



# Zinc based metal–organic framework for nickel adsorption in water and wastewater samples by ultrasound assisted-dispersive-micro solid phase extraction coupled to electrothermal atomic absorption spectrometry

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## ARTICLE INFO:

Received 14 Sep 2020

Revised form 15 Nov 2020

Accepted 30 Nov 2020

Available online 29 Dec 2020

## Keywords:

Metal–organic framework,  
Nickel,  
Adsorption,  
Dispersive- micro solid phase  
extraction,  
Water sample,  
Electrothermal atomic absorption  
spectrometry

## ABSTRACT

In this research,  $Zn_2(BDC)_2(DABCO)$  metal–organic framework (MOF) as a solid phase was used for separation and preconcentration toxic nickel ions (Ni) from water samples by ultrasound assisted-dispersive-micro solid phase extraction coupled to electrothermal atomic absorption spectrometry (USA-D- $\mu$ -SPE/ET-AAS). The MOF nanostructure was characterized by field emission-scanning electron microscope (FE-SEM) and transmission electron microscopy (TEM) for presentation of morphology and size of MOF synthesis. By procedure, 25 mg of  $Zn_2(BDC)_2(DABCO)$  as MOF adsorbent was added to 25 mL of water samples and then, Ni ions chemically adsorbed based on dative bonding of nitrogen in DABCO (1,4-diazabicyclo [2.2. 2]octane);  $N_2(C_2H_4)_3$  at pH=8. The adsorbent was separated from liquid phase by syringe cellulose acetate filters (SCAF, 0.2  $\mu$ m) and Ni ions back extracted from MOF adsorbent before determined by ET-AAS. The maximum recovery of MOF for nickel ions as a physically and chemically adsorption was obtained 34.6% and 98.8% at pH=3 and 8, respectively. The capacity adsorption of  $Zn_2(BDC)_2(DABCO)$ , MOF for nickel was acquired 125.7 mg g<sup>-1</sup> at pH=8. By procedure, the preconcentration factor (PF), LOD, and linear range were achieved 48.7, 0.03  $\mu$ g L<sup>-1</sup> and 0.10-2.88  $\mu$ g L<sup>-1</sup>, respectively (RSD<1.26). The validation of proposed method was successfully obtained by ICP- MS analysis in real samples.

## 1. Introduction

The water pollution is one of the most important issues in the world today [1-2]. The high concentration of heavy metals in environment has been attributed to population growth, economic

development and rapid industrialization in recent years [3-5]. These toxic metals can enter to the human body after release into the environment. Exposure to heavy metals causes to poisoning, mutagenicity, carcinogenicity and disease in humans, as well as a serious threat to the environment and public health [6]. Nickel is one of the most toxic heavy metal for humans even in

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<https://doi.org/10.24200/amecj.v3.i04.123>

low concentrations. Nickel toxicity causes some disorders in human body such as bone diseases, damage to the liver and the kidney, bronchitis, lung cancer and CNS problem [7, 8]. Nickel ions enter into environment from waste water, water and air from industries and factories such as battery Company, mining and electroplating. Normal range of nickel in human serum ( $0.2 \mu\text{g L}^{-1}$ ) is reported by *American conference of governmental industrial hygienists (ACGIH)*. Also, the nickel values in water samples are ranges from 3 to  $10 \mu\text{g L}^{-1}$  and average levels in drinking water is between  $2.0\text{--}4.3 \mu\text{g L}^{-1}$  [7,8]. Recently, the different techniques include, flame atomic absorption spectrometry (F-AAS) [9], electrothermal atomic absorption spectrometry (ET-AAS) [10], ultrafiltration [11], ion-exchange [12], chemical precipitation [13], electrodialysis [14], adsorption [15], spectrophotometry [16] and inductively coupled plasma-mass spectrometry (ICP-MS) [17] were used for nickel determination in water and human biological samples. As difficulty matrixes and trace concentration in drinking waters and wastewater, the sample preparation must be used to separation Ni ions from samples. The different procedures for sample preparation of Ni were reported in water samples. For examples, the solid-phase extraction (SPE), the functionalized magnetic SPE [18], the dispersive liquid-liquid microextraction method (DLLME) [19], ultrasound-assisted solid phase extraction (USA-SPE) [20] and micro SPE (D- $\mu$ -SPE) [21] were previously presented for preparation of water samples by researchers. Today, the nanotechnology has led to significant advances in different fields of science and product innovation [22]. Nanomaterials have been developed due to their special properties and various application potentials [23, 24]. Recently, the metal-organic frameworks (MOFs) have expanded as porous hybrid organic-inorganic materials [25, 26]. These materials synthesized via self-assembly of primary building blocks including metal ions (or metal clusters) as metal centers, and bridging ligands as linkers [27]. MOFs have been synthesized by different

methods such as solvothermal, hydrothermal, ionic liquids, microwave, sonochemical, diffusion, electrochemical, mechanochemical, and laser ablation [28]. MOFs have received great attention because of their unique properties in many areas [28-29]. The ultrasound assisted-dispersive ionic liquid-suspension solid phase micro extraction is a good candidate method for Ni extraction from waters [30].

In the present study, the nickel absorption is one of the most considerable applications of  $\text{Zn}_2(\text{BDC})_2(\text{DABCO})$  MOF in waters. So, The Zn-MOF adsorbent based on USA-D- $\mu$ -SPE procedure was used for nickel adsorption/extraction from water samples and the concentration of nickel ions determined by ET-AAS.

## 2. Experimental

### 2.1. Materials

All reagents with high purity and analytical grade were purchased from Merck (Darmstadt, Germany). Materials including zinc acetate dihydrate ( $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ ), 1,4 benzenedicarboxylic acid (BDC), 1,4-diazabicyclo [2.2.2] octane (DABCO), dimethylformamide (DMF) were purchased and used for synthesis of  $\text{Zn}_2(\text{BDC})_2(\text{DABCO})$  MOF. The syringe cellulose acetate filters (SCAF,  $0.2 \mu\text{m}$ ) purchased from Sartorius, Australia (Minisart® Syringe Filters). The GBC 932, electrothermal atomic absorption spectrophotometer (ET-AAS, model 932, Australia) equipped with a graphite furnace were used for the determination of nickel in water samples. The samples were injected to graphite tube with auto-sampler ( $20 \mu\text{L}$ ). The ICP-MS was used for determining of ultra-trace nickel in water samples (Perkin Elmer, 1200 W;  $2.0 \text{ L min}^{-1}$ ; 1-1.5 sec per mass;  $\text{N}_2$  gas). The pH meter with the glassy electrode was used for measuring pH in water samples (Metrohm, E-744, Switzerland). The shacking of water and wastewater samples were done by vortex mixer (Thermo, USA). The standard solution of nickel nitrate (1%,  $\text{Ni}(\text{NO}_3)_2$ ) was purchased from Sigma, Germany. All of Ni standard 0.5-5 ppb was daily prepared

by dilution of the standard Ni solution with DW. Ultrapure water was prepared from RIPI Co. (IRAN). The pH was adjusted from 5.5 to 8.0 by sodium phosphate buffer solution (0.2 M, Merck, Germany).

## 2.2. Characterization

The MOF was characterized by scanning electron microscope (FESEM) (SIGMA VP) and transmission electron microscope TEM (EM10C) microscopes from Zeiss Company. X-ray diffraction (XRD) spectrum were prepared by a Seifert TT 3000 diffractometer (Germany) using wavelength 0.15 nm. The Fourier transform infrared spectrophotometer (FTIR, IFS 88, Bruker Optik GmbH, Germany) was used in the 200-4000  $cm^{-1}$ . Determination of nickel was performed with ET-AAS.

## 2.3. Synthesis of MOF

The  $Zn_2(BDC)_2(DABCO)$  MOF was prepared via the self-assembly of  $Zn^{2+}$  ion as a connector, DABCO as a bridging ligand, and BDC as a chelating ligand. In a typical reaction, Zn (OAc) $_2$ ·2H $_2$ O (0.132 g, 2 mmol), BDC (0.1 g, 2 mmol), and DABCO (0.035 g, 1 mmol) were added to 25 ml DMF [4]. The reactants were sealed under reflux and stirred at 90 °C for 15 min. Then, the reaction mixture was cooled to room temperature, and filtered. The white crystals were washed with DMF to remove any metal and

ligand remained, and dried in a vacuum. DMF was removed from white crystals with a vacuum furnace at 150 °C for 5 h.

## 2.4. General procedure of nickel adsorption

By proposed method, the  $Zn_2(BDC)_2(DABCO)$  as metal–organic framework (MOF) was used for extraction of toxic nickel ions ( $Ni^{2+}$ ) from water samples by USA-D- $\mu$ -SPE procedure (Fig.1). Firstly, 25 mg of  $Zn_2(BDC)_2(DABCO)$  adsorbent added to 25 mL of water samples included Ni standard solution and Ni ions chemically adsorbed based on dative bonding of nitrogen groups in DABCO material after shaking for 10 min at pH=8. Secondly, the  $Zn_2(BDC)_2(DABCO)$  adsorbent separated from water samples by SCAF (10 mL, 0.2  $\mu$ m) and then the Ni loaded on the MOF was back-extracted from solid-phase based on changing pH by nitric acid solution (0.2 M, 0.25 mL). After dilution, the remained solution was determined by ET-AAS after dilution with DW up to 0.5 mL. Also, the adsorptions of the  $Zn_2(BDC)_2(DABCO)$  adsorbent were evaluated in different pH by USA-D- $\mu$ -SPE procedure and capacities adsorption was obtained. The proposed procedure was used for a blank solution without any analyte (Ni) for 10 times. The calibration curve for nickel in was prepared from LLOQ to ULOQ ranges (0.1-2.88  $\mu$ g L $^{-1}$ ) and the PF obtained by the curve-fitting rule.

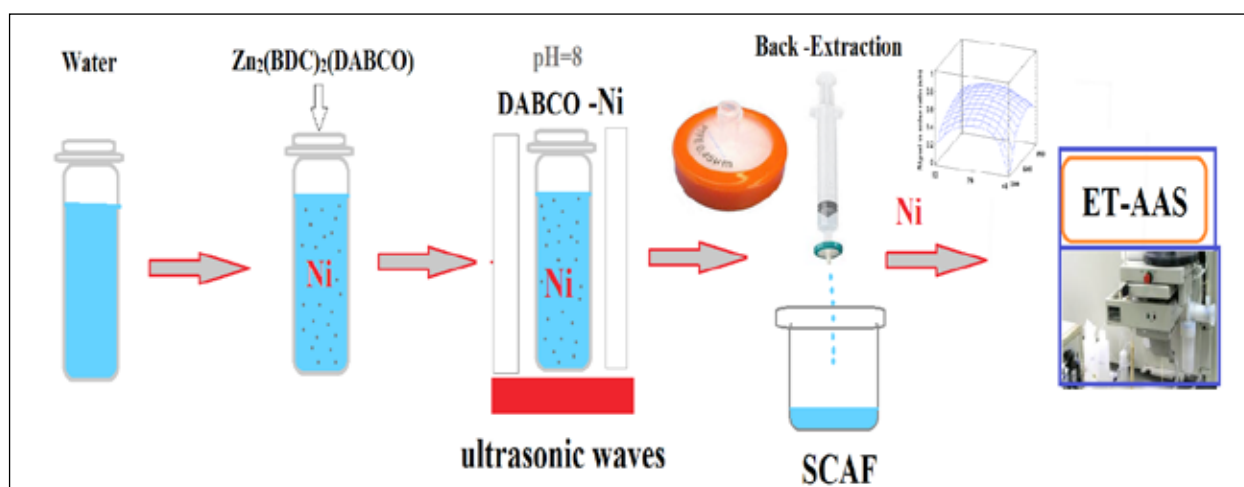
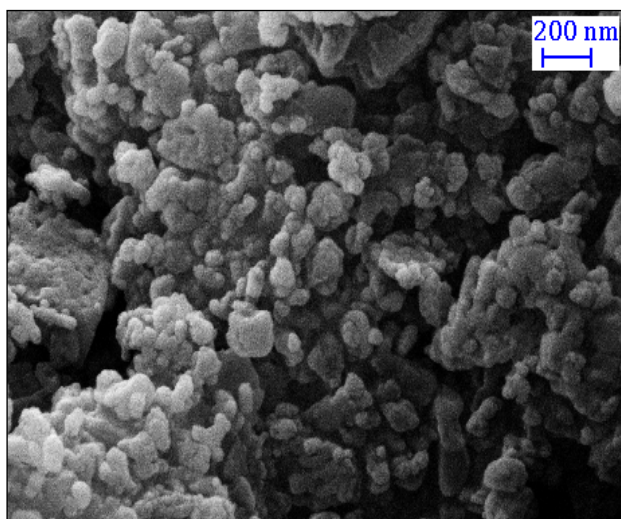
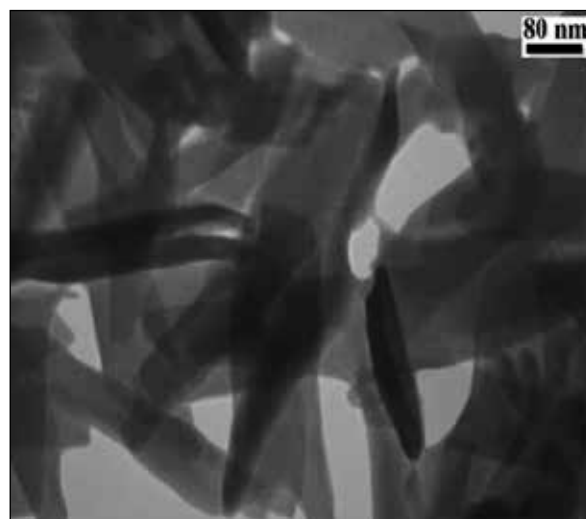


Fig. 1. Extraction procedure for nickel ions in water by  $Zn_2(BDC)_2(DABCO)$  adsorbent



**Fig. 2a.** FESEM of  $Zn_2(BDC)_2(DABCO)$  MOF



**Fig. 2b.** TEM of  $Zn_2(BDC)_2(DABCO)$  MOF

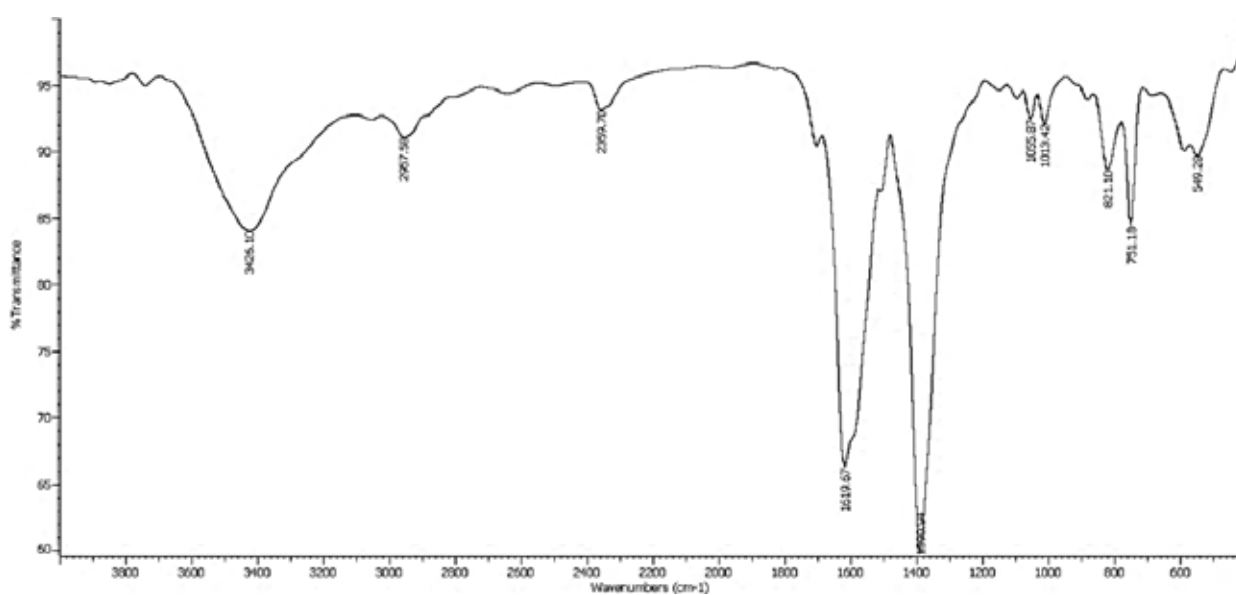
### 3. Results and Discussion

#### 3.1. FE-SEM and TEM

Field emission scanning electron microscope (FE-SEM) was used for evaluation of morphology of MOF [ $Zn_2(BDC)_2(DABCO)$ ] with an average diameter of 100 nm (**Fig. 2a**). Transmission electron microscope (TEM) was used for evaluation of nanoparticles size and morphology of the MOF. TEM showed the pore shape and size, the pore has rod-shaped with many pore with different sizes from 20-80 nm (**Fig. 2b**).

#### 3.2. FTIR of $Zn_2(BDC)_2(DABCO)$ MOF

The organic material and functional groups such as NH, CO, SH in different adsorbents were identified by FTIR analysis. The FTIR spectrum of  $Zn_2(BDC)_2(DABCO)$  MOF was obtained after calcination in KBr matrix (250 °C). As results, there is no peak based on impurities and and it confirm the completion of the synthesis. Also, various peaks were presented such as 705  $cm^{-1}$  and 1000  $cm^{-1}$  for ZnO bonds, 3000  $cm^{-1}$  - 3500  $cm^{-1}$  for OH of carboxylic acid, 1600  $cm^{-1}$  for CO stretching



**Fig. 3.** FTIR spectrum of the  $Zn_2(BDC)_2(DABCO)$  MOF.

bond and  $1440\text{ cm}^{-1}$ ,  $1358\text{ cm}^{-1}$ ,  $1429\text{ cm}^{-1}$  and  $1550\text{ cm}^{-1}$  for aromatic compounds (Fig.3).

### 3.3. XRD of $Zn_2(BDC)_2(DABCO)$ MOF

By application of XRD technique, the essential information can obtain based on crystal structure and product purity by XRD analysis. The XRD pattern for the  $Zn_2(BDC)_2(DABCO)$  MOF was shown in Figure 4. By results, all peaks are clear. In addition, the XRD pattern for the  $Zn_2(BDC)_2(DABCO)$  has no peak belong to impurities. The crystal structure of the  $Zn_2(BDC)_2(DABCO)$  confirm by sharp peaks of XRD pattern. The size of the  $Zn_2(BDC)_2(DABCO)$  MOF was achieved about 45 nm by Debye-Scherrer equation.

### 3.4. The pH optimization

The pH is the effective factor on adsorption and extraction of nickel ions by USA-D- $\mu$ -SPE procedure. So, the different pH between 2-10 was studied for extraction of Ni (II) in water and wastewater samples. The experimental results showed us, the  $Zn_2(BDC)_2(DABCO)$

MOF was simply extracted Ni (II) ions from water samples in a pH 7.5-8.5. Moreover, the extraction efficiency was achieved about 98.7% in pH of 8 but, the recoveries were reduced at acidic pH less than 7 and basic pH more than 9.0. So, the optimum pH of 8 was used for further works in this study. The extraction mechanism of nickel ions in water samples based on  $Zn_2(BDC)_2(DABCO)$  MOF take place by the coordination of dative covalent bond of N group as negative charge with the positively charged Ni ions ( $Ni \rightarrow :N$ ) at pH=8. At lower pH ( $pH < pK_{pzc}$ ), the surface of  $Zn_2(BDC)_2(DABCO)$  MOF have positively charged and extraction efficiency decreased as repulsion. Also, the surface of  $Zn_2(BDC)_2(DABCO)$  MOF have negatively charged at pH=8 and so the negative charge between nitrogen group and  $Ni^{2+}$  caused to increased recovery. At pH more than 8, the Ni ions started to participate ( $Ni(OH)_2$ ) and so, the recovery decreased (Fig. 5). The best pH for physical adsorption was achieved at pH between 3-4 with the mean recovery of 34.6%.

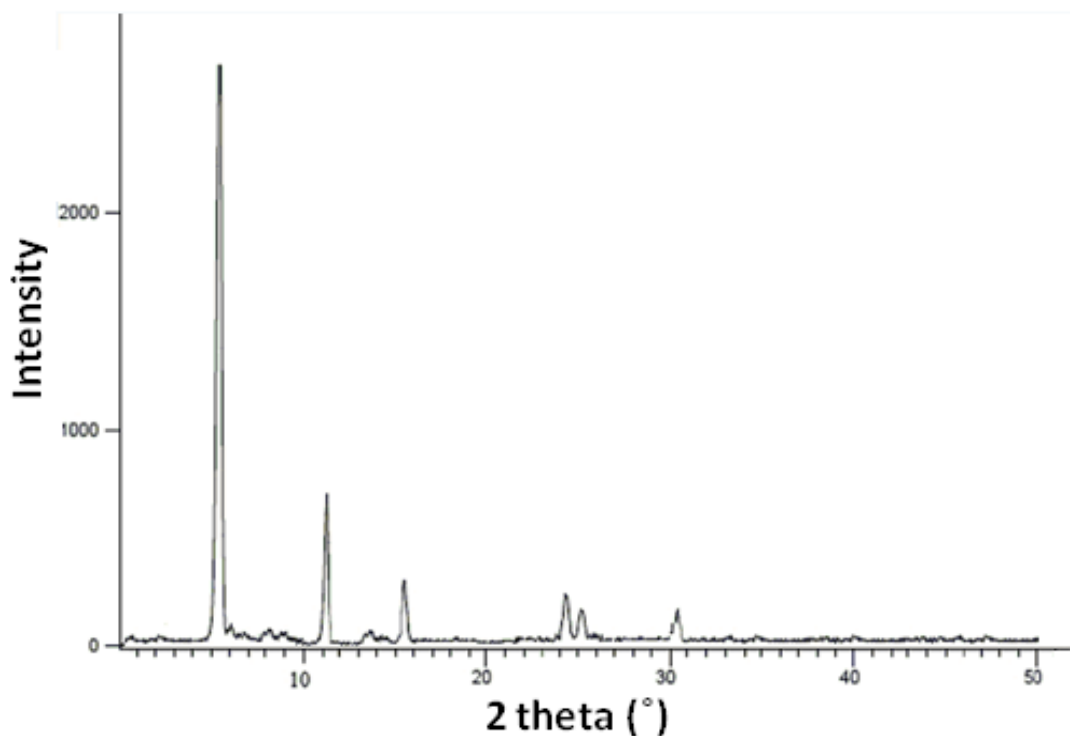
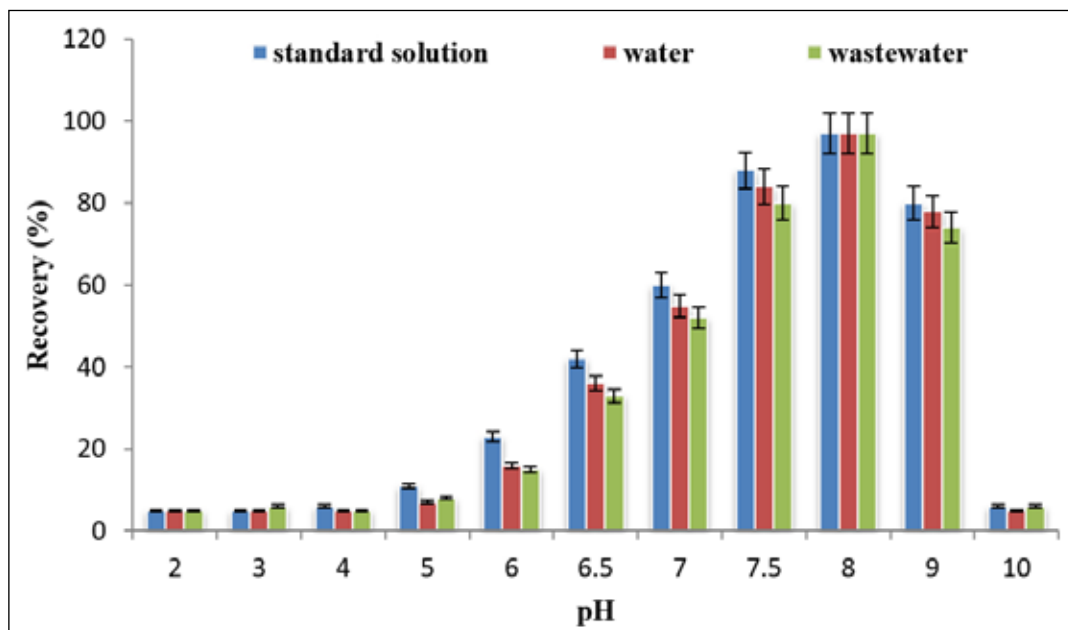


Fig.4. XRD pattern of the synthesized  $Zn_2(BDC)_2(DABCO)$  MOF

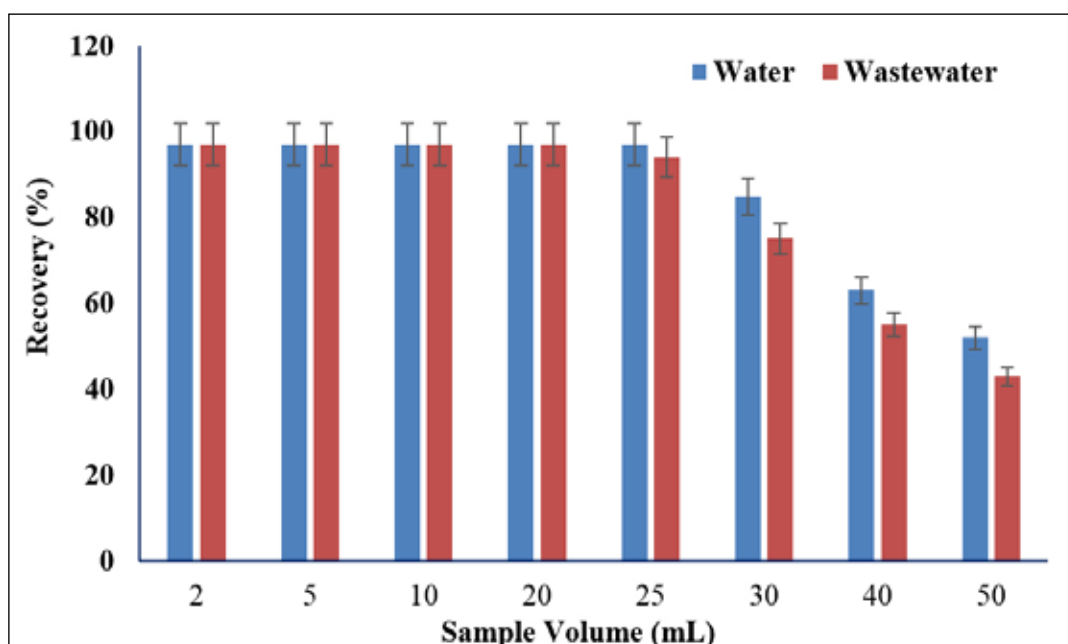


**Fig. 5.** The effect of pH on nickel extraction in water samples based on  $Zn_2(BDC)_2(DABCO)$  MOF by USA-D- $\mu$ -SPE procedure

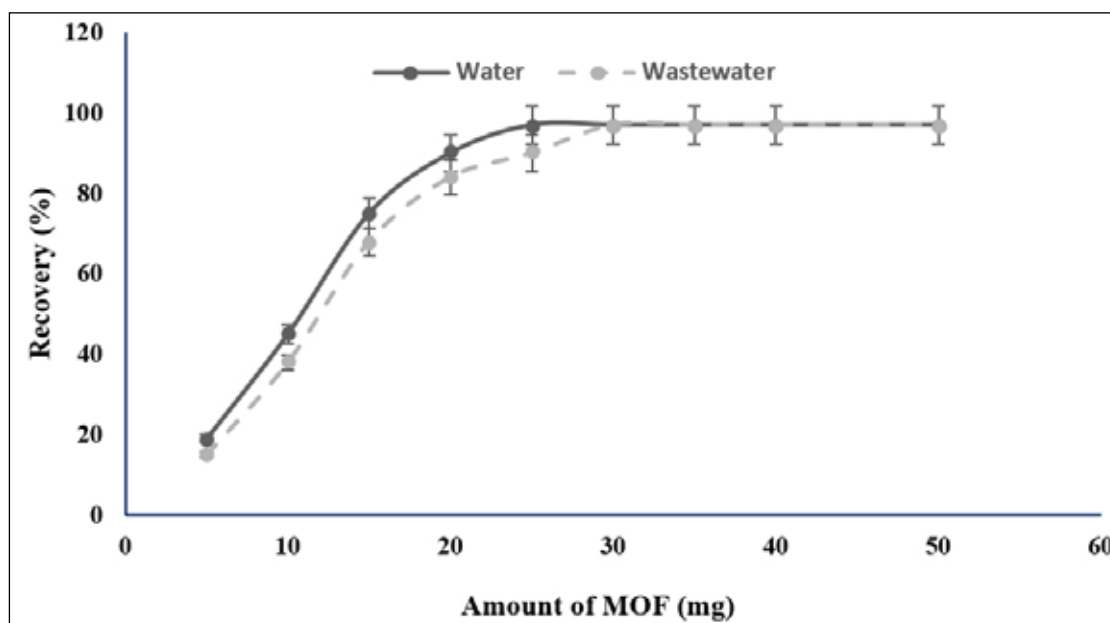
### 3.5. The effect of sample volume

The influence of sample volume for Ni extraction based on  $Zn_2(BDC)_2(DABCO)$  MOF was studied between 5-50 mL in water and wastewater samples with LLOQ and ULLOQ ranges ( $0.1-2.88 \mu\text{g L}^{-1}$ ). The results showed us the high recoveries were

achieved for 25 mL of water samples and wastewater samples. So, 25 mL of sample was selected as optimum volume for nickel extraction in water and wastewater samples at pH=8. By increasing the sample volume more than 25 mL, the extraction recoveries were reduced between 43-52% (**Fig. 6**).



**Fig. 6.** The effect of sample volume on nickel extraction in water samples based on  $Zn_2(BDC)_2(DABCO)$  MOF by USA-D- $\mu$ -SPE procedure



**Fig. 7.** The effect of MOF mass for nickel extraction in water samples based on  $Zn_2(BDC)_2(DABCO)$  MOF by USA-D- $\mu$ -SPE procedure

### 3.6. The effect of $Zn_2(BDC)_2(DABCO)$ MOF

For efficient recovery, the amount of  $Zn_2(BDC)_2(DABCO)$  MOF must be evaluated and optimized. Therefore, the amounts of  $Zn_2(BDC)_2(DABCO)$  MOF between 5-50 mg were examined for Ni(II) adsorption/extraction by the USA-D- $\mu$ -SPE procedure. The results showed that the quantitative recoveries in water samples were obtained with 22 mg of  $Zn_2(BDC)_2(DABCO)$  MOF for nickel extraction at pH=8. So, 25 mg of  $Zn_2(BDC)_2(DABCO)$  MOF was used as optimum of MOF mass for further process (Fig. 7). The results showed us the extra dosage of MOF had no effect on the extraction value in water samples.

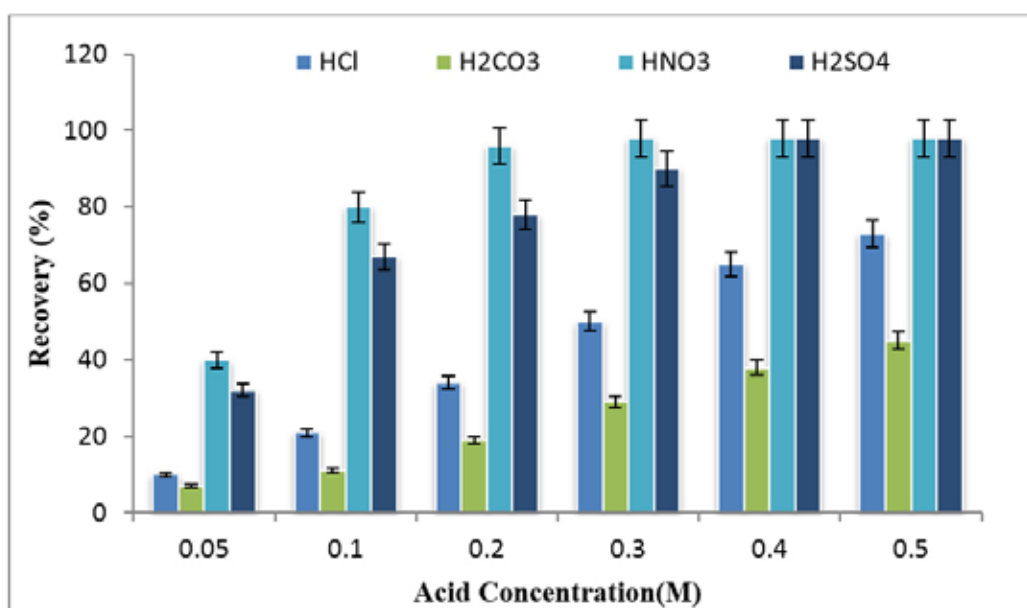
### 3.7. The effect of eluent

The eluents with different volume and concentration was used for back-extraction of nickel ions from  $Zn_2(BDC)_2(DABCO)$  MOF. Acidic pH cause to breakdown the dative bond between nitrogen group in MOF and nickel ions (MOF-N: ..... Ni) and then, the Ni (II) ions release into the eluent phase. Therefore, a different volume of acid solution such as HCl,  $HNO_3$ ,  $H_2SO_4$  and  $H_2CO_3$  with various concentration was examined for back extraction

Ni(II) in water samples ( $0.1-1 \text{ mol L}^{-1}$ ,  $0.1-0.5 \text{ mL}$ ) by syringe cellulose acetate filters (SCAF,  $0.2 \mu\text{m}$ ). The results showed that  $0.2 \text{ mol L}^{-1}$   $HNO_3$  as elution phase can efficient released the Ni (II) ions from  $Zn_2(BDC)_2(DABCO)$  MOF to liquid phase. So,  $0.2 \text{ mol L}^{-1}$  of  $HNO_3$  ( $0.1 \text{ mL}$ ) was selected as the optimum concentration and volume of  $HNO_3$  eluent in this study. As a result, the elution of solid phase ( $Zn_2(BDC)_2(DABCO)$  MOF) with nitric acid ( $0.2 \text{ M}$ ,  $0.1 \text{ mL}$ ) was simply back extracted nickel ions from MOF (Fig.8).

### 3.8. Validation

By USA-D- $\mu$ -SPE procedure, the nickel extraction based on  $Zn_2(BDC)_2(DABCO)$  MOF was obtained in water and wastewater samples. The experimental results showed a validated data for Ni (II) in tab water, drinking water, river water and wastewater samples at pH=8 (Table 1). The accuracy of the data were confirmed by spiking of nickel standard solution to water samples based on  $Zn_2(BDC)_2(DABCO)$  MOF adsorbent. Due to results the efficient recovery for extraction Ni ions in wastewater and water samples was achieved by nanoparticles of  $Zn_2(BDC)_2(DABCO)$  MOF.



**Fig. 8.** The effect of eluents on nickel extraction based on  $Zn_2(BDC)_2(DABCO)$  MOF

The perfect extraction demonstrated that the USA-D- $\mu$ -SPE technique had satisfactory results for nickel in real samples at pH=8. In addition,

the standard reference materials (SRM) were used for validating of DIL-S- $\mu$ -SPE procedure (**Table 2**).

**Table 1.** Validation of methodology for nickel extraction and determination in water samples by spiking of samples by USA-D- $\mu$ -SPE procedure coupled to ET-AAS

Sample	Added ( $\mu\text{g L}^{-1}$ )	*Found ( $\mu\text{g L}^{-1}$ )	Recovery (%)
Tab Water	---	$0.454 \pm 0.022$	---
	0.5	$0.948 \pm 0.045$	98.80
Drinking Water	---	$1.641 \pm 0.072$	---
	1.5	$3.103 \pm 0.147$	97.46
<sup>a</sup> Wastewater	---	$1.723 \pm 0.084$	---
	1.0	$2.745 \pm 0.133$	102.22
Well water	---	$0.832 \pm 0.042$	---
	0.5	$1.311 \pm 0.058$	95.81
River water	---	$1.074 \pm 0.053$	---
	1.0	$2.108 \pm 0.105$	103.42
<sup>b</sup> Sea Water	---	$1.824 \pm 0.092$	---
	1.0	$2.787 \pm 0.128$	96.30

\*Mean of three determinations of samples  $\pm$  confidence interval (P = 0.95, n = 10)

<sup>a</sup> wastewater dilution with DW (1:10)

<sup>b</sup> Sea water dilution with DW (1:5)



**Table 2.** Determination of nickel in water samples based on Zn<sub>2</sub>(BDC)<sub>2</sub>(DABCO) MOF by standard reference materials (SRM)

Sample	Added ( $\mu\text{g L}^{-1}$ )	SRM Value ( $\mu\text{g L}^{-1}$ )	*Found ( $\mu\text{g L}^{-1}$ )	Recovery(%)
<sup>a</sup> 1643f	-----	1.5	1.49 $\pm$ 0.06	-----
	1.5	-----	2.91 $\pm$ 0.13	94.6
<sup>a</sup> 1643e	-----	1.5	1.59 $\pm$ 0.07	-----
	1.5	-----	3.15 $\pm$ 0.15	104.1
<sup>a</sup> 1640a	-----	0.6	0.63 $\pm$ 0.03	-----
	0.5	-----	1.12 $\pm$ 0.05	98.0
<sup>b</sup> 3136	-----	1.0	1.02 $\pm$ 0.05	-----
	1.0	-----	1.98 $\pm$ 0.08	96.0

\* Mean of three determinations of samples  $\pm$  SD (P = 0.95, n = 10)

<sup>a</sup> Standard Reference Material 1643f (1.50), 1643e (1.50) and 1640a (0.6), trace elements in water, after dilution with DW (1:40)

<sup>b</sup> NIST, SRM 3136, Sigma, after dilution with DW the concentration of 1.0  $\mu\text{g L}^{-1}$  daily prepared

### 3.9. Comparing with other methods

The USA-D- $\mu$ -SPE procedure was compared to other published articles for extraction and determination of Ni ions in water samples (Table 3). Due to table 3, the different methodology and adsorbents compared for nickel extraction in water samples. Many parameters such as LOD,

PF, RSD%, sample volume, capacity adsorption and etc. compared together. The results showed us, the USA-D- $\mu$ -SPE procedure was comparable to other presented works in Table 3. Therefore, the Zn<sub>2</sub>(BDC)<sub>2</sub>(DABCO) MOF with favorite properties can be used for extraction of nickel in water samples in optimized conditions.

**Table 3.** Comparing of USA-D- $\mu$ -SPE procedure with other published method for nickel extraction in different matrixes

Methods	Instrument	Metal	Matrix	LOD( $\mu\text{g L}^{-1}$ )	EF/PF	%RSD	Ref
SPE	F-AAS	Ni/Cu	Water and biological samples	0.6	200	3.1	[31]
IIPSPE	UV-VIS	NI	Water	1.0	125	2.4	[32]
SPE	F-AAS	Ni, Ca, Co, Cu	Tea, Water	1.0	10	2.0	[33]
ISSADSPE	F-AAS	Ni	Water	0.7	50	2.5	[34]
NH-IS-SPE	$\mu$ S-FAAS	Ni,Cr,Co	Water and Food	2.74	205	3.5	[35]
SPE	ICP-OES	Ni	Water	0.025	80	2.6	[36]
PPT-SPE	F-AAS	Ni	Water	2.7	120	4.4	[37]
USA-D- $\mu$ -SPE	ET-AAS	Ni	Water	0.03	48.7	1.26	This week

SPE: solid phase extraction

IIPSPE: Ion imprinted polymer- solid phase extraction

ISSADSPE: In-syringe solvent-assisted dispersive solid phase extraction

NH-IS-SPE: Needle hub in-syringe solid phase extraction

$\mu$ S-FAAS: micro-sampling flame atomic absorption spectrometry

PPT-SPE: Pipette tip Solid phase extraction

#### 4. Conclusions

In this study, the  $Zn_2(BDC)_2(DABCO)$  MOF adsorbent was synthesized by solvothermal method at 90 °C via the self-assembly metal centers and linkers using DMF solvent. Based on the results, the MOF was propped as a good candidate for nickel adsorption/extraction from water samples by USA-D- $\mu$ -SPE procedure at pH=8. The syringe cellulose acetate filters (SCAF, 0.2  $\mu$ m) was used for separation of  $Zn_2(BDC)_2(DABCO)$  MOF from liquid phase and back-extraction of Ni ions from adsorbent before determined by ET-AAS. The  $Zn_2(BDC)_2(DABCO)$  MOF had the high recovery between 94.6-104.1 for Ni extraction from water samples. The proposed USA-D- $\mu$ -SPE method had low LOD and RSD% with good reusability about 21 times for water samples. Therefore, the  $Zn_2(BDC)_2(DABCO)$  MOF caused to create the efficient extraction of Ni ions in water samples based on chemical adsorption. The nickel concentration in remain solution has simply determined by ET-AAS after back-extraction and dilution with DW.

#### 5. Acknowledgement

The authors wish to thank from Department of Medical Nanotechnology, Tehran Medical Sciences, Islamic Azad University (IAUMS), Iranian Research Institute of Petroleum Industry (RIPI) and Iranian Petroleum Industry Health Research Institute (IPIHRI) for supporting this work.

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