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# Adsorption and determination of Lead in water and human urine samples based on $Zn_2(BDC)_2(DABCO)$ MOF as polycaprolactone nanocomposite by suspension micro solid phase extraction coupled to UV–Vis spectroscopy

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## **ABSTRACT**

Today, the safety of water resource is the most important challenges which was reported by health and environment organizations. Water pollution can be created by hazardous contaminants of environmental pollutions. Lead as a heavy metal has carcinogenic effects in humans. Metal organic framework (MOF) is a highly porous material with different application. The  $Zn_{2}(BDC)_{2}(DABCO)$ is a good candidate of MOF based on zinc metal (Zn-MOF) with potential adsorption/extraction. In this work, Zn<sub>2</sub>(BDC)<sub>2</sub>(DABCO) MOF as polycaprolactone (PCL) nanocomposite were applied for lead adsorption/extraction from 50 mL of aqueous solution by ultraassisted dispersive suspension-micro-solid phase extraction procedure (USA-S-  $\mu$ -SPE) at pH=8. The samples were characterized by the FTIR, the XRD analysis, the FE-SEM and the BET surface area. The effect of parameters was investigated on lead absorption before determined by UV-Vis spectroscopy. The linear range, the detection limit (LOD) and enrichment factor of adsorbent were obtained 0.05-1 mg L<sup>-1</sup>, 0.25  $\mu$ g L<sup>-1</sup> and 48.7, respectively (r = 0.9992, RSD%=3.65). The absorption capacity of Zn,(BDC),(DABCO) MOF for 50 mg L<sup>-1</sup> of standard lead solution were obtained 133.8 mg g-1 for 0.25 g of adsorbent. The results indicate that this nanocomposite can have a good potential to develop different adsorbents.

# 1. Introduction

Heavy metals are considered one of the major pollutants with harmful effects on the environment and living organisms [1]. Lead is one of heavy metals with many industry applications. Lead element is a very strong poison and major environmental health problem. This non-biodegradable pollutant can be

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caused detrimental effects on human health [2]. The world health organization (WHO) has identified lead as a hazardous material that needed to protect the health of workers, children and women of childbearing age. Threshold limit value (TLV) is the weighted average concentration of the risk factor in the atmosphere [1-3]. According to the results of workers in battery storage plants, TLV (working day of eight hours) was obtained about 0.1 mg m<sup>-3</sup> and normal lead concentration in urine of workers was less than 50  $\mu$ g L<sup>-1</sup>. The US Environmental

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Protection Agency (EPA) has reported 5-100  $\mu$ g L<sup>-1</sup> as a reference value in bottle and drinking water [3]. The lead effects on human health and causes the different diseases in humans such as, CNS defect, the nerve system damage, the renal/liver/bone dysfunction. The organic lead compound such as Triethyl and methyl lead with the Pb(II) as inorganic lead are toxic for the humans [3]. Lead emitted to environment with  $(C_2H_2)_2/(CH_2)_2$ -Pb and Pb(II) forms and can be dispersed by oil/gasoline additives [4]. The organic lead is used in for industries, which can simply enter to human body by the skin and respiratory system. The organic lead with good hydrophobicity in organic solvent and foods has toxic effect in humans [5]. So, determination lead in water and human liquid samples (urine) is very important. Various methods have been developed to removal of each toxic heavy metal from water [6,7] such as the chemical precipitation [8], the ion exchange [9], the reverse osmosis [10], and the adsorbent process [11]. Recently, lead adsorbent from aqueous solution is a real challenge due to use widespread all over the world [12]. The adsorption process is the most efficient and extensive method for lead removal from wastewater [13]. The various adsorbents included, the graphene/graphene oxide [14], the nanofibers in different samples [15], the carbon nanotubes (CNTs) [16], the magnetic doped with carbon quantum dots(MDCQDs) [17], and the silica nanostructure [18] were widely used for lead extraction in water samples. Metal organic frameworks (MOFs) are a new class of porous coordination polymers with a variety of applications [19, 20]. They are formed of organic ligands as linkers and metal ions or clusters as metal centers [21, 22]. Recently, the MOFs have attracted a great attention because of unique properties [23, 24]. Zn<sub>2</sub>(BDC)<sub>2</sub>(DABCO) MOF is metal organic framework based on zinc metal (Zn-MOF) by connection of Zn<sub>4</sub>O units and 1,4-benzenedicarboxylate (BDC) and 1,4-diazabicyclo [2.2.2] octane (DABCO) ligands via self-assembly such as solution [25], solvothermal [26] and other methods. The common adsorbent compounds have expanded based on MOFs [27]. Zn<sub>2</sub>(BDC)<sub>2</sub>(DABCO) MOF was loaded with various materials such as mercury [28], the gentamicin [29], the Pd(II) [30], the methane [31], the azobenzene [32] and etc.

Easy separation of sorbent from the water is beneficial for reuse of materials and removal of heavy metals during treatment. Therefore, the adsorbents were developed based on magnetic [33-36] and polymer [33, 37] materials. Polycaprolactone is one of the most common polymers for the removal of heavy metals from aqueous solutions as hazardous, carcinogenic, and toxic pollutants. According to previous report, polycaprolactone nanofibrous were modified by clay mineral and zeolite nanoparticles for lead adsorption [38]. Also in another report, cyclodextrin-polycaprolactone titanium dioxide nanocomposites were used as a adsorbent for the removal of lead in aqueous waste samples [39]. The different techniques included, the graphite furnace coupled with atomic absorption spectrometry(GF-AAS) [40], the anodic stripping voltammetry (ASV) [41], the flame atomic absorption spectrometry (F-AAS) [42], the inductively coupled plasma atomic emission spectrometry (ICP-AES) [43] and the UV-Vis were used for lead determination in water samples. In present study, Zn<sub>2</sub>(BDC)<sub>2</sub>(DABCO) MOF/PCL nanocomposites were prepared by a simple method and lead absorption was investigated by MOF and its nanocomposites from aqueous solution at optimized pH.

#### 2. Experimental

#### 2.1. Reagents and Materials

All reagents with high purity and analytical grade were purchased from Merck (Darmstadt, Germany). Ultra-pure water was used for the preparation of all reagent's solutions. Zinc acetate ehydrate (Zn(Oac)<sub>2</sub>.2H<sub>2</sub>O, CAS N:5970-45-6, Sigma, Germany), 1,4 benzenedicarboxylic acid (CAS N: 652-36-8, Sigma), 1,4-diazabicyclo [2. 2.2] octane (CAS N: 280-57-9, Sigma), N,N-dimethylformamide anhydrous (DMF, CAS N: 68-12-2) were used for synthesis of MOF. The lead acetate salt and poly  $\varepsilon$ -Caprolactone (97%, CAS N: 502-44-3, Sigma, 1400 g mol-1, molecular weight) were applied for preparation of lead and polymer solution respectively.

#### 2.2. Sample preparations

For sampling, all glass tubes were washed with a 2.0 mol L<sup>-1</sup> HNO<sub>3</sub> solution for at least 12 h and rinsed 8 times with DW. The lead concentrations in humans have low concentration (ppb) in urine/water and even minor contamination for sampling and determination caused to effect on the accuracy of the results. By procedure, 50 mL of the urine samples were prepared from workers of batteries factories in Iran (Men, 25-55 age), based on ethical low. Clean and sterilized bottles were prepared for urine or water sampling. The water samples were prepared based on ASTM sampling and storage in 2% HNO<sub>3</sub>.

#### 2.3. MOF Synthesis

For preparation of  $Zn_2(BDC)_2(DABCO)$  MOF, Zn  $(OAc)_2.2H_2O$  (0.132 g, 2.0 mmol) to production of  $Zn^{2+}$  ions as a connector, BDC (0.1 g, 2.0 mmol) as a chelating ligand, and DABCO (0.035 g, 1.0 mmol) as a bridging ligand were added to 25 ml DMF as a solvent [28]. The reactants were sealed under reflux and stirred at 90 °C for 3 h. 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. Based on lead absorption, polycaprolactone nanocomposites cannot be prepared by solution casting method. In fact, the pores of MOF filled up with solvent and there is not any residual porosity for lead absorption. In this work, PCL nanocomposites were prepared by press method with different percentages of MOF for the first time. First, PCL polymer was dissolved in chloroform solvent under magnetic stirring. The final solution was transferred to the plate and allowed to dry. Then film surface was subjected to a hot press for 10 minutes. Finally, the certain amount of MOF powder was uniformly transferred to a cold press under the pressure on the film surface. Based on lead absorption, PCL nanocomposites with 5 and 10 percentage of MOF were shown better results and it was not possible to form a uniform nanocomposite with a higher percentage of MOF. Finally, the lead absorption was investigated in different values of lead concentrations, pH and temperature solution by MOF and its nanocomposite at different times. Figure 1 shows general procedure of Zn<sub>2</sub>(BDC)<sub>2</sub>(DABCO) MOF synthesis and lead adsorption by MOF.



Fig. 1. General procedure for Zn<sub>2</sub>(BDC)<sub>2</sub>(DABCO) MOF synthesis and lead adsorption by MOF.



Fig. 2. Extraction/Adsorption procedure based on Zn<sub>2</sub>(BDC)<sub>2</sub>(DABCO) MOF adsorbent for lead analysis

#### 2.4. Characterization

FTIR spectra were recorded on a Shimadzuir 460 spectrometer in a KBr matrix in the range of 400– 4000 cm<sup>-1</sup>. The crystalline structure of sample was investigated by X-ray diffraction utilizing Cu Kα X-ray radiation with a voltage of 40 kV and a current of 30 mA by X'pert pro diffractometer (X' Pert Pro model, Panalytical, Peru). Field emission scanning electron microscope was employed to observe morphology and size (Sigma VP model, ZEISS, Germany). The surface area was determined using nitrogen gas sorption by MOF samples at 298 K and 0.88 atmosphere pressure (BEISORP Mini model, Microtrac Bel Corp, Japan). Lead absorption was evaluated by UV–Vis spectroscopy (GENESYS 30 model, Thermo Scientific, America).

# 2.5. Extraction/Adsorption Procedure

By the USA-S-  $\mu$ -SPE method, 50 mL of urine and water samples were used for extraction and determination lead ions by Zn<sub>2</sub>(BDC)<sub>2</sub>(DABCO) MOF adsorbent. 0.25 g of Zn<sub>2</sub>(BDC)<sub>2</sub>(DABCO) MOF added to urine/water or standard solution (0.05-1 mg L<sup>-1</sup>) at pH=8. After sonication for 5.5 min, the Pb (II) ions were extracted/chemically adsorbed with the N group of the DABCO as a dative covalent bond in the optimized pH (Pb<sup>2+</sup> $\rightarrow$ : N---MOF). After centrifuging, the lead adsorbed on Zn<sub>2</sub>(BDC)<sub>2</sub>(DABCO) MOF was separated from liquid phase in the bottom of the centrifuging tube (50 mL, 5.0 min; 3500 rpm). The liquid phase was removed and the lead ions back-extracted from the  $Zn_2(BDC)_2(DABCO)$  MOF in acidic pH (HNO<sub>3</sub>, 0.2M, 0.5 mL). The remained solution determined by UV-Vis after diluted with 0.5 mL of DW (Fig. 2). The calibration curve for lead in the standards solutions was prepared based on a LLOQ and ULOQ range with (0.05-1 mg L<sup>-1</sup>) and without a preconcentration procedure (2- 50 mg L<sup>-1</sup>) and finally, the enrichment factor (EF) calculated by slop of the two calibration curves(m1/m2)..

# 3. Results and discussions

# 3.1. FTIR spectra for MOF

The FTIR absorption spectra of the samples were recorded in the range of 400-4000 cm<sup>-1</sup> with KBr pellets. FTIR spectra of MOF were presented before and after lead absorption (Fig. 3). The C-H aromatic bands are shown at 3423 cm<sup>-1</sup>. The IR bands of N–H and O-H stretching vibrations are characteristic at 3300 cm<sup>-1</sup>. The aliphatic C–H asymmetric stretching is assigned at 2958 cm<sup>-1</sup>. The O-H....O valance stretching vibration band is reported at 2600 cm<sup>-</sup> <sup>1</sup>. The high intensity peak of C=O stretching is assigned at 1635 cm<sup>-1</sup> for Zn<sub>2</sub>(BDC)<sub>2</sub>(DABCO) MOF. The bands of aromatic C=C stretching are shown at 1593 cm<sup>-1</sup>. The high intensity peak of C=O carboxylic group is specified at 1390 cm<sup>-1</sup>. The peaks of obtained results has similar to the previous report [20, 25, 26]. The bands between 800 and 500 cm<sup>-1</sup> are ascribed to Pb(II) adsorptions that according to the previous reports [44].



Fig. 3. FTIR spectra of MOF a) before and b) after lead adsorption.

# 3.2. XRD analysis

The XRD pattern of samples was measured in  $2\theta$  range 5-50° that used to identify the crystalline structure (Fig. 4). The XRD pattern of MOF is similar to a previously reported pattern [25, 28] and its crystalline structure is preserved after the

absorption based on the previous report [27]. The XRD of PCL was approved the crystalline structure according to the previous report with two characteristic peaks [45]. The high percentage of polymer in the nanocomposite was caused no observation of MOF characteristic peaks.



Fig. 4. XRD Pattern of a) MOF, b) MOF after lead adsorption,c) PCL polymer and d) MOF/PCL nanocomposite

#### 3.3. FE-SEM images

The FE-SEM images were shown for MOF before and after lead adsorption (Fig. 5). SEM results were shown MOF nanoparticles with size of between 40-90 nm (before lead adsorption) and less than 100 nm (after lead adsorption). Lead absorption was caused the increase of particle size due to phenomenon of swelling. This result presented for the first time.

# 3.4. The Brunauer–Emmett–Teller (BET) analysis

The Brunauer–Emmett–Teller (BET) analysis was used for determination of surface area of MOF by  $N_2$  adsorption before and after lead adsorption (Fig. 6). The surface area of MOF was decreased with lead adsorption from 762 m<sup>2</sup> g<sup>-1</sup> to 21 m<sup>2</sup> g<sup>-1</sup>. The results indicate that there is almost no porosity after absorption and approximately the pores filled up lead.



C 200 nm

Fig. 5. FE-SEM images of a) MOF before lead adsorption before, b) MOF after lead adsorption, and c) MOF/PCL nanocomposite in 200 nm scale bare.



Fig. 6. The absorption/desorption N<sub>2</sub> curve related to MOF a) before and b) after lead adsorption.

# 3.5. Optimization study

The lead absorption was investigated by UV–Vis spectroscopy. The calibration curve of lead was examined at  $\lambda_{max} = 208$  nm with concentration of 0.1, 0.2, 0.4, 0.6, and 0.8 ppm (Fig. 7a). Lead adsorption diagram was investigated by different MOF amount including 0.1, 0.25, and 0.5 g for lead concentration at 0.6 ppm at various times (Fig. 7 b). Based on the result, the increase of MOF amount was resulted to the increase of lead adsorption due to increase of surface area.

The lead absorption was evaluated in different lead concentrations by MOF and its nanocomposite at different times (Fig. 8a). The lead concentrations were included 0.4, 0.4, 0.8, and 1.0 ppm for absorption investigation of 0.25 g MOF. The increase of lead concentration was resulted to increase of adsorption by MOF. The absorption of MOF/PCL nanocomposite was examined at a constant concentration of 0.6 ppm for lead solution (Fig. 8b). According to nanocomposite result, the increase of MOF percentage was resulted to increase of lead absorption. If fact, the increase of MOF was created the higher lead absorption due to increase of surface area.

Lead adsorption was studied in different pH of solution including acidic (pH=2), neutral, and basic (pH=10) for 0.25 g MOF with 0.6 ppm of lead concentration and 10% nanocomposite with 0.6 ppm of lead concentration (Fig. 9). The higher pH was caused more surface active sites, a competition between positive charges(Pb), and increase lead adsorption through the electrostatic force of attraction. However, the optimum pH in ranging from 7.5 to 8.5 for the divalent lead ions cased to preservation of MOF stability for efficiency improvement of chemical adsorption based on nitrogen dative bond more than 95% and have less than 32 % at pH 3-5 by physical adsorption.

Lead adsorption was evaluated in various temperature including 25 (ambient), 40, 60, and 80 °C for 0.25 g MOF and 10% nanocomposite with 0.6 ppm of lead concentration (Fig. 10). The increase of temperature was resulted to increase of lead adsorption because of kinetic energy and Brownian motion. Based on the previous report, temperature is directly related to the potential for adsorption by sorbent [19].







Fig. 7. a) The calibration curve of lead and b) the diagram of lead adsorption in different MOF amount



**Fig. 8.** The diagram of lead adsorption by **a**) MOF and **b**) MOF/PCL nanocomposite in different lead concentrations



Fig. 9. The diagram of lead adsorption by a) MOF and b) MOF/PCL nanocomposite in different pH.



Fig. 10. The diagram of lead adsorption by a) MOF and b) MOF/PCL nanocomposite in different temperature.

### 3.6. Validation of USA-S- µ-SPE / UV-Vis

By the USA-S- µ-SPE method, 50 mL of urine and water samples were used for extraction and determination lead ions by 0.25 g of MOF adsorbent (0.05-1.0 mg L<sup>-1</sup>, 100-1000 µg L<sup>-1</sup>, pH=8). The validated results were achieved for real samples by spiking of the standard solution of lead (Pb) to 50 mL of samples. The recoveries of spiked samples showed that the method was acceptable results for lead extraction and determination in urine and water samples. (Table 1) Also, the mean lead concentrations for five wastewater samples in paint factory, Karaj were obtained (325.4± 13.8, n=5) by the ET-AAS which was near to the USA-S- µ-SPE/UV-Vis procedure (320.6± 15.2, n=5) as 98.4 % recovery. The results confirmed the accuracy and precision of methodologyfor lead adsorption by MOF.

# 4. Conclusions

In this research, the MOF and MOF/PCL

nanocomposite were used for lead adsorption. The effect of different parameter including pH and temperature of solution,  $Zn_2(BDC)_2(DABCO)$  MOF and concentration of sorbent was shown on lead adsorption by MOF and its PCL nanocomposite. The results presented that MOF and its PCL nanocomposite can represent an economical source of lead sorbent from aqueous solution to develop environmental applications. The future prospects can be developed great application of this nanocomposites.

The working range and the relative standard deviation range (RSD%) for proposed procedure were obtained 0.05-5 mg L<sup>-1</sup>and 2.13-5.24, respectively (r = 0.9992). The absorption capacity of Zn<sub>2</sub>(BDC)<sub>2</sub>(DABCO) MOF for standard lead solution were ranged from 121.5 to 148.7 mg g<sup>-1</sup> in optimized conditions. The method was validated by the F-AAS.

Sample*	Added (µg L <sup>-1</sup> )	*Found (µg L <sup>-1</sup> )	Recovery (%)
Well Water		$178.9 \pm 7.2$	
	150	$323.5 \pm 15.6$	96.4
Waste water		397.8±17.7	
	500	$903.6 \pm 41.5$	101.2
Waste water		492.1 ± 22.3	
	500	$986.3 \pm 44.6$	98.8
Urine		$62.4\pm2.8$	
	50	$110.8 \pm 4.7$	96.8
Drinking water		ND	
	50	$48.6 \pm 2.1$	97.2
		$55.8 \pm 2.4$	
Urine	50	$107.1 \pm 3.3$	102.6

Table 1. Validation of USA-S- μ-SPE/UV-Vis method for Pb(II) determination in urine and water samples based onZn<sub>2</sub>(BDC)<sub>2</sub>(DABCO) MOF adsorbent by spiking real samples

\*Mean of three determinations of samples  $\pm$  confidence interval (P = 0.95, n = 10) ND: Not detected

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