



# Zirconium-based highly porous metal-organic framework (MOF-545) as an efficient adsorbent for vortex assisted-solid phase extraction of lead from cereal, beverage and water samples



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## ABSTRACT

In this study, zirconium-based highly porous metal-organic framework, MOF-545, was synthesized and characterized. The surface area of MOF-545 was found to be 2192 m<sup>2</sup>/g. This adsorbent was used for the first time as an adsorbent for the vortex assisted-solid phase extraction of Pb(II) from cereal, beverage and water samples. Lead in solutions was determined by FAAS. The optimal experimental conditions were as follows: the amount of MOF-545, 10 mg; pH of sample, 7; adsorption and elution time, 15 min; and elution solvent, 2 mL of 1 mol L<sup>-1</sup> HCl. Under the optimal conditions of the method, the limit of detection, preconcentration factor and precision as RSD% were found to be 1.78 µg L<sup>-1</sup>, 125 and 2.6%, respectively. The adsorption capacity of the adsorbent for lead was found to be 73 mg g<sup>-1</sup>. The method was successfully verified by analyzing two certified reference materials (BCR-482 Lichen and SPS-WW1 Batch 114) and spiked chickpea, bean, wheat, lentil, cherry juice, mineral water, well water and wastewater samples.

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## 1. Introduction

Toxic elements are usually present at low concentrations in environmental samples with a complex matrix and the analytes cannot be accurately detected. Therefore, pre-treatment techniques prior to instrumental analysis are imperative to improve sensitivity and effectively eliminate matrix interferences from the samples. Lead is one of the most toxic elements for humans, animals and plants. It has an accumulative effect causing serious hematologic, brain and kidney malfunction problems. Furthermore it is nonbiodegradable (Maratta, Vázquez, López, Augusto, & Pacheco, 2016; Mehdinia, Shoormeij, & Jabbari, 2017) and the consumption of food with high concentrations of this element can produce problems for human health. Therefore, it is very important to accurately determine trace lead concentrations found in environmental and food samples. The maximum tolerable concentration limits of lead in fruit juices and cereals are 0.05 mg kg<sup>-1</sup> and 0.2 mg kg<sup>-1</sup>, respectively (Codex Alimentarius, 1995). For lead, the Environmental Protection Agency (EPA, 2017) describes the Criteria Maximum Concentration of 65 and 210 µg L<sup>-1</sup> for fresh and salt waters, respectively. World Health Organization (WHO,

2004) establishes a recommended limit of 10 µg L<sup>-1</sup> in drinking water. Compared with other pre-treatment techniques, solid phase extraction (SPE) is one of the most widely used sample pre-treatment techniques due to its high recovery, high enrichment factor, low consumption of organic solvents, and ease of automation and operation (Yavuz, Tokalioğlu, Şahan, Berberoğlu, & Patat, 2017; Tokalioğlu & Livkebabcı, 2009; Ma et al., 2016). The sorbent material plays a key role in SPE. It is very important for achieving high enrichment efficiency and high adsorption capacity. Moreover, the nature of the sorbent determines the selectivity of the extraction method (Liu et al., 2017; Tokalioğlu et al., 2016). Novel sorbents have been fabricated to enhance the performance of the SPE technique. Many novel nanomaterials, such as graphene (Wang, Gao, Zang, Li, & Ma, 2012; Yavuz, Tokalioğlu, Şahan, & Patat, 2013a; Sitko, Zawisza, & Malicka, 2013; Wang, Liu, Lu, & Qu, 2014), ionic liquid coated carbon nanospheres (Tokalioğlu et al., 2016), metal oxide nanoparticles (Yavuz, Tokalioğlu, Şahan, & Patat, 2013b; Yavuz, Tokalioğlu, Şahan, & Patat, 2016; Suleiman, Hu, Pu, Huang, & Jiang, 2007; Xu, Wu, Ye, Yuan, & Feng, 2016), and metal-organic frameworks (MOFs) (Ahmed & Jhung, 2017; Khan & Jhung, 2017) have been used as sorbent in extraction.

One of the most promising types of materials that have been developed in the last few years is MOFs. Recently, MOFs have

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attracted growing interest in the fields of adsorption and separation due to their ultra high porosity, enormous surface areas and tunable pore size (Jia et al., 2016). MOFs are comparable to traditional porous materials because of their large internal surface areas, extensive porosity, and high degree of crystallinity. They are hybrid materials whose inorganic-organic frameworks consist of two major components: a metal ion or cluster of metal ions and an organic chelating linker connecting two metal components (Ahmed & Jung, 2017). MOFs have been considered in different research areas, including energy applications, drug delivery/biomedicine, adsorption/storage in gas and liquid phases, for the separation of chemicals, catalysis, sensing and explosive detection, polymerization, magnetism and luminescence (Furukawa, Cordova, O’Keeffe, & Yaghi, 2013; Demir, Usta, Tamar, & Ulusoy, 2017).

In the last few years, different kinds of MOFs have been used for the removal of heavy metal ions due to their high porosity and ultrahigh specific surface areas, for instance, UiO-66 (Zr)-2COOH for the selective removal of  $\text{Cu}^{2+}$  over  $\text{Ni}^{2+}$  from aqueous solution (Zhang et al., 2015); phenyl bromine-appended MOFs (Br-MOFs) for elemental mercury ( $\text{Hg}^0$ ) removal from simulated flue gas (Zhang, Shen, Zhu, Xu, & Tian, 2016); a Zr-based MOF (UiO-66) sensor for the visual detection and removal of ultra-traces of some toxic metal ions such as Bi(III), Zn(II), Pb(II), Hg(II) and Cd(II) in aquatic samples (Shahat, Hassan, & Azzazy, 2013); the determination of trace levels of lead based on magnetic solid-phase extraction with a dithizone functionalized magnetic MOF( $\text{Fe}_3\text{O}_4/\text{Cu}_3(\text{BTC})_2\text{-H}_2\text{Dz}$ ) (Wang, Xie, Wu, Ge, & Hu, 2013); selective and sensitive detection of  $\text{Fe}^{3+}$  with a three-dimensional Tb-BTB framework as a luminescent sensor (Xu, Hu, Cao, & Zhao, 2015); determination of mercury from tea and mushrooms with a MOF based on copper (JUC-62) (Wu et al., 2016); TMU-16- $\text{NH}_2$  MOF as a new sorbent for the removal of Cd(II) ions from water samples (Roushani, Saedi, & Baghelani, 2017); and electrochemical detection in tap water samples of cadmium with two isorecticular nanoporous Zn(II)-MOFs (Roushani, Valipour, & Saedi, 2016). There are few studies for the preconcentration by solid phase extraction of heavy metal ions from samples using MOF as an adsorbent.

Zirconium-based MOFs (Zr-MOFs) exhibit relatively high chemical, thermal and mechanical stability which is a requisite for practical applications. Their stability is attributable to the oxophilic nature of the  $\text{Zr}_6$  clusters and coulombic attraction between these cationic Zr clusters and anionic linkers (Ahn et al., 2016). The MOF-545,  $[\text{Zr}_6\text{O}_8(\text{H}_2\text{O})_8(\text{TCPP-H}_2)_2]_n$  used in this study consists of octahedral  $\text{Zr}_6\text{O}_8(\text{CO}_2)_8(\text{H}_2\text{O})_8$  building units and porphyrine tetracarboxylates (Tcpp- $\text{H}_2$ ) formed via deprotonation of tetrakis (4-carboxyphenyl) porphyrin ( $\text{H}_4\text{-Tcpp-H}_2$ , aka known meso-tetra phenylporphine-4,4',4'',4'''-tetracarboxylic acid). We chose MOF-545 as an adsorbent because it has high thermal and chemical stability and has micro- and mesopores which facilitate the diffusion of analytes. To the best of our knowledge, there is no information in the literature about the use of MOF-545 as SPE adsorbent for the preconcentration of lead from cereal, beverage and water samples.

The aim of this study is to determine the effectiveness of the synthesized Zr-based MOF-545 as an adsorbent in SPE to preconcentrate lead from cereal, beverage and tap water samples. The MOF-545 was characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), Brunauer, Emmett and Teller (BET) surface area and zeta potential measurements. Lead determination was made by flame atomic absorption spectrometry (FAAS). The properties of the MOF-545 as an adsorbent for high SPE efficiency and the parameters affecting the recovery values of Pb(II) were investigated. Factors such as sample pH, adsorption and elution contact times, eluent type and concentration, sample volume,

amount of MOF-545, adsorption capacity, and interfering ion effects were studied in detail.

## 2. Experimental

### 2.1. Reagents and materials

All reagents were of analytical grade. Starting materials (zirconyl chloride octahydrate, Sigma-Aldrich; porphyrin,  $\text{H}_4\text{-Tcpp-H}_2$ , TCI) and solvents (Merck) were purchased and used without further purification. Ultra high purity water (UHP, 18.2 M $\Omega$  cm) obtained from a Milli-Q system (Millipore Corp., Bedford, MA, USA) was used to prepare all solutions. Standard solution of Pb(II) ions was prepared by diluting a stock solution of 1000 mg L $^{-1}$ . A phosphate buffer solution ( $\text{H}_3\text{PO}_4/\text{NaH}_2\text{PO}_4$ ) for pH 2 and 3, acetate buffer solution ( $\text{CH}_3\text{COOH}/\text{CH}_3\text{COONa}$ ) for pH 4–6.5, ammonium acetate solution ( $\text{CH}_3\text{COONH}_4$ ) for pH 7 and 7.5 and ammonia buffer solution ( $\text{NH}_3/\text{NH}_4\text{Cl}$ ) for pH 8 and 9 were used in the pH experiments.

### 2.2. Instrumentation

The CHN contents were determined with a LECO TruSpec Micro CHNS analyzer. Powder X-ray diffraction (PXRD) data were collected on a Rigaku/SmartLab diffractometer operated at 3000 W power (40 kV, 30 mA) using Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) and a  $2\theta$  range of 3 to 50°.  $\text{N}_2$  adsorption isotherms were measured using a Quantachrome NOVA 4200e instrument at 77 K. To determine the BET specific surface area ( $\text{m}^2/\text{g}$ ), ~100 mg of the MOF-545 sample was evacuated on a Quantachrome FloVac degasser under vacuum for 18 h at 120 °C. The BET specific surface area was calculated using the BET equation from the adsorption isotherm. Scanning electron microscopy (SEM) images of the samples were taken with a JEOL JSM-6610 (20 kV accelerating voltage under vacuum). The zeta potential of the MOF-545 suspension was measured with a Malvern Instruments Zetasizer Nano system (England) in water. A Perkin Elmer AAnalyst 800 model flame atomic absorption spectrometer with deuterium lamp for background correction (Waltham, MA, USA) was used to determine lead. For the measurements, the lead hollow cathode lamp was operated at 10 mA. The wavelength was set at 283.3 nm with a spectral band width of 0.7 nm. All measurements were carried out in an air/acetylene flame (2.0/17.0 L min $^{-1}$ ). A Sartorius PT-10 model (Göttingen, Germany) pH-meter was used for pH adjustments. An Annita ALC PK120 model centrifuge (Buckinghamshire, England) and a vortex stirrer (Wiggen Hauser, Malaysia) were used to centrifuge and stir the solutions.

### 2.3. Synthesis of MOF-545

The MOF-545,  $[(\text{Zr}_6(\text{H}_2\text{O})_8\text{O}_8(\text{C}_{48}\text{N}_4\text{O}_8\text{H}_{26})_2)]$  was prepared by following the published protocol (Morris et al., 2012). Briefly, zirconyl chloride octahydrate (37.5 mg, 0.111 mmol) and  $\text{H}_4\text{-Tcpp-H}_2$  (6.5 mg, 0.037 mmol) (5 mL) were dissolved in dimethylformamide (DMF) by sonication. The  $\text{H}_4\text{-Tcpp-H}_2$  solution was then added to the Zr solution. After two minutes of sonication, formic acid (7 mL) was added to the solution. The solution was heated at 120 °C for six days in a 20 mL scintillation vial. The crystals were collected by filtration and washed with DMF ( $3 \times 10 \text{ mL}$ ) and the DMF was then replaced with acetone ( $3 \times 20 \text{ mL}$ ) over a three-day period. Finally, the acetone was removed by heating at 120 °C under vacuum for 18 h.  $[(\text{Zr}_6(\text{H}_2\text{O})_8\text{O}_8(\text{C}_{48}\text{N}_4\text{O}_8\text{H}_{26})_2)] = 2393 \text{ g/mol}$ ; composition (%): C 48.0 (48.2); H 2.77 (2.86); N 4.41 (4.68). Before use as an adsorbent, it was washed with UHP water,

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