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Synthesis and characterization of magnetic metal-organic framework (MOF) as a novel sorbent, and its optimization by experimental design methodology for determination of palladium in environmental samples

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ABSTRACT

This paper describes the synthesis and application of novel magnetic metal-organic framework (MOF) [(Fe_3O_4–Pyridine)/$Cu_3(BTC)_2$] for preconcentration of Pd(II) and its determination by flame atomic absorption spectrometry (FAAS). A Box–Behnken design was used to find the optimum conditions for the preconcentration procedure through response surface methodology. Three variables including amount of magnetic MOF, extraction time, and pH of extraction were selected as factors for adsorption step, and in desorption step, four parameters including type, volume, and concentration of eluent, and desorption time were selected in the optimization study. These values were 30 mg, 6 min, 6.9, K_2SO_4+NaOH, 6 mL, 9.5 (w/v %)+0.01 mol L^{-1}, 15.5 min, for amount of MOF, extraction time, pH of extraction, type, volume, and concentration of the eluent, and desorption time, respectively. The preconcentration factor (PF), relative standard deviation (RSD), limit of detection (LOD), and adsorption capacity of the method were found to be 208, 2.1%, 0.37 ng mL^{-1}, and 105.1 mg g^{-1}, respectively. It was found that the magnetic MOF has more capacity compared to Fe_3O_4–Py. Finally, the magnetic MOF was successfully applied for rapid extraction of trace amounts of Pd (II) ions in fish, sediment, soil, and water samples.

1. Introduction

Palladium is an element with increasing demand in today's industries. In 2007, 192 t of palladium has been sold in the world market. It's used in different areas of science and technology, like metallurgy, and it is extensively used as a catalyst especially in hydrogenation and dehydrogenation of some of the important organic compounds. Due to electrical conductivity and durability, Pd(II) is widely used in electronic applications for production of multi-layer ceramic (chip) capacitors, conductive tracks in hybrid integrated circuits, plating connectors and lead frames, and jewelry [1–2]. One of the most important applications of Pd(II) is the production of catalytic converters for car engines [3]. Palladium can also be used in biomedical devices, as a catalyst in fuel cells, and as anti-pollution devices for automobile industry. Consequently, Pd(II) is released into the environment in considerable amounts as a new pollutant, and especially by the technical use of automobile catalyst convertors which contain the active palladium metal [4–7]. Palladium may enter the environment and interact with complex materials such as humic substances [8]. Palladium has no biological role, and all of its compounds should be regarded as highly toxic and carcinogenic [9–10]. Therefore, monitoring trace levels of palladium in environmental samples has a great importance with respect to estimation of future risks of human health and the ecosystem. The toxicity of palladium requires practical techniques to remove it from the environment. Furthermore, because of the high economical value of Pd(II), its separation even in trace amounts is beneficial. Due to widespread applications, toxicity, and economic importance of palladium, many methods for determination or separation of this metal has been already proposed. Some of the valuable techniques, including ET-AAS [11–12], ICP-AES [13], FAAS [14], ICP-MS [15], and total reflection XRF-spectrometry [16] have been used for palladium determination. The mentioned methods do not have adequate sensitivity and selectivity for complex matrixes of real samples [11–16]. Therefore, preconcentration techniques are essential for determination of trace amounts of palladium in diluted or complex samples for increasing the sensitivity and selectivity. So far, different methods including liquid–liquid extraction (LLE) [17], cloud point extraction (CPE) [18] dispersive

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liquid–liquid microextraction (DLLME) [19], solvent extraction [20], and solid phase extraction (SPE) [21–22] have been used for determination and preconcentration of trace levels of Pd(II).

SPE technique is more flexible and efficient than LLE in terms of simplicity, cleanness, low consumption of reagents and organic solvents, and high enrichment factor. Recently, SPE has been extensively used for preconcentration of trace amounts of palladium prior to its determination [23]. Different solid phases such as activated carbon [24], ion exchange [25], silica gel [26,27], Diaion resin [28], chelating sorbent [29–31], hydrogel [32], polyurethane foam [33], amberlite XAD resins [34], and modified silica gel [35] have been used for preconcentration–determination of palladium.

In this work for the first time magnetic MOF with cavities immobilized by Fe_3O_4–Py has been utilized. Metal–Organic Frameworks (MOFs) are crystalline solids consisting of metal ions coordinated by organic ligands to form rigid three dimensional frameworks with unique properties such as high surface area, high pore volume, and chemical tenability. MOFs have shown great potential in gas storage, separation, chemical sensing, drug delivery, and heterogeneous catalysis applications [36,37]. In general, the flexible and highly porous structure of MOFs allow guest molecules such as metals to diffuse into the bulk structure, and the shape and size of the pores lead to selectivity over the guests that may be adsorbed. These features make MOFs an ideal sorbent in solid phase extraction of heavy metals. However, there is little information about MOFs as a solid phase extraction system [38].

Magnetic properties of the sorbent help rapid and easy separation of the new solid phase from the solution. Pyridine in the sorbent helps the new solid phase to have selectivity towards palladium, and cavities of MOF can increase the adsorption capacity of the new sorbent. In this study, a novel magnetic MOF has been synthesized for fast extraction and separation of Pd(II) ions from various matrixes. Characterization of the sorbent was evaluated by Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), scanning electron microscopy (SEM), thermogravimetry (TG), and differential thermal analysis (DTA). A Box–Behnken design was used to find the optimum conditions for the method through response surface methodology. Finally, the sorbent was used for preconcentration and determination of Pd(II) ions in different real samples.

2. Experimental

2.1. Reagents and solutions

All reagents of analytical grade were purchased from Merck (Darmstadt, Germany) or from Fluka (Buchs SG, Switzerland) and used without further purification. Standard solution of 1000 mg L^{-1} of Pd(II) was purchased from Merck. All solutions were prepared using double distilled water.

2.2. Instrument

AA-680 Shimadzu (Kyoto, Japan) flame atomic absorption spectrometer with a deuterium background corrector was used for determination of Pd (II) ions. A palladium hollow cathode lamp (HCL) was used as the light source operated at 10 mA. The wavelength was set at 244.8 nm resonance line and the spectral band width was set at 0.5 nm. All measurements were carried out in an air/acetylene flame. A digital pH meter, WTW Metrohm 827 Ion analyzer (Herisau, Switzerland), equipped with a combined glass calomel electrode was used for the pH adjustments at 25 ± 1 °C temperature. Heidolph heater stirrer model MR 3001 (Germany) was used for heating and stirring of the solutions. IR spectra were recorded on a Bruker IFS-66 FT-IR Spectrophotometer. High angle X-ray diffraction patterns were obtained on a Philips-PW 17C diffractometer with Cu Kα radiation. Scanning electron microscopy (SEM) was performed by gently distributing the powder sample on the stainless steel stubs, using SEM (KYKY-3200, Beijing, China) instrument. The thermal properties of samples were determined, using a BAHR-Thermoanalyse GmbH (Germany) with employing, heating and cooling rates of 10 °C min^{-1} and using a condenser as the coolant. The samples were weighed as a thin film and carefully packed into a clean aluminum pan (19.01–19.15 mg), and sealed by crimping an aluminum lid on the pan (Shimadzu universal crimper). An Al_2O_3 empty pan sealed with a cover pan was used as a reference sample. A scanning range of 10 to 800 °C was used for samples at 10 °C min^{-1} in nitrogen gas.

2.3. Synthesis of Fe_3O_4–Py, MOF, and magnetic MOF

2.3.1. Synthesis of Fe_3O_4–Py

Fe_3O_4 nanoparticles were synthesized according to the previously reported procedure [39] and their formation was established by X-ray powder diffraction. N-[3 (triethoxysilyl)propyl]isonicotinamide (TPI) was synthesized according to the earlier report [40] and characterized by ^{1}H NMR. Finally, for Preparation of Pyridine functionalized Fe_3O_4 nanoparticles, 1.0 g of Fe_3O_4 nanoparticles was suspended in 70 mL of toluene, afterward 1.0 g of TPI was added and the mixture was refluxed for 24 h. The solid phase was filtered, separated, and washed 3 times with 50 mL of ethanol in order to remove the impurities and then dried at room temperature. Functionalization of Fe_3O_4 nanoparticles was confirmed by IR spectroscopy, and thermal and elemental analysis.

2.3.2. Synthesis of Cu_3 $(BTC)_2$ MOF

$Cu_3(BTC)_2$ MOF (BTC=benzene-1,3,5-tricarboxylate) was synthesized according to the previously reported procedure [41]. A solution consisting 0.84 g of trimesic acid and 1.75 g of $Cu(NO_3)_2.3\ H_2O$ in 50 mL of Ethanol was refluxed under rigorous stirring. After a few hours, a blue solid started to precipitate. The resulting solid was kept under reflux conditions for 48 h, and subsequently cooled to room temperature. The obtained blue powder was recovered by filtration, washed once with water and then it was washed with Ethanol for the second time. Thereafter, the sample was dried under vacuum at 100 °C for 12 h and then kept under dry nitrogen until further use (sample A). The synthesized MOF was characterized by IR spectroscopy, TG, DTA, SEM, and XRD.

2.3.3. Synthesis of magnetic MOF

Magnetic MOF was synthesized according to the previously reported procedure [42]. Pyridine functionalized Fe_3O_4 and synthesized magnetic MOF are shown in Fig. 1a and b, respectively. H_3BTC (0.5 g, 2.38 mmol) was dissolved in a mixed solution of DMF/ethanol (1:1, 80 mL). After that 20 mL of ethanol solution containing 0.1 g Fe_3O_4–Py was prepared, and then, 2 mL (for sample B), 5 mL (for sample C), and 10 mL (for sample D), were added to the mixture under magnetic stirring, and then it was heated to 70 °C. After adding 40 mL aqueous solution of $Cu(OAc)_2.H_2O$ (0.86 g, 4.31 mmol) to the reaction mixture, the reaction was carried out at 70 °C with stirring for a further 4 h. Finally, the product was collected by centrifugation and washed with water (50 mL) and ethanol (10 mL×3). Magnetic MOF was characterized by IR spectroscopy, TG, DTA, SEM, and XRD.

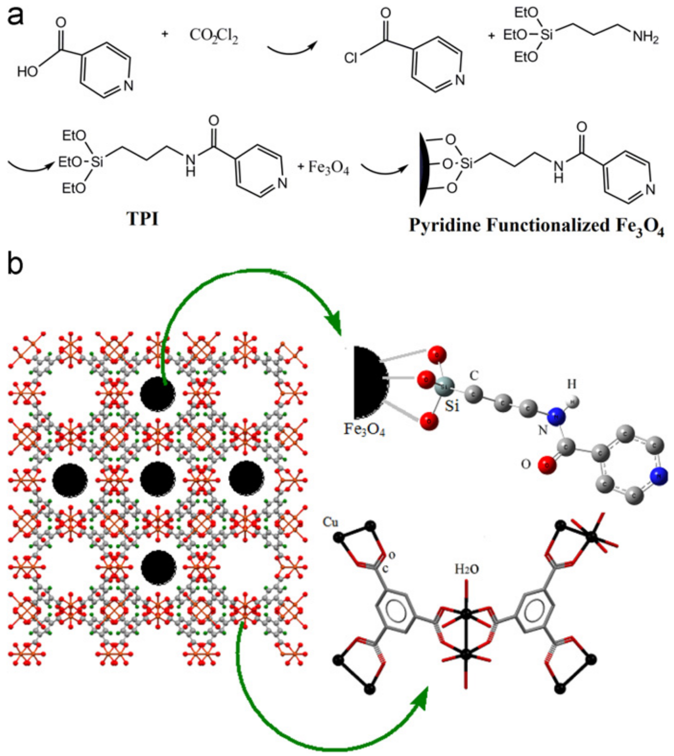

Fig. 1. (a) A schematic diagram of Pyridine-functionalized Fe_3O_4. (b) Schematic illustration of synthesized magnetic MOF.

2.4. Preparation of standard solution

Reference material was digested with 6 mL of HCl (37% (v/v)) and 2 mL of HNO_3 (65% (v/v)) in a microwave digestion system. Digestion was carried out for 2 min at 250 W, 2 min at 0 W, 6 min at 250 W, 5 min at 400 W, 8 min at 550 W, and then venting for 8 min. The residue from digestion was then diluted with double distilled water [43].

Standard Stock solutions (1000 mg L^{-1}) of K^+, Na^+, Ca(II), Pb(II), Ni(II), Mn(II), Fe(III), Zn(II), Cu(II), Cd(II), Al(III), and Ag(I) were prepared in 2% (v/v) HNO_3. The used standard solutions were prepared by appropriate dilution of the stock solution with double distilled water. All of these solutions were stored in ambient temperature.

2.5. Adsorption and desorption step

Adsorption of palladium from aqueous solutions was investigated by batch experiments. Adsorptions were performed in test tubes containing 30 μg of palladium ions in 15 mL of double distilled water. According to a preliminary experimental design, the pH was adjusted by drop-wise addition of 1 mol L^{-1} sodium hydroxide and 1 mol L^{-1} hydrochloric acid; and then magnetic MOF particles were added to the solutions. After that, the mixture was shaken for an appropriate time to completely extract palladium ions from the solution. Finally, the test tubes were placed in a magnetic field, where permanent magnet in the wall causes the particles to aggregate on one side of the test tube. The adsorbed amounts of palladium were determined using FAAS from the concentration change of palladium in solution after adsorption. The instrument response was periodically checked with known palladium standard solutions. Extraction percent of palladium was calculated from the following equation:

$$\text{Extraction}\% = \frac{C_A - C_B}{C_A} \times 100$$

C_A and C_B are the concentrations of palladium ions before and after extraction in the solution, respectively.

In desorption step, magnetic MOF that adsorbed Pd(II) ions of the solution was eluted with 6 mL of 0.01 mol L^{-1} NaOH in 9.5 (w/v %) K_2SO_4 solution as an eluent by batch experiments and the amount of desorption was determined by FAAS.

2.6. Real samples pretreatment

2.6.1. Fish and sediment

Fish and sediment samples were collected from two different sites in Moosa creek. Moosa creek is located in Northwest of Persian Gulf, and has several subsidiary creeks. Among them, Jafare creek was chosen as a polluted site and Behad creek as a reference site which is far from petrochemical industries. The fish samples (platycephalus indicus) were placed in ice box and transported to the laboratory and stored at −20 °C prior to analysis. Fish samples were dissected with clean plastic knife and a part of the muscles was taken out quickly and was dried in an oven at 70 °C for 48 h. Analysis were carried out according to the procedure by Yilmaz (2003) [44]. A porcelain mortar was used to grind dry tissues. 0.5 g of each sample was digested with 5 mL of concentrated HNO_3 in Teflon beakers for 4 h at 100 °C. The content was filtered in to 25 ml standard flask and diluted up to 25 mL with double distilled water. Sediment samples were collected from the two mentioned sites using Peterson grab sampler, and stored in a plastic bag in ice and transported to the laboratory and were kept at −20 °C until analysis. 1.0 g of sediment was digested with 6 mL of HCl (37%) and 2 mL of HNO3 (65%) in a microwave digestion system. Digestion was carried out for 2 min at 250 W, 2 min at 0 W, 6 min at 250 W, 5 min at 400 W, 8 min at 550 W and then venting for 8 min. The residue resulted from digestion was then diluted to 100 mL with double distilled water.

2.6.2. Soil sample

Soil sample was collected from Sarcheshme Mine (Kerman, Iran). At the same time, soil sample was digested according to the digestion method for sediment sample.

2.6.3. Water samples

The proposed method was applied to different water samples such as distilled, tap (Tehran, Iran), Amirie River (Tehran, Iran), and mineral water (Sarcheshme Mine, Kerman, Iran) samples. The water samples were stored in cleaned polyethylene bottles and were filtered through nylon filters (Millipore). Before the analysis, the pH of samples was adjusted to 6.9.

2.7. Reference material

Ore polymetallic gold and two mine stone samples were collected with a certified palladium content which was reported by the Geological Survey of Iran.

At the same time, standard material was digested according to the mentioned procedure for sediment and blank digestion. The pH of solution was adjusted to 6.9 for separation and preconcentration of Pd(II) ions form the solution. Finally, the preconcentration procedure mentioned above was applied to the resulted solutions.

2.8. *Experimental design methodology*

To fully understand the way in which experimental variables affect the extraction and preconcentration of Pd(II), individual factors must be considered along with nonlinear effects and interaction terms. The chemometric approach has a rational experimental design, which allows the simultaneous variation of all experimental factors, and saves materials and time. The Box–Behnken design (BBD) is probably the most widely used experimental design applied for fitting a second-order response surface. This cubic design is characterized by set of points lying at the midpoint of each edge of a multidimensional cube and center point replicates whereas the 'missing corners' help the experimenter to avoid the combined factor extremes. This property prevents a potential loss of data in those cases [45].

Analysis of the experimental design data and calculation of predicted responses were carried out using the StatGraphics plus 5.1 packages.

3. Results and discussion

3.1. *Characterization studies*

3.1.1. *FT-IR spectra*

The FT-IR spectra of MOF, and magnetic MOF were recorded using KBr pellet method (Fig. 2). In the IR spectra of MOF absorptions due to C=O (1640 cm^{-1}), C–H (2940 cm^{-1}) corresponding to aromatic groups, and –O–C–O–(1550 and 1430 cm^{-1}) were observed. In the IR spectra of magnetic MOF, the same absorptions were witnessed with a little shift that indicates the successful immobilization of Fe_3O_4–Py. In addition, as shown in Fig. 2 absorptions due to N–H (3490 cm^{-1}) was observed which confirms the immobilization of MOF by Fe_3O_4–Py. Furthermore, elemental analysis showed the presence of 0.239% N in the structure of magnetic MOF which indicates that Fe_3O_4–Py had been sufficiently immobilized in the structure of magnetic MOF (C: 56.125%, H: 7.356%, N: 0.239%, O: 15.324%).

3.1.2. *Thermogravimetric analysis*

Thermal stability of the magnetic MOF and MOF was evaluated by thermo gravimetric analysis. Fig. 1S shows the thermogravimetry (TG) and differential thermal analysis (DTA) plots for (a) MOF and (b) magnetic MOF (sample D). In DTA plots of MOF, exothermic peaks were observed at 295.1, 326.4, 349.1, and 445.3 °C but in DTA plots of magnetic MOF exothermic peaks were observed at 301.9, 390.2, and 450.3 °C. As it is shown in TG plots, weight loss for MOF was about 72%, and the remaining 28% is related to the presence of Cu^{2+} in the MOF structure. However, decrease in weight for magnetic MOF was about 68%. In the remaining 32%, about 28% is related to Cu^{2+}, and about 4% is due to presence of $Fe^{2+}$and Fe^{3+} ions in the structure of magnetic MOF. The observations indicate that the formation of magnetic MOF was performed successfully.

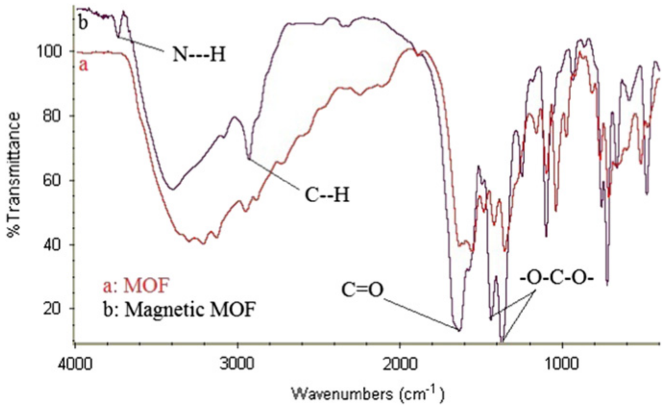

Fig. 2. (a) The FT-IR spectra of (a) MOF (b) magnetic MOF.

3.1.3. *Scanning electron microscopy*

To investigate the surface morphology of the MOF and magnetic MOF, the samples were characterized by SEM (Fig. 3). The crystals of original $[Cu_3(BTC)_2(H_2O)_3]_n$ sample are octahedral with a smooth surface and have an average size of 10 μm (Fig. 3a). However, surface of the magnetic MOF tends to be rougher after immobilization by Fe_3O_4–Py (Fig. 3b–d).

3.1.4. *X-ray diffraction*

For further study, MOF and magnetic MOF (sample A, B, C, and D), were investigated by XRD. All of the diffraction peaks for Fe_3O_4–Py immobilized samples B and C show that the sketch of the MOF crystal is well retained even after the modification with Fe_3O_4–Py, because all diffraction peaks of the immobilized MOF can readily be indexed to $[Cu_3(BTC)_2(H_2O)_3]_n$ (Fig. 4a–c). For sample D however, modification of $[Cu_3(BTC)_2(H_2O)_3]_n$ with excessive Fe_3O_4–Py resulted in loss of crystalline order of the framework, as evidenced by significant decrease in diffraction intensities (see Fig. 4d), which is due to partial decomposition of the crystalline $[Cu_3(BTC)_2(H_2O)_3]_n$ [38]. Although in diffraction peak of sample D, the structure of MOF cannot be observed; the presence of Cu and Fe ions in the structure can be determined by FAAS.

3.2. *Optimization of the preconcentration procedure*

3.2.1. *Adsorption step*

The optimization step for the magnetic MOF method was carried out using Box–Behnken design (BBD). Several variables that could potentially affect the extraction efficiency were chosen: pH, amount of magnetic MOF, and extraction time. Other parameters involved in the extraction were kept constant, especially the concentration of Pd(II) (2 mg L^{-1}). This design permitted the responses to be modeled by fitting a second-order polynomial, which can be expressed as the following equation:

$$Y=\beta_0+\beta_1x_1+\beta_2x_2+\beta_3x_3+\beta_{12}x_1x_2+\beta_{13}x_1x_3 +\beta_{23}x_2x_3+\beta_{11}x_1^2+\beta_{22}x_2^2+\beta_{33}x_3^2$$

where, x_1, x_2, and x_3 are the independent variables, β_0 is an intercept, $\beta_1-\beta_{33}$ are the regression coefficients, and Y is the response (removal % or recovery %). The number of experimental points (N) is defined by the expression below:

$$N=2\,\mathrm{K}(K-1)+C_o$$

where K is the number of variables and C_o is the number of center points [46]. In this study, K and C_o were set at 3 and 3, respectively, which meant that 15 experiments had to be done.

The levels of the factors are listed in Table 1. The ANOVA results produced the Pareto chart of main and interaction effects are shown in Fig. 5. The standard effect was estimated for computing the t-statistic for each effect. The vertical line on the plot shows statistically significant effects. The bar extracting beyond the line corresponds to the effects that are statistically significant at 95% confidence level [47]. Furthermore, the positive or negative sign (corresponding to a colored or colorless response) can be enhanced or reduced, respectively, when passing from the lowest to the highest level set for the specific factor. According to Fig. 5, the pH of solution has the largest influence on the extraction efficiency and a positive effect upon the extraction.

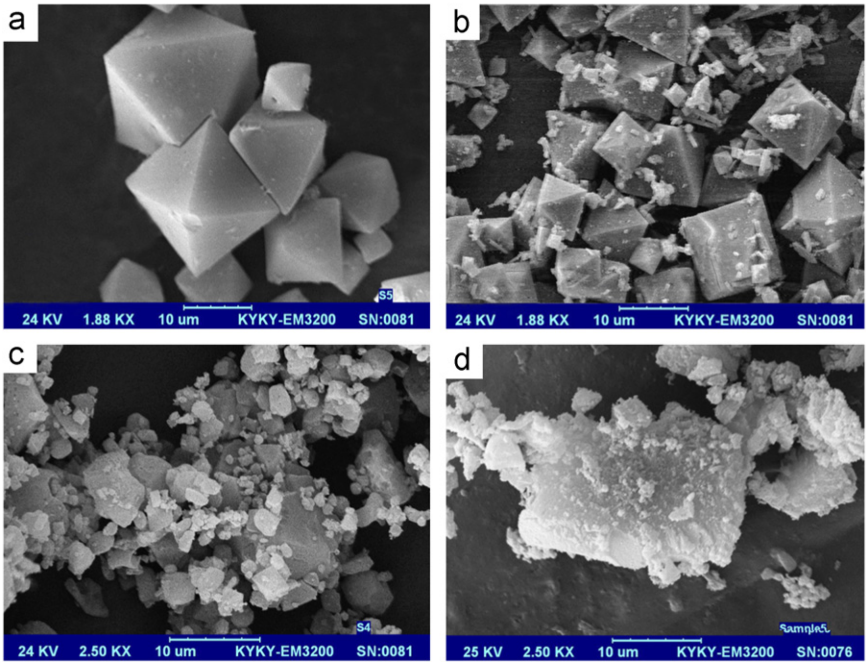

Fig. 3. The SEM images of MOF (sample A) and magnetic MOF (sample: B, C, D).

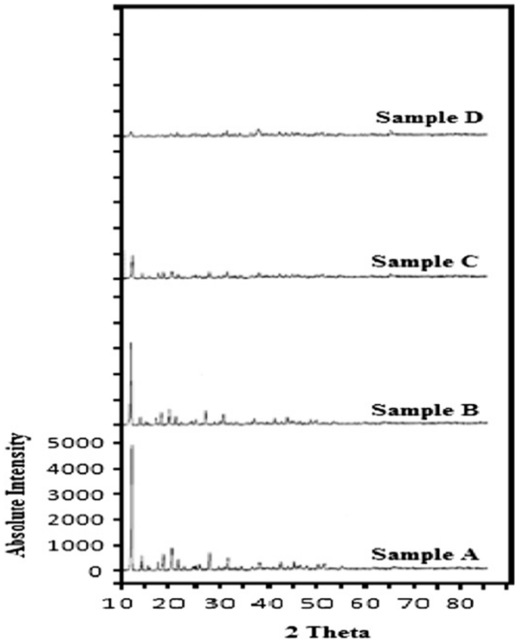

Fig. 4. XRD patterns of MOF (sample A) magnetic MOF (B, C, D).

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

		Level		
		Lower	Central	Upper
Extraction step	A: pH	1.0	4.0	7.0
	B: Extraction time ($_{\text{min}}$)	1.0	3.0	7.0
	C: amount of polymer (mg)	10.0	20.0	30.0
Desorption step	A: Time ($_{\text{min}}$)	2.0	11.0	20.0
	B: Eluent concentration (% w/v)	0.0	6.0	12.0
	C: Eluent volume (mL)	2.5	5.0	7.5

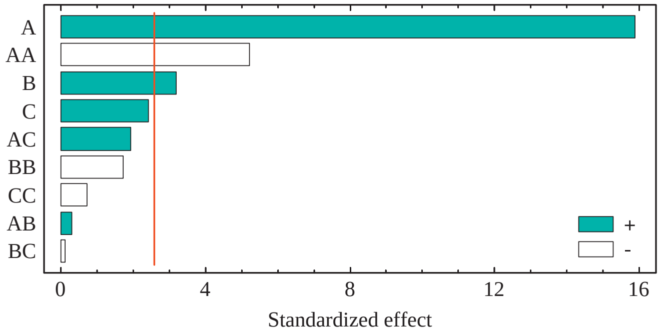

Fig. 5. Pareto chart of the main effects in the BBD. AA, BB and CC are the quadratic effects of the pH, extraction time and amount of polymer, respectively. AB, AC and BC are the interaction effects between pH and extraction time; pH and amount of polymer and extraction time and amount of polymer, respectively.

The adsorption of Pd(II) increases as the pH increases. In acidic solution, adsorption is very low. This observation is due to protonation of the active sites of the magnetic MOF. As the pH increases, the protonation of active sites decreases and the condition becomes more favorable for complex formation and adsorption of Pd(II) ions to the magnetic MOF.

The Response Surface Methodology (RSM) (Fig. 2Sa) was applied to analyze simultaneous effects of time and pH variables on the response and the two-dimensional countour plot (Fig. 2Sb) that displayed the interaction between independent variables. The adsorption of Pd(II) ions increased along with the increase in pH but the time factor has no significant effect on the extraction of Pd(II) ions.

Extraction time and amount of magnetic MOF showed a positive but non-significant effect on the extraction efficiency. According to the overall results of the optimization study, the following experimental conditions were chosen: pH, 6.9; extraction time, 6 min; amount of magnetic MOF, 30 mg.

3.2.2. Selection of desorption solvent

In this work five eluents (HCl, HNO_3, $K_2\,SO_4$, NaOH and KCl) were chosen as the desorption solvent. Other factors were kept constant during the optimization (pH, 6.9; extraction time, 6 min; amount of magnetic MOF, 30 mg; elution volume, 5 mL; elution time, 20 min). Results showed that HCl, HNO_3, and NaOH decompose the structure of magnetic MOF but 0.01 mol L^{-1} NaOH increases the recovery without any decomposition of magnetic MOF structure. Based on measurements, the best quantitative recovery was obtained with 0.01 mol L^{-1} NaOH in K_2 SO_4 solution as the desorption solvent.

3.2.3. *Desorption step*

Three factors were studied in desorption step using experimental design: elution volume (mL), elution time ($_{min}$), and concentration of eluent (% w/v). In these conditions, a response surface design could be done without previously performing a screening design. The BBD was chosen because it requires the least number of experiments (15 run).

The data obtained were evaluated by ANOVA. The effects determined by the analysis are shown using Pareto chart in Fig. 3S. Based on BBD, volume and concentration of eluent showed a positive and significant effect on the recovery of Pd(II) but elution time has positive and non-significant effect. As Fig. 3S shows, eluent volume has the greatest influence on the extraction recovery and a positive effect upon the extraction efficiency.

The RSM (Fig. 6a) was applied to analyze simultaneous effects of elution time and elution volume variables on the responses. The two-dimensional countour plot (Fig. 6b) displays the interaction between independent variables. The extraction efficiency of Pd(II) ions increased along with the increase in elution time and elution volume.

According to the overall results of the optimization study, the following experimental conditions were chosen: elution volume, 6 mL; elution time, 15.5 min; and concentration of eluent, 0.01 mol L^{-1} NaOH in 9.5 (w/v %) K_2SO_4 solution.

3.3. *Effect of breakthrough volume*

In the analysis of real samples, the sample volume is one of the important parameters affecting the preconcentration factor. Therefore, the effect of sample volume on quantitative adsorption of Pd(II) ion was investigated. For this purpose, 30 mg of magnetic MOF was suspended in different sample volumes (25, 50, 100, 250, 500, 750, 1000, 1250, 1400, and 1500 mL), and the total amount of loaded Pd(II) was kept constant to 10 μg. All the solutions were extracted under the optimum conditions for the proposed method. As the volume increased up to 1250 mL, the sample solution recovery was constant but in high volumes, the recovery was decreased. The maximum sample volume can be obtained in 1250 mL with 98% recovery, and therefore the preconcentration factor (PF) was calculated to be 208 since the final elution volume was 6 mL.

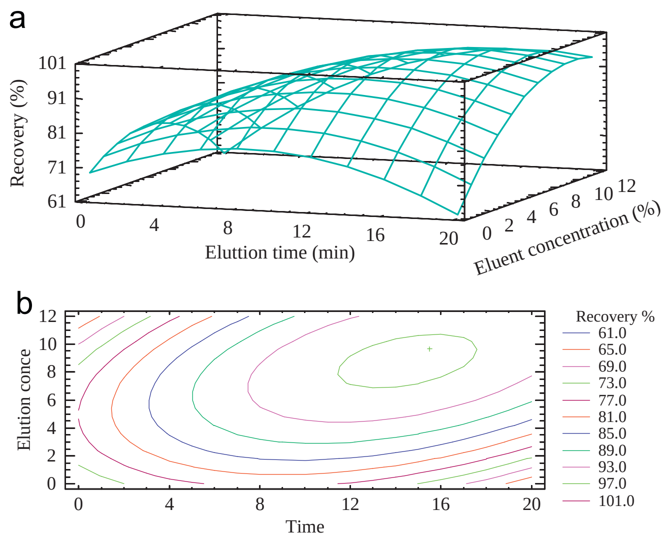

Fig. 6. (a) RSM and (b) contour plot obtained by plotting of elution time vs elution concentration using the BBD.

3.4. *Maximum adsorption capacity*

The sorption capacity which is defined as the maximum amount of metal ion sorbed per gram of the magnetic MOF is an important factor to evaluate the synthesized magnetic MOF. In order to investigate the adsorption capacity of magnetic MOF particles, a standard solution containing 100 mg L^{-1} of Pd(II) was used. In order to evaluate the maximum adsorption capacity, the difference between concentration of the solution before passing through the column and the concentration of the solution after passing through the column was calculated. Based on a measurement, the sorption capacity of the magnetic MOF was calculated to be 105.1 mg g^{-1}.

3.5. *Effect of matrix ions*

In order to investigate the effect of various cations existed in natural samples; elements that are known as alkaline, alkaline earth, and transition metals were added to 100 mL of solution containing 0.1 mg of palladium ions. The degree of tolerance for some alkaline, alkaline earth, and transition metal ions is presented in Table 2. From the tolerance data, it can be found that the foreign ions have no significant effects on preconcentration of palladium ions at pH 6.9.

Table 2
The tolerance limit of various ions on the determination of palladium.

Foreign ion	Tolerable concentration ratio X/Pd	R^a (%) $\pm S^b$
K^+	10000	98.0 ± 2.0%
Na^+	10000	98.0 ± 2.0%
Ca^{2+}	1000	97.0 ± 1.8%
Al^{3+}	1000	99.0 ± 1.4%
Ag^+	1000	98.0 ± 1.6%
Cu^{2+}	1000	97.0 ± 1.7%
Fe^{3+}	1000	96.0 ± 2.0%
Cd^{2+}	1000	99.0 ± 2.0%
Pb^{2+}	1000	95.0 ± 1.6%
Mn^{2+}	1000	98.0 ± 1.8%
Zn^{2+}	1000	99.0 ± 2.0%

Conditions: sample pH=6.9, sample volume=100 ml, 100 μg L^{-1} of Pd (II), sorption time=6 min; eluent=6 mL, 0.01 mol L^{-1} NaOH in K_2SO_4 (9.5 W/v %) desorption time=15.5 min. X: Concentration of diverse ions.

[a] Recovery.

[b] standard deviation (N=3).

3.6. *Statistical and calibration parameters*

Under optimum conditions that have been described, the magnetic MOF showed a linear calibration curve within concentration ranging from 1 to 100 μg L^{-1}. The least square equation at above dynamic linear range was as follows:

$$A = 0.01C_{Pd}(\mu g\ L^{-1}) + 0.02, (R^2 = 0.998)$$

The limit of detection (LOD), which is defined as $C_{LOD}=3S_b/m$, where S_b is the standard deviation of 8 replicate blank signals and m is the slope of the linear section of calibration curve after preconcentration, for a sample volume of 750 mL, was found to be

Table 3
(a) Analysis of Pd(II) in different real samples. The results are the mean of three measurements. (b) Determination of Pd(II) recovery in certified reference material.

(a)

Sample	C_{added} (ng kg^{-1})	C_{found} (ng kg^{-1})	Recovery %	RSD %
Fish sample in Behad creek	–	–	–	–
	5.0	4.84	96.8	1.8
Fish sample in Jafare creek	–	6.23	–	1.6
	5.0	11.52	102.6	2
Sediment sample Behad creek	–	3.29	–	1.5
	5.0	8.17	98.6	1.7
Sediment sample Jafare creek	–	28.6	–	1.8
	5.0	32.8	97.6	1.7
Water sample	C_{added} (ng L^{-1})	C_{found} (ng L^{-1})	Recovery %	RSD %
Distilled water	–	–	–	–
	5.0	4.94	98.8	1.6
Tap water	–	–	–	–
	5.0	4.96	99.2	1.7
mineral water	–	62.3	–	1.9
	5.0	67.8	100.7	2.1
River water	–	–	–	–
	5.0	4.92	98.8	1.8

(b)

Sample	Element	Concentration(ng g^{-1})		Relative error (%)
		Certified	Found	
GBW 07293	Pd	568	559	98.4
Certified 1[a]	Pd	1.7	1.64	96.5
Certified 2[a]	Pd	4.0	3.82	95.5

[a] Certified concentration of the elements were reported by Geological Survey of Iran (Tehran, Iran).

0.37 ng mL^{-1} for Pd(II) ions. The relative standard deviation (RSD) for six separate batch experiments with 30 mg of sorbent for determination of 8 µg Pd(II) in 100 mL of water was calculated to be 2.1%.

3.7. Certified reference material and real sample analysis

In order to assess the accuracy of the method, it was applied to extraction and separation of Pd(II) ions from different certified reference materials and real samples including fish, sediment, soil, tap, river, distilled, and mineral water samples. The results were summarized in Table 3 for three replicate analysis of each sample. Primary analysis of the certified reference materials and real samples showed that most of them had Pd(II) ions. All of the samples were spiked with 5 µg L^{-1} of Pd(II) ions, and a good correlation was obtained between the added and measured amounts. Generally, the recoveries of Pd(II) ions were obtained in the range between 96.8 to 102.5%.

4. Conclusion

Magnetic MOF is a novel sorbent for extraction and preconcentration of Pd(II) ions from different matrixes. The proposed method has many advantages such as high sample clean-up, high extraction recovery, selectivity, and high preconcentration factor. Furthermore, the extraction method has higher adsorption capacity compared to Fe_3O_4–Py. In general, the performance of the method was excellent in extraction of trace amounts of Pd(II) from different real samples. In addition, the method is very environmental friendly and can be used in complex matrices with high selectivity.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2012.05.030.

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