefore, this is a practicable method for palladium trace analysis in a variety of matrices in order to reduce its hazardous effects on environment and ecosystem.

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