



Determination of cadmium in rice samples using amino-functionalized metal-organic framework by a pipette tip solid phase extraction

Mohammad Abbaszadeh^a, Ali Miri^a, and Mohammad Reza Rezaei Kahkha^{a,*}

^a Department of Environmental Health Engineering, Faculty of Health, Zabol University of Medical Sciences, Zabol, Iran

ARTICLE INFO:

Received 21 May 2022

Revised form 2 Aug 2022

Accepted 28 Aug 2022

Available online 29 Sep 2022

Keywords:

Cadmium,
Amino functionalized metal-organic framework,
Pipette tip extraction,
Rice samples,
Atomic adsorption spectrometer

ABSTRACT

In this study, the amino-functionalized metal-organic framework (NH₂-MOFs) was used as an adsorbent for the extraction of cadmium in rice samples based on the pipette tip solid phase extraction (PT-SPE) before determined by the flame absorption spectrometry (F-AAS). The pH of the sample solution, initial concentration of the cadmium, the volume of the sample, elution conditions, and the amount of adsorbent on the recovery of the cadmium were investigated and optimized. The results showed that the best extraction efficiency of cadmium was obtained at pH 5.0, 2500.0 µL of cadmium solution, and 20.0 µL of HCl (10% V/V) as eluent solvent. First, the cooking rice was transferred to a beaker and hydrochloric acid/nitric acid was added to it as a digestion process before analysis by the PT-SPE procedure. The limit of detection of this method was found to be 0.03 µg L⁻¹ with a relative standard deviation of ≤ 2.5 % (for seven replicate analyses of 50 µg L⁻¹ of cadmium). The linear and dynamic ranges were achieved at 0.3 -14.5 µg L⁻¹ and 0.3 -150 µg L⁻¹, respectively. The adsorption capacity of sorbent and enrichment factor was 175 mg g⁻¹ and 125 folds, respectively. The proposed method was successfully applied for the determination of cadmium in rice samples.

1. Introduction

Pollution of foods with heavy metals (HMs) is a serious problem for public health and the community due to its toxicity and carcinogenicity. Therefore, monitoring and controlling the amount of HMs in food samples is critical. Cadmium is one of the most dangerous HMs that enters food samples from various sources, including mining, industrial production and other ways such as agricultural runoff [1]. According to the US Environmental Protection Agency, the maximum acceptable level of cadmium in rice and wheat is 200 µg. kg⁻¹ [2]. On the other hand, the accumulation of cadmium

ions in food samples such as rice, wheat, and other species is unavoidable[3]. In these food samples, the effect of matrices is a serious problem for its measuring because of the low concentration of cadmium, therefore, a preconcentration technique is necessary before quantification[4]. Various techniques have been applied for this purpose such as dispersive liquid- liquid microextraction [5], cloud point extraction [6] and solid phase extraction (SPE) [7]. The pipette tip (PT), a micro-scale format of SPE, that used for the preconcentration and extraction of various samples[8]. Using a small amount of sorbent (insert into a pipette tip) and low solvent consumption without a special auxiliary device is the advantage of PT-SPE compared to conventional SPE cartridges [9,10].

*Corresponding Author: M. R. Rezaei Kahkha

Email: m.r.rezaei.k@gmail.com

<https://doi.org/10.24200/amecj.v5.i03.208>

Recently PT-SPE was applied for the determination and extraction of several analytes in food samples such as bisphenol a [11], estradiol in milk [12], and antibiotic residues Metal-organic frameworks (MOFs) are a new class of hybrid porous materials consisting of organic linkers coordinated to inorganic metal nodes that are used in solid phase extraction because of their thermal and chemical stability[14]. Recently, several adsorbents such as silica nanoparticles [15], molecularly imprinted polymer [16], and other sorbents were applied for determination of cadmium in food samples[17]. Hence, based on the above remarks and our research interest in applications of porous materials [18-21]we utilized the highly stable amino functionalized metal organic framework (Fig. 1) for the determination and extraction of cadmium in imported rice samples. Many other papers were presented about extraction methods by previous researchers [22-24]. Parameters affecting PT-SPE were studied and optimized. To the best of our knowledge, the MOF with the properties mentioned above was applied for the first time as a solid phase sorbent in a pipette-tip microextraction mode.

2. Material and methods

2.1. Reagents and instrument

All reagents and solutions were analytical grades. Methyl 4-formylbenzoate (CAS N: 1571-080, Sigma, Germany), pyrrole (CAS N: 109-97-7, pH >6, Merck), the trifluoroaceticacid (CAS N: 76-05-1, EC Number 200-929-3, TFA) from Sigma-Aldrich, propionic acid (CAS N: 79-09-4, MW: 74.08, Sigma-Aldrich), $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (CAS N.: 13520-92-8, 98%, Sigma-Aldrich), 1000 mg.L^{-1} standard solution of cadmium (CAS N: 7440-43-9 Sharlou, Spain), *N,N'*-dimethylformamide (CAS N: 68-12-2, DMF), benzoic acid (>98%, CAS N: 65-85-0; EC N: 200-618-2, Sigma), acetone ($\geq 99.5\%$; CAS N: 67-64-1, Sigma, Germany), tetrahydrofuran (THF, CAS N: 109-99-9 EC N: 203-726-8, Sigma), methanol (CAS N: 67-56-1), and KOH (CAS N: 1310-58-3, Sigma, Germany) were purchased from commercial sources and used as received. The flame atomic absorption spectrometer based on a double beam spectrophotometer (FAAS, AA7800, Shimadzu, Japan) was used for cadmium detection. The mixture of C_2H_2 gas and the D_2 was tuned for the cadmium determination by FAAS.

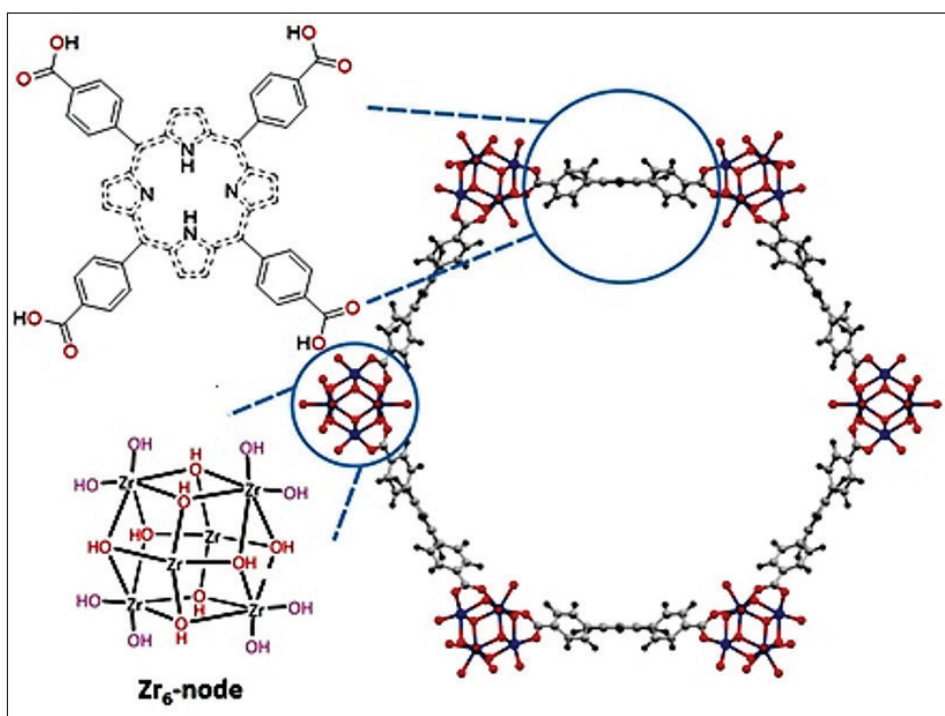


Fig.1. A schematic of amino functionalized MOF.

2.2. Synthesis of amino-functionalized metal-organic framework

The sorbent was synthesized in a similar way that we have previously reported [25]. Briefly, 200 mg of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, 3.0 g of benzoic acid, and 20 mL of DMF were added into a 30-mL vial (solution A); and in other 30-mL vial, 100 mg of H_2TCPP and 20 mL of DMF were added (solution B). Both solutions A and B were sonicated for 30 min and then incubated at 100 °C in an oven for 1 h. Next, 1 mL of A solution, 1 mL of B solution, and 0.05 mL of trifluoroacetic acid were added and mixed by swirling for 5 s. The vials were then incubated and immersed in an oven at 120 °C for 30 h. A dark purple precipitate started to form in the vials. After cooling to room temperature, the suspension was transferred into a centrifuge tube and centrifuged for 5 min (7500 rpm) to remove the supernatant. The solid was washed with fresh DMF (3×30 mL) before soaking in 40 mL of fresh DMF and 1.5 mL of 8 M HCl (activation with HCl). It was then heated at 120 °C for 12 h to remove the benzoic acid. The sample was subsequently washed with fresh DMF (3×30 mL), THF (3×30 mL), and acetone (3×30 mL). After soaking in acetone overnight, the solid was collected, and then dried in a vacuum oven

at 120 °C for 12 h to give the MOF. SEM of the amino-functionalized metal-organic framework is seen in Figure 2.

2.3. Pipette-tip extraction procedure

Appropriate amounts of sorbent were inserted into a pipette-tip (DRAGON, China) which was then attached to a 5000 μL micro pipette (DRAGON LAB, China). Then 2500 μL of the aqueous sample was withdrawn into the sorbent and dispensed back into the same tube for 20 cycles. Elution was performed by 20 μL of 10% HCl into a 1-mL vial. The desorption step was also performed by 20 aspirating/dispensing cycles. The extraction recovery of cadmium was calculated by comparing the absorbance of 50 $\mu\text{g L}^{-1}$ of cadmium standard solution by results of optimization experiments (Fig.3).

3. Results and discussion

3.1. Optimization of affecting parameter on the extraction procedure

To optimize the extraction conditions, parameters affecting extraction were optimized as below. All optimizations were performed on a 50 $\mu\text{g L}^{-1}$ of cadmium solution, made by diluting of 1000 mg L^{-1} standard solution.

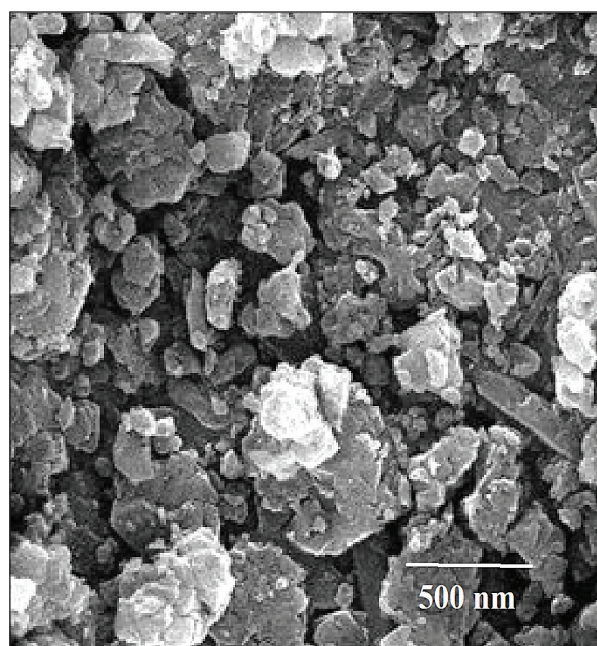
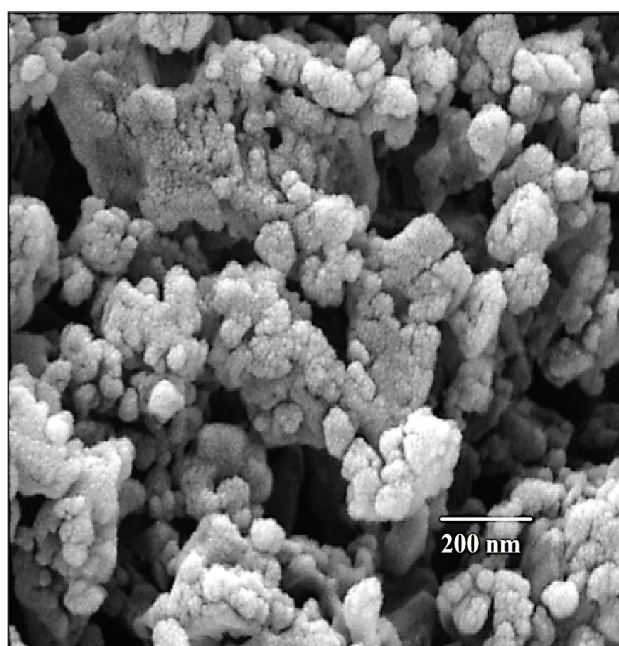


Fig.2. SEM images of synthesized NH_2 -MOFs

3.1.1. Effect of pH

The effect of sample pH on the extraction efficiency of cadmium was investigated by adjusting pH of it between 2.0 and 9.0. Either 0.1 M NaOH or 0.1 M HCl was used. As depicted in Figure 4, a solution with the pH values between 4.0 and 6.0 showed the highest

extraction efficiency (optimal pH = 5). In alkaline media, produced hydroxide ions can form a complex with cadmium ions, and a precipitation ($\text{Cd}(\text{OH})_2$) is created. Results showed that the extraction efficiency of cadmium based on NH₂-MOFs was decreased. So, pH 5.0 was selected as the optimum value.

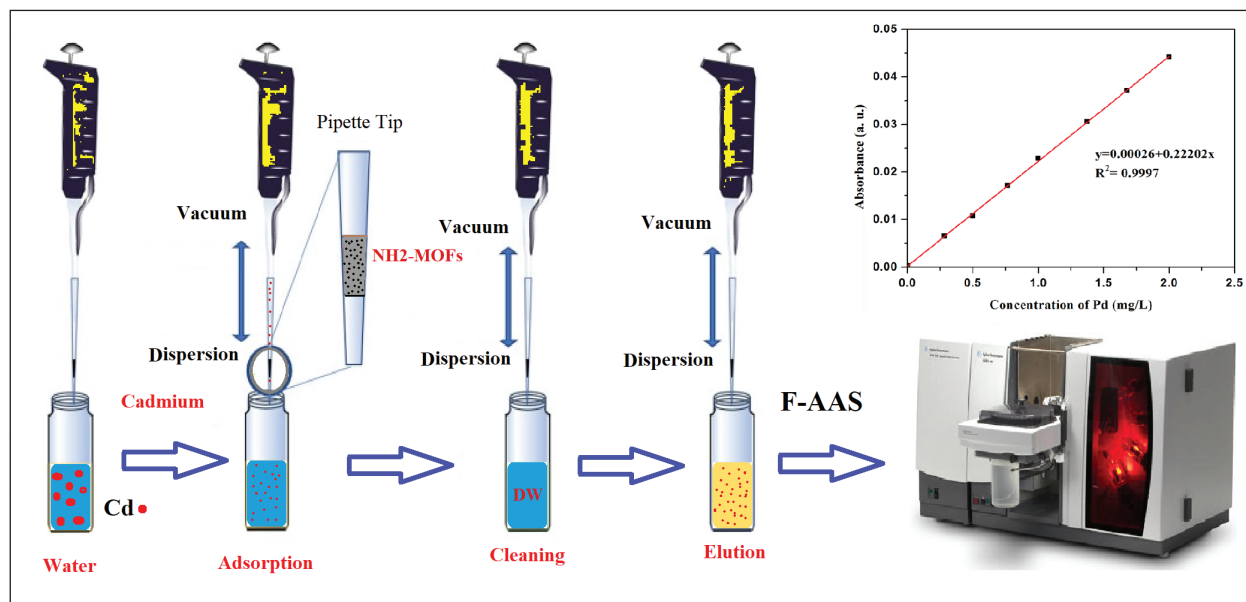


Fig. 3. Cadmium extraction based on NH₂-MOFs adsorbent and Pipette-tip- SPE procedure

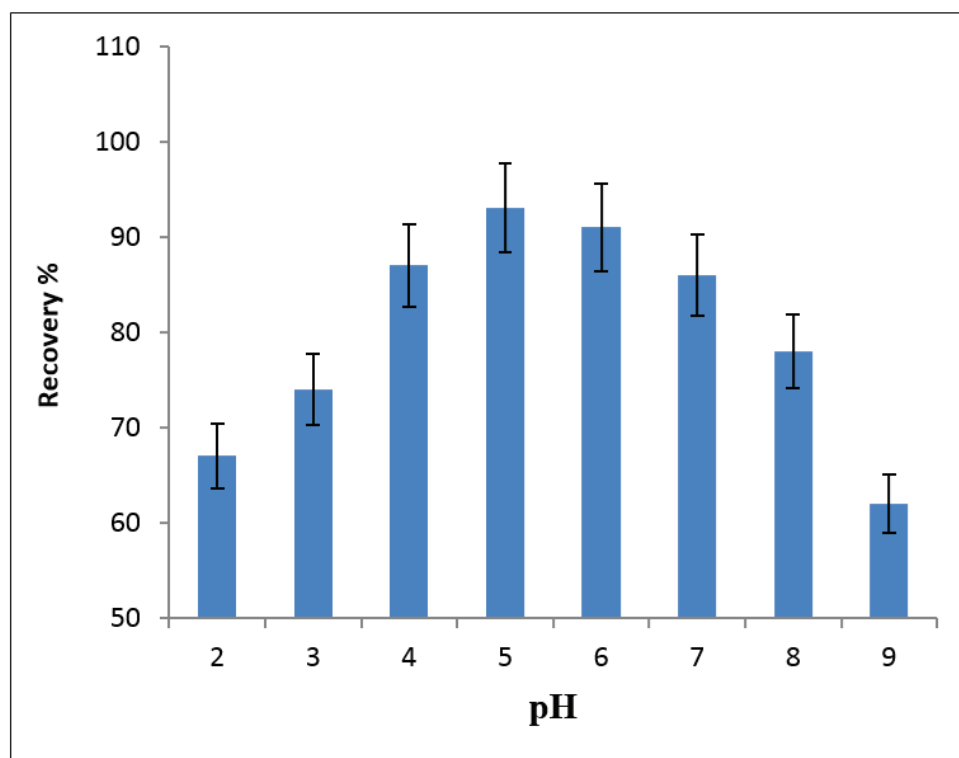


Fig. 4. Effect of pH on recovery of cadmium

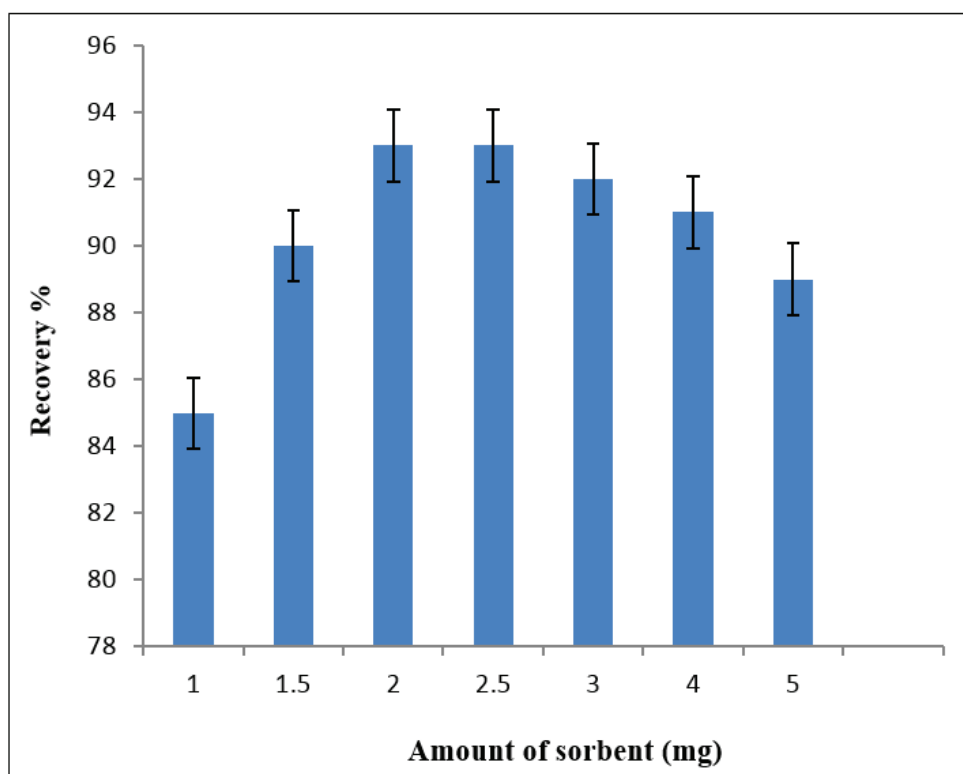


Fig. 5. Effect of amount of sorbent on recovery of cadmium.

3.1.2. Effect of amount of sorbent

To obtain the best extraction efficiency and good recoveries of cadmium ions, the amount of sorbent was examined between 1-5 mg. The adsorption ability of the adsorbent was increased by increasing the amount of sorbent up to 2 mg; therefore, the optimum amount of 2 mg was chosen (Fig. 5).

3.1.3. Effect of volume of the eluting solvent

Several strong acidic solvents including different concentrations of HNO_3 (2-10% V/V) and HCl (2-10% V/V) were studied to select an optimized eluting solvent. Among them HCl 10% showed the highest extraction efficiency for cadmium ions. To achieve the highest enrichment factor, we tried to obtain the smallest HCl volume of 10%. Volumes between 5 to 50 μL of HCl 10% were examined for the extraction of 1000 μL of a standard solution containing 50 $\mu\text{g L}^{-1}$ of the cadmium in deionized water. As shown in Figure 6, at the volume of 20 μL of the eluting solvent, the recovery of cadmium is at its highest value.

Therefore, the eluting volume of 20 μL was selected for further experiments.

3.1.4. Effect of volume of sample solution

Amount of sample solution taken for the analysis is an important parameter in solid phase extraction [5]. Different volumes of sample solution were tested at the range of 200 to 4000 μL containing 50 $\mu\text{g L}^{-1}$ of cadmium. As can be seen in Figure 7, the extraction recovery of cadmium increased with the increase of the volume up to 2500 μL . So, the extraction efficiency (more than 95%) and a preconcentration factor of 125 for cadmium extraction were achieved based on 20 μL of eluent with the PT-SPE procedure before determination by the F-AAS.

3.1.5. Effect of number of aspirating/dispensing of sample and elution solvent

The number of aspirating/dispensing cycles of eluent solvent and the volume of solution that passed through the extractor resembles the extraction time. The results showed the highest recoveries

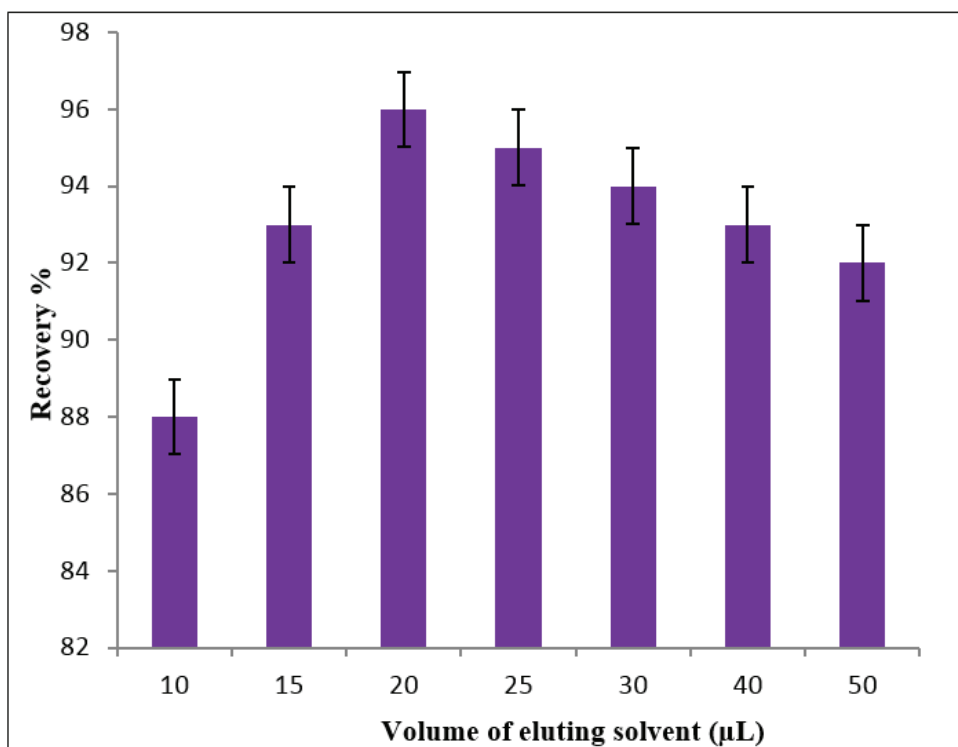


Fig. 6. Effect of volume of eluting solvent (HCl 10%) on recovery of cadmium

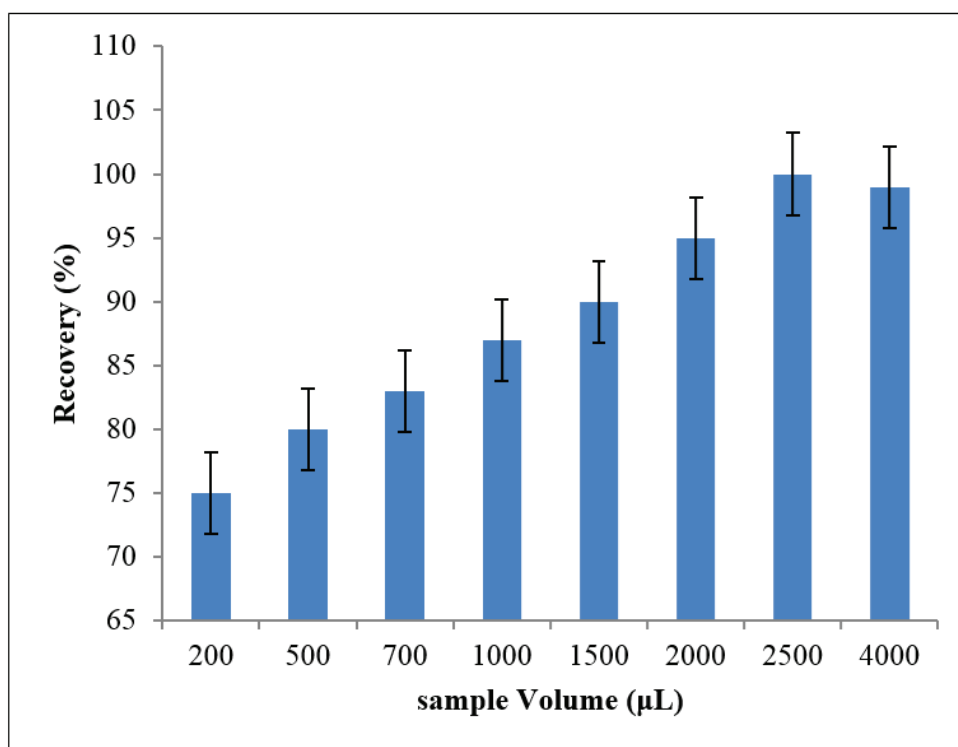


Fig. 7. Effect of sample volume on recovery of cadmium

for cadmium obtained at 20 cycles, when 2500 μL of a sample containing 50 $\mu\text{g L}^{-1}$ of the standard solution was used. During desorption, the analyte was eluted from the extractor into a 2.0 mL glass test tube by repetitive aspirating/dispensing of 20 μL of the HCl 10% (V/V) through the tip. The optimal number of aspirating/dispensing cycles for desorption of adsorbed analytes (provided the highest recovery) was found to be 20 cycles at 12min.

3.1.6. Reusability of the adsorbent

The reusability of the sorbent was investigated by washing of the column with HCl 10% V/V and then five cycles with deionized water. After that, several extraction and elution operation cycles were carried out under the optimized conditions. The results indicated that the amino functionalized MOF could be regenerated and reused at least ten times without significantly decreasing extraction recoveries.

3.1.7. Sorption capacity

To investigate of the adsorption capacity of the functionalized MOF, a standard solution containing 100 mg L^{-1} of cadmium ions was applied. The maximum sorption capacity is defined as the total amount of cadmium ions adsorbed per gram of the sorbent. The obtained capacity of the adsorbent was found to be 175 mg g^{-1} .

3.1.8. Effect of interfering ions

The effect of common co-existing ions that often companion with cadmium ions in real samples on cadmium determination was studied in optimum conditions by analyzing 100 $\mu\text{g L}^{-1}$ of cadmium after addition of varying concentrations of Na^+ , K^+ , Ca^{2+} , Cu^{2+} , Zn^{2+} , Ni^{2+} , Mn^{2+} , and Fe^{2+} . The concentration ratio of other ions was as follow: 1750 for Na^+ , K^+ ; 1500 for Ca^{2+} , Mg^{2+} ; 1250 for Cu^{2+} , Zn^{2+} , Fe^{2+} , Ni^{2+} , Mn^{2+} . Results showed that interference ions do not influence on extraction recovery of cadmium. Hence, the method was selective for preconcentration and extraction of cadmium (Table 1).

3.2. Analytical performance of suggested method

The analytical performance of the suggested pipette-tip solid phase extraction was evaluated, and the results are summarized in Table 2. The limit of detection (LOD) was obtained based on a signal-to-noise ratio of 3. The linearity range was studied by varying the concentration of the standard solution from 0.3 to 150 $\mu\text{g L}^{-1}$. The repeatability of the method, expressed as relative standard deviation (RSD), was calculated for seven replicates of the standard at an intermediate concentration (50 $\mu\text{g L}^{-1}$) of the calibration curve. The precision of the method was determined by repeatability (intraday precision) and intermediate precision (inter-day precision) of both standard and sample solutions.

Table 1. The effect of interfering ions on the recovery of Cd (II) ions in water samples by PT-SPE procedure coupled to F-AAS

Interfering Ions(M)	Mean ratio (C_M/C_{Cd})	Recovery (%)
	Cd(II)	Cd(II)
Al^{3+}	750	97.5
Na^+ , K^+	1750	97.8
Cu^{2+} , Zn^{2+} , Fe^{2+} , Ni^{2+} , Mn^{2+}	1250	98.2
I^- , Br^- , F^-	1100	97.7
Ca^{2+} , Mg^{2+}	1500	98.0
Co^{2+} , Pb^{2+}	950	97.9
Ag^+ , Au^{3+}	250	96.5

Table 2. Analytical figures of merit for proposed methods

Parameter	Analytical feature
Dynamic range ($\mu\text{g L}^{-1}$)	0.3 -150
R^2 (determination coefficient)	0.99
Repeatability (RSD ^a %)	2.45
Limit of detection ^b (ng.L^{-1})	15
Enrichment factor (fold)	125
Total extraction time (min)	≤ 12

^aRSD, relative standard deviation, for 5 replicate measurements of $50 \mu\text{g.L}^{-1}$ of the analyte

^bLimit of detection was calculated based on the $3S_0/m$ criterion for 10 blank measurements

Precision was determined in seven replicates of both cadmium standard solution ($100 \mu\text{g L}^{-1}$) and sample solution ($100 \mu\text{g L}^{-1}$) on the same day (intra-day precision) and daily for 8 times over a period of one week (inter-day precision). The results are represented as % RSD and indicated that intra-day precision and inter-day precision of the method were 5.0% and 3.5%, respectively.

3.3. Determination and validation of cadmium in rice samples

Rice samples were purchased from several local markets. About 50 gr of rice was weighed and cooked in the oven for 8 hours at the temperature is 80°C with the aim of removing moisture

and determining weight. It was dry. After drying and reaching constant weight, 10 gr of rice was transferred to a 250.0 ml beaker. Samples for 48 hours at a temperature of 105°C it placed. Then 5 ml of 37% hydrochloric acid and 15 ml of 65% nitric acid were added to them and after 120 minutes at the laboratory temperature, it dissolved slowly and heated until its volume reached less than 20 ml. Then the obtained clear solution was cooled, filtered and used for the determination of cadmium according to the above PT-SPE method. As can be seen in Table 3 concentrations of cadmium in all samples in comparison to the maximum acceptable level ($200 \mu\text{g g}^{-1}$) are adequate.

Table 3. Determination of cadmium in different rice samples under optimized conditions^a

Rice Sample	Added ($\mu\text{g g}^{-1}$)	Found ($\mu\text{g g}^{-1}$)	Recovery (%)	RSD % (n=3)
1	0	45	-	-
	50	94.2	98.2	2.7
	150	194.5	74.3	3.2
2	0	40	-	-
	50	89.3	98.7	1.7
	100	139.2	98.1	2.8
3	0	55	-	-
	50	104.7	98.7	3.6
	100	154.5	98.5	2.8

^aThe maximum acceptable level of cadmium in the rice reported by WHO is $200 \mu\text{g g}^{-1}$

4. Conclusion

In this research, for the first time, we employed an amino functionalized MOF with a high surface area and large porosity for PT-SPE of cadmium. This method is very simple, fast, solvent-free and applicable for the extraction of cadmium. The total time of analysis, was less than 12 minutes and the functionalized-MOF sorbent was used for at least 10 extractions without any change in its capacity. Only 2mg of the sorbent was enough to fill the PT. Moreover, evaluation of intra-day and inter-day showed a notable precision with RSD below 5 and 3.5%, respectively. This method was applied successfully for the determination of cadmium in three rice samples. Real samples spiked with three concentration levels and results indicated that sorbent can be applied in the complicated matrix for analysis of heavy metals such as cadmium. Also, analysis of real samples showed that the concentration of cadmium in all samples is below the acceptable range.

5. Conflict of Interest and Ethical approval

The authors have declared no conflict of interest.

6. References

- [1] P.K. Rai, Heavy metals in food crops: Health risks, fate, mechanisms, and management, *Environ. Int.*, 125 (2019) 365-385. <https://doi.org/10.1016/j.envint.2019.01.067>.
- [2] Y. Mao, Research Progress of Soil Microorganisms in Response to Heavy Metals in Rice, *J. Agri. Food Chem.*, 70 (2022) 8513-8522. <https://doi.org/10.1021/acs.jafc.2c01437>.
- [3] C. Mao, Human health risks of heavy metals in paddy rice based on transfer characteristics of heavy metals from soil to rice, *Catena*, 175 (2019) 339-348. <https://doi.org/10.1016/j.catena.2018.12.029>
- [4] W.A. Khan, M.B. Arain, M. Soylak, Nanomaterials-based solid phase extraction and solid phase microextraction for heavy metals food toxicity, *Food Chem. Toxicol.*, 145 (2020) 111704. <https://doi.org/10.1016/j.fct.2020.111704>
- [5] M.H. Habibollahi, Extraction and determination of heavy metals in soil and vegetables irrigated with treated municipal wastewater using new mode of dispersive liquid-liquid microextraction based on the solidified deep eutectic solvent followed by GFAAS, *J. Sci. Food Agri.*, 99 (2019) 656-665. <https://doi.org/10.1002/jsfa.9230>.
- [6] S.S. Arya, A.M. Kaimal, Novel, energy efficient and green cloud point extraction: technology and applications in food processing, *J. food Sci. Technol.*, 56 (2019) 524-534. <https://doi.org/10.1007/s13197-018-3546-7>
- [7] H.L. Jiang, N. Li, L. Cui, Recent application of magnetic solid phase extraction for food safety analysis, *TrAC Trends Anal. Chem.*, 120 (2019) 115632. <https://doi.org/10.1016/j.trac.2019.115632>
- [8] H. Sun, J. Fung, Recent advances in micro-and nanomaterial-based adsorbents for pipette-tip solid-phase extraction, *Microchim. Acta*, 188 (2021) 1-24. <https://doi.org/10.1007/s00604-021-04806-0>
- [9] M. Shirani, F. Salari, Needle hub in-syringe solid phase extraction based a novel functionalized biopolyamide for simultaneous green separation/preconcentration and determination of cobalt, nickel, and chromium (III) in food and environmental samples with micro sampling flame atomic absorption spectrometry, *Microchem. J.*, 152 (2020) 104340. <https://doi.org/10.1016/j.microc.2019.104340>
- [10] M.A. Habila, Z.A. Alothman, Activated carbon cloth filled pipette tip for solid phase extraction of nickel (II), lead (II), cadmium (II), copper (II) and cobalt (II) as 1, 3, 4-thiadiazole-2, 5-dithiol chelates for ultra-trace detection by FAAS, *Int. J. Environ. Anal. Chem.*, 98 (2018) 171-181. <https://doi.org/10.1080/03067319.2018.1430794>
- [11] M.R.R. Kahkha, Fast determination of bisphenol a in spiked juice and drinking water samples by pipette tip solid phase extraction using cobalt metal organic framework as sorbent, *Bull. Chem. Soc. Ethiopia*, 32 (2018) 595-602. <https://doi.org/10.4314/bcse.v32i3.17>

- [12] Y. Zhang, Covalent organic framework Schiff base network-1-based pipette tip solid phase extraction of sulfonamides from milk and honey, *J. Chromatogr. A*, 1634 (2020) 461665. <https://doi.org/10.1016/j.chroma.2020.461665>
- [13] T.G. Aqda, Graphene oxide-starch-based micro-solid phase extraction of antibiotic residues from milk samples, *J. Chromatogr. A*, 1591 (2019) 7-14. <https://doi.org/10.1016/j.chroma.2018.11.069>
- [14] Y. Su, S. Wang, Zr-MOF modified cotton fiber for pipette tip solid-phase extraction of four phenoxy herbicides in complex samples, *Ecotoxicol. Environ. Safe.*, 201(2020)110764. <https://doi.org/10.1016/j.ecoenv.2020.110764>
- [15] A. Girgin, N. Atsever, Determination of cadmium in mineral water samples by slotted quartz tube-flame atomic absorption spectrometry after peristaltic pump assisted silica nanoparticle based pipette tip solid phase extraction, *Water Air Soil Pollu.*, 232 (2021) 1-10. <https://doi.org/10.1007/s11270-021-05386-8>
- [16] M.M. Moein, Advancements of chiral molecularly imprinted polymers in separation and sensor fields: A review of the last decade, *Talanta*, 224 (2021) 121794. <https://doi.org/10.1016/j.talanta.2020.121794>
- [17] M. Arjomandi, H. Shirkhanloo, A review: analytical methods for heavy metals determination in environment and human samples, *Anal. Methods Environ. Chem. J.*, 2 (2019) 97-126. <https://doi.org/10.24200/amecj.v2.i03.73>
- [18] M. Abbaszadehbezi, M. R. Rezaei Kahkha, A. Khammar, Application of pipette-tip solid-phase extraction technique for fast determination of levofloxacin from wastewater sample using cobalt metal-organic framework, *Anal. Methods Environ. Chem. J.*, 5 (2) (2022) 51-59. <https://doi.org/10.24200/amecj.v5.i02.185>
- [19] M.R.R. Kahkha, M. Kaykhaii, B. Rezaei Kahkha, H. Khosravi, Simultaneous removal of heavy metals from wastewater using modified sodium montmorillonite nanoclay, *Anal. Sci.*, 36 (2020) 1039–1043. <https://doi.org/10.2116/analsci.19P300>
- [20] M.R.R. Kahkha, Magnetic bentonite nanocomposite for removal of amoxicillin from wastewater samples using response surface methodology before determination by high performance liquid chromatography, *Anal. Methods Environ. Chem. J.*, 3 (03) (2020) 25-31. <https://doi.org/10.24200/amecj.v3.i03.108>
- [21] M.R.R. Kahkha, G. Ebrahimzadeh, A. Salarifar, Removal of Metronidazole residues from aqueous solutions based on magnetic multiwalled carbon nanotubes by response surface methodology and isotherm study, *Anal. Methods Environ. Chem. J.*, 3(03) (2020) 44-53. <https://doi.org/10.24200/amecj.v3.i03.110>
- [22] M. Tuzen, A. Sarı, Polyamide magnetic palygorskite for the simultaneous removal of Hg(II) and methyl mercury; with factorial design analysis, *J. Environ. Manage.*, 211 (2018) 323-333. <https://doi.org/10.1016/j.jenvman.2018.01.050>
- [23] T.A. Saleh, A. Sarı, M. Tuzen, Optimization of parameters with experimental design for the adsorption of mercury using polyethylenimine modified-activated carbon. *J. Environ. Chemical Eng.*, 5 (2017) 1079-1088. <https://doi.org/10.1016/j.jece.2017.01.032>
- [24] M. Tuzen, A. Sarı, M.R. Afshar Mogaddam, S. Kaya, K.P. Katin, N. Altunay, Synthesis of carbon modified with polymer of diethylenetriamine and trimesoyl chloride for the dual removal of Hg (II) and methyl mercury ([CH₃Hg]⁺) from wastewater: Theoretical and experimental analyses. *Mater. Chem. Phys.*, 277 (2022) 125501. <https://doi.org/10.1016/j.matchemphys.2021.125501>
- [25] M. R. Rezaei Kahkha, S. Daliran, The mesoporous porphyrinic zirconium metal-organic framework for pipette-tip solid-phase extraction of mercury from fish samples followed by cold vapor atomic absorption spectrometric determination, *Food Anal. Methods*, 10 (2017) 2175-2184. <https://doi.org/10.1007/s12161-016-0786-x>