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# Functional group effect of Isoreticular metal-organic frameworks on heavy metal ion adsorption

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#### ABSTRACT

Evaluating the relationship between structure and function of metal-organic frameworks (MOFs) is an interesting issue that has been discussed in this work. Here, four isoreticular 3D porous zinc(II) MOFs with *pcu* topology, including  $[Zn(oba)(4-bpmb)_{0.5}] \cdot (DMF)_{1.5}$  (TMU-6),  $[Zn(oba)(bpmn)_{0.5}] \cdot (DMF)_{1.5}$  (TMU-21),  $[Zn_2(oba)_2(bpfb)] \cdot (DMF)_5$  (TMU-23) and  $[Zn_2(oba)_2(bpfn)] \cdot (DMF)_2$  (TMU-24),  $H_2oba = 4,4'$ -oxybisbenzoic acid, bpmb = N,N'-bis-(4-pyridylmethylene)-1,4-benzenediamine, bpmn = N,N'-bis-(4-pyridylmethylene)-1,5-naphthalenediamine, bpfb = N,N'-bis-(4-pyridylformamide)-1,4-benzenediamine and bpfn =

N,N'-bis(4-pyridylformamide)-1,5-naphthalenediamine, containing imine- (TMU-6 and TMU-21) and amide- (TMU-23 and TMU-24) decorated pores, have been successfully synthesized by mechanochemical method. Then, adsorption efficiency of these four MOFs for some heavy metal ions was studied to evaluate the effect of type of the functional groups of the pillars in different MOFs on adsorption process. The results indicated that the amide-decorated MOFs show a better adsorption efficiency toward metal ions than the imine-decorated MOFs. In the following, TMU-23 was used as an efficient sorbent for extraction and removal of some heavy metal ions ( $Co^{+2}$ ,  $Cd^{+2}$ ,  $Cu^{+2}$ ,  $Cr^{+3}$ ,  $Fe^{+2}$ , and  $Pb^{+2}$ ) and its analytical performance was evaluated and determined. In addition, DFT calculations were performed on possible coordination modes between cations and simplified functional groups of the related pillars in each MOF and probable interaction mechanism of the MOFs and the metal ions was evaluated.

#### **1. INTRODUCTION**

Since the beginning of the industrial growth, human activities and natural processes have been entering numerous potential hazardous trace heavy metal ions into the environment. Many of these metals, such as chromium (Cr), copper (Cu), iron (Fe), and cobalt (Co) are necessary for plants, living organisms, and the human body, [1, 2] whereas in large quantities, the same elements are toxic. Cadmium (Cd) and lead (Pb) show extreme toxicity even at low concentrations. Therefore, there has been an increasing necessity for analytical chemists to evaluate the environmental and healthy quality based on an accurate determination of heavy metal ions in environmental samples. [3-6]

While the determination of trace heavy metal ions in environmental samples is highly desired, it is also restricted by two main difficulties: first, the interfering effects of the matrix, second, the

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usual low concentrations of heavy metal ions which may be lower than the detection limit of many analytical techniques. There is a crucial need for extraction and preconcentration of trace elements from applied matrix before analyzing them through analytical techniques. [7-9] Solid phase extraction (SPE) is currently being used as a preconcentration or separation method for analyzing trace analyte ions existing in various materials and complexes. [10, 11] SPE has several advantages such as large preconcentration factors, low cost because of lower consumption of reagent, simplicity in phase separation and ease of automation. [12, 13] In SPE procedure, selection of suitable sorbent to achieve higher analytical performance (i.e., analytical sensitivity, selectivity, and precision) is the most crucial step. So studying the relationship of structure and function of a sorbent may be a fascinating subject in the analytical chemistry.

Metal-organic frameworks (MOFs) are crystalline materials combined of organic linkers and inorganic metal ions which are self-assembled through coordination bonds. [14] The diversity of metal ions and organic linkers makes it possible to generate architectures with tunable porosity. [15, 16] High thermal resistivity, large surface area, uniform nanosized structural cavity and porosity makes MOFs as good candidates for diverse applications such as gas storage, [17, 18] catalyst, [19, 20] separation, [21] drug delivery, [22, 23] sensing, [24, 25] biomedical imaging [26] and analytical applications. [27, 28]

Analytical chemists enjoy the potential of novel MOF materials for their application in analytical methods. As sorbents for sampling, solid phase extraction (SPE) [29, 30] and solid phase microextraction (SPME) [31, 32] as well as stationary phases for liquid and gas chromatography [33] providing them with a solution to the challenges such as extraction, sample collection, improving sensitivity, selectivity and limit of detection. Considering all of these applications, it is difficult to find an appropriate MOF for sample preparation. [34]

MOFs show great promise in the analytical applications such as the capture of heavy metal ions by the chelating effect between metal ions and functional group in the linker. [35, 36] The shape and size of the pores lead to selectivity over the guests that may be adsorbed. Immobilization of functional groups modifies the surface for the engineering of interface properties of solid substrates, while the fundamental of their geometry and mechanical strength remains unchanged. [2, 37]This article is developed in the following order: first, synthesis of MOFs with various functional groups. Second, discuss the effects of different functional groups in MOFs on extraction efficiency. There are a lot of reports about the extraction and removal of heavy metal ions with MOFs but in this work we try to explain the results that accrue with small change in the linker and such investigation may open up new possibilities for the rational design and synthesis of nanoporous materials for particular applications. [38]

Recently, we successfully introduced two acylamide-containing threefold interpenetration pcu-MOFs; TMU-23 ( $[Zn_2(oba)_2(bpfb)]$ ·(DMF)<sub>5</sub>), and TMU-24 ( $[Zn_2(oba)_2(bpfn)]$ ·(DMF)<sub>2</sub>) (H<sub>2</sub>oba = 4,4'-oxybis(benzoic acid, bpfb = N,N'-bis-(4-pyridylformamide)-1,4-benzenediamine and bpfn DMF N,N'-bis(4-pyridylformamide)-1,5-naphthalenediamine, N.Nwhere is =dimethylformamide) [39], and studied their  $CO_2$  sorption properties. The study revealed that not only the insertion of amide functional groups on the MOFs pore surface but also the accessibility of the functional groups could affect their CO<sub>2</sub> sorption and CO<sub>2</sub>/N<sub>2</sub> separation properties. Inspired by our previous works, [40, 41] herein we report the mechanochemical synthesis of TMU-23 and TMU-24 for the first time and investigate the capability of these amide-decorated MOFs as sorbents for adsorption of heavy metal ions. For further investigation of the role of the functional groups of the MOFs in capturing of metal ions, two other isoreticular

mechanosynthesized Zn(II)-based MOFs,  $[Zn(oba)(4-bpmb)_{0.5}] \cdot (DMF)_{1.5}$  (TMU-6) and  $[Zn(oba)(bpmn)_{0.5}] \cdot (DMF)_{1.5}$  (TMU-21), (bpmb = N,N'-bis-(4-pyridylmethylene)-1,4benzenediamine and bpmn = N,N'-bis-(4-pyridylmethylene)-1,5-naphthalenediamine), were selected in which the pores surface are decorated by imine functional groups [39] (Scheme 1). This investigation helped us to examine the role of the basicity of the different N-donor ligands (containing amide or imine group) and the oxygen containing groups in metal ion capturing and to compare the adsorption efficiencies in four MOFs.

Also, maximum adsorption capacity of all the MOFs were examined and compared. Subsequently, according to results of the preliminary experiments, TMU-23 was selected as an efficient sorbent for extraction and preconcentration of trace amounts of some heavy-metal ions including Cd(II), Co(II), Cr(III), Cu(II), Fe(II) and Pb(II) from aqueous samples, followed by their determination by flow-injection inductively coupled plasma-optical emission spectrometry (ICP-OES), and potential parameters affecting the performance of the target metal ions extraction were evaluated in detail. Eventually, the proposed method was applied for the preconcentration and determination of the heavy metal ions in real environmental water samples. Also, DFT calculations were performed to study type of the interaction of the metal ions with functional groups (amide or imine) of four MOFs and the obtained results were compared with 1the experimental studies results.

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Figure1: advantage of mechanochemical methods for preparation of MOF compared to other methods.

[42, 43]

#### 2. EXPERIMENTAL SECTION

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#### 2.1. Materials and Physical Techniques

All starting materials, including Zinc(II) nitrate hexahydrate, zinc(II) acetate dihydrate, and 4,4'oxybis(benzoic acid) (H<sub>2</sub>oba) were purchased from Aldrich and Merck. The ligands N,N'-bis-(4pyridylformamide)-1,4-benzenediamine N,N'-bis(4-pyridylformamide)-1,5-(bpfb). naphthalenediamine (bpfn), N,N'-bis-(4-pyridylmethylene)-1,4-benzenediamine (bpmb) and N,N'-bis-(4-pyridylmethylene)-1,5-naphthalenediamine (bpmn) were synthesized according to the previous reported methods. [39] Stock standard solutions (1000 mg L<sup>-1</sup>) of Cd(II), Co(II), Fe(II), Cr(III), Cu(II), and Pb(II) were prepared by dissolving appropriate amounts of analyticalgrade Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O, Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Cr (NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, Fe(NO<sub>3</sub>)<sub>2</sub>.9H<sub>2</sub>O, Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O, and Pb(NO<sub>3</sub>)<sub>2</sub> salts, respectively, from Merck in ultrapure water. Fourier transform infra-red (FT-IR) spectra were recorded on a Bruker Tensor 27FTIR spectrometer equipped with a Golden Gate diamond attenuated total reflection (ATR) cell, in absorption mode at room temperature. Powder X-ray diffraction (PXRD) measurements were collected on a Philips X'pert diffractometer with monochromatic Cu-K $\alpha$  radiation ( $\lambda_{Cu} = 1.5406$  Å). For synchronous determination of the target elements we used a simultaneous inductively coupled plasma-optical

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emission spectrometry (ICP-OES) on a Varian Vista-PRO instrument (Springvale, Australia) having a radial torch coupled to a concentric nebulizer and a Scott spray chamber carrying a charge-coupled detector (CCD). To introduce the final solution into the ICP-OES nebulizer a six-port two-position injection valve from Tarbiat Modares University equipped with a 250  $\mu$ L injection loop constructed from silicon tubing was used. Table S1 in the Supporting Information (SI) lists the optimal conditions of instruments and the emission lines used for determining the metal ions by ICP-OES.



Scheme 1. Chemical Structures of H<sub>2</sub>oba, bpfb, bpfn, bpmb and bpmn.

#### **Computational details**

All DFT calculations were performed using the GAMESS suite of programs. The geometry of the ligands was optimized at the B3LYP/6-31+G\* level of theory. The LANL2DZ basis set with the corresponding effective core potential was used for the metal cations. Molecular electrostatic potentials (MEPs) of the isolated ligand were obtained on the 0.001 atomic unit surface by means of the SAS-WFA program using the wavefunctions generated at the aforementioned level of theory. The Mulliken charge density analysis of the free ligands was performed at the B3LYP/6-31+G\* level using the GAMESS.

#### 2.2. Extraction Procedure

The procedure for the solid-phase extraction of heavy metal ions was conducted by the following steps: Initially a 100 mL aliquot of aqueous sample including the target metal ions was added in a 200 mL glass beaker containing 10 mg of the MOF as sorbent. The pH value of the solution was adjusted to 8. After stirring the solution for 10 min to speed up the adsorption of the analytes onto the MOF, the solution was centrifuged at 6000 rpm for 2 min. Then the sorbent was separated from the solution, and the adsorbed analytes were desorbed from the sorbent with 200  $\mu$ L of the eluent containing 0.4 M ethylenediaminetetraacetic acid (EDTA) by powerful vortex for 2 min. After centrifuging, the eluate of volume 200  $\mu$ L was subjected into the nebulizer of the ICP-OES instrument using the six-way two-position injection valve for further determination.

To investigate the adsorption capacity of all the MOFs, 3 mg of each MOF was added to 15 mL of the metal ions solutions at different concentrations in the range of 20-200 mg  $L^{-1}$  and after pH adjusting to 6, stirred for 15 min at room temperature. As the equilibrium point was reached, the sorbent was separated centrifugally, and the concentrations of the residual ions in solution after equilibrium adsorption were determined by ICP-OES.

#### 3. RESULTS AND DISCUSSION

#### **3.1.** Characterization of the MOFs

Knowing the isoreticularity concept first disclosed by Yaghi and co-workers, [44] four pillared MOF structures (TMU-6, TMU-21, TMU-23 and TMU-24) with the same network topology, bearing different N-donor ligands were prepared. The original preparation method and the crystallographic data of TMU-6, TMU-21, TMU-23 and TMU-24, which respectively contain imine/amide pillars of bpmb, bpmn, bpfb and bpfn have been recently addressed by our research group. [39]

In order to achieve more facile preparation route of these MOFs, all MOFs were prepared via mechanochemical method. In a typical synthesis, TMU-6, TMU-21, TMU-23 and TMU-24 were prepared by the mechanochemical reaction (grinding by hand) of a mixture of  $Zn(OAc)_2 \cdot 2H_2O$ ,  $H_2oba$ , and N-donor ligand; bpmb, bpmn, bpfb and bpfn (Figure S1), respectively for 15 min (SI). Comparison between the simulated and the experimental (resulting from the mechanosynthesized powder) PXRD patterns revealed that the mechanosynthesized TMU-6, TMU-21, TMU-23 and TMU-24 were structurally identical to their original structures prepared by conventional heating (Figure 2).

TMU-6, TMU-21, TMU-23 and TMU-24 are neutral threefold interpenetrated MOFs formed by {Zn(oba)} layers connected through the N,N-pillar ligands. In these structures, each nonlinear dicarboxylate oba ligand is coordinated to three Zn(II) centers forming the  $\{Zn(oba)\}$  layers along the *ab*-plane. Because of the dinuclear nature of the metal cluster, these layers are formed by two sheets of parallel oba ligands that form  $\pi$ - $\pi$  stacking interactions between them. These  $\{Zn(oba)\}\$  layers are then pillared by the linear imine/amide-functionalized ligands, extending the structure in three dimensions with 6-connected net and *pcu* topology. Although all compounds are threefold interpenetrated, they still possess apparent 1D pore channels ( $\sim 8.1 \times$ 7.4 Å<sup>2</sup>, ~8.2 × 7.0 Å<sup>2</sup>, ~6.8 × 6.4 Å<sup>2</sup> and ~6.7 × 5.5 Å<sup>2</sup>-including van der Waals (vdW) radii-for TMU-6, TMU-21, TMU-23 and TMU-24, respectively) running along the (101) direction and noticeable free space (33%, 30%, 32% and 30% for TMU-6, TMU-21, TMU-23 and TMU-24, respectively) (Figure ). As we previously reported, all the MOFs are nonporous to N<sub>2</sub> at 77 K but are porous to CO<sub>2</sub> at various temperatures. CO<sub>2</sub> uptakes at 203 K were calculated to be 9.0, 4.5, 7.2, and 6.3 mmol.g<sup>-1</sup> and the observed pore volumes were 0.32, 0.16, 0.27 and 0.22 cm<sup>3</sup>.g<sup>-1</sup> for TMU-6, TMU-21, TMU-23, and TMU-24, respectively. [39]

Thermogravimetric analyses (TGA) of the mechanosynthesized MOFs showed a plateau in the range of 30-~370 °C revealing that their pore channels were devoid of any guest molecules (Figure S4, SI). Above these temperatures, the MOFs started to decompose. The prepared MOFs were also soaked in water and some organic solvents such as ethanol, acetonitrile and dichloromethane for at least 24 h at room temperature to determine whether they are stable in these solvents. The PXRD patterns before and after immersion were consistent, confirming that the structures have high stabilities in these solvents (Figure S5, S6FI).



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**Figure 2.** Comparison of PXRD patterns of TMU-6, TMU-21, TMU-23 and TMU-24: (a,d,g,j) simulated, (b,e,h,k) as-synthesized and (c,f,i,l) mechanosynthesized, respectively.



**Figure 3.** Representation of the pores highlighting the imine and amide groups in (a) TMU-6, (b) TMU-21, (c) TMU-23 and (d) TMU-24 (presented in space-filling) pointing toward the pores of the frameworks. All hydrogen atoms and the disordered guest molecules are omitted for clarity.

#### **3.2. Optimization of Extraction Parameters**

The primary experiments demonstrated that the MOF containing amide functional group has higher metal ions adsorption efficiency than the MOF with imine group. Accordingly, TMU-23 was selected as the SPE sorbent for extraction and preconcentration of heavy metal ions, including Cd(II), Co(II), Cr(III), Cu(II), Fe(II) and Pb(II) to evaluate its analytical performance. In order to achieve the best efficiency various factors influencing the extraction efficiency such as concentration of the eluent, sample pH, times of adsorption and desorption, and sample and eluent volumes were investigated and optimized. The optimization was carried out on an aqueous solution containing mixture of 100  $\mu$ g L<sup>-1</sup> of each metal ion and the above mentioned variables were performed by modifying one at a time and keeping the remaining constants.

The pH of aqueous solution plays an important role in the chelation of the metal ion species with free coordination sites of the MOF as well as in the following extraction process. The effect of the sample pH was tested in the range of 5-11. As demonstrated in Figure S7, the maximum peak areas were obtained at pH 8, so it was chosen as the optimum value at further studies. Decrease in extraction efficiency by further increasing the sample pH from 8 to 11, can be attributed to precipitation of the metal ions in hydroxide forms.

To obtain the maximum extraction efficiencies for the target analytes, amount of the sorbent was optimized by varying its amount in the range of 5-15 mg for extraction of 100  $\mu$ g L<sup>-1</sup> of the analytes from 30 mL of the sample solution. In order to gain satisfactory recoveries of the target metal ions, a certain amount of sorbent is required. The results shown in Figure S8 indicated, indicated that the best extraction efficiencies were achieved by using 10 mg of the MOF, hence this amount of the MOF was employed in the subsequent studies.

It is necessary to determine optimum volume of the eluent to achieve the highest enrichment and recovery of the adsorbed analytes. Eluent volume should be enough to can soak the sorbent and on the other hand it should not be excessive to dilute the eluate. Considering these, different volumes (200-600  $\mu$ L) of 0.4 M EDTA as eluent was examined and the results revealed that analytes quantitative recoveries could be achieved by using 200  $\mu$ L of the eluent. Accordingly, desorption of the target metal ions was performed using 200  $\mu$ L of 0.4 M EDTA in subsequent experiments Figure S9.

To examine effect of the sample volume on the analytical performance, experiments were performed by changing the sample solution volume, spiked with 20  $\mu$ g of the target analytes, in the range of 30-250 mL using 10 mg of the MOF. The results revealed that the extraction

efficiency was nearly constant in the volume range of 30-100 mL, and after that, a decrease was observed in the signal intensity. Therefore, 100 mL was chosen as the optimal sample volume.

The influence of the concentration of EDTA on desorption of target ion was studied. For desorbing 100µg.L<sup>-1</sup> of target ion, already adsorbed on 10 mg of sorbent, 200µl of different concentration of eluent (EDTA) have been used. As a result of experiments, 200 µl of  $0.4 \text{ mol } \text{L}^{-1}$  EDTA solutions that give maximum recovery was found as optimum eluents. A concentration of 0.4 mol  $l^{-1}$  of EDTA was selected for further studies (Figure S10). To obtain the highest sensitivity and precision, the equilibrium time of the adsorption process should be determined. For this purpose, further experiments were performed for study of the extraction time by changing the time in the range of 2-20 min. As can be seen in Figure S11, it was observed that there is an increase of the extraction efficiency along with the increasing extraction time from 2-10 min while further increasing in time had no significant on recovery. Thus, time of 10 min was applied for further experiments. This rapid adsorption process can be attributed to the short diffusion route of the metal ions to the MOF and the MOF high porosity and surface area that cause to reaching equilibrium in a shorter contact time. The effect of the desorption time was also studied, and it was revealed that after 2 min, no substantial change occurs in the desorption efficiency. (Figure S12)

#### 3.3. Method validation

The practical applicability of the proposed extraction method was evaluated by establishing a number of performance parameters as the figures of merit such as linearity, limit of detection (LOD), preconcentration factor (PF), repeatability, and extraction recovery for extraction of the target analytes from the aqueous solutions under the optimum conditions. As summarized in Table 1, calibration curves plotted using ten spiking levels of the metal ions with three replicate

measurements for each point, were found to be linear in the range of 0.2–200  $\mu$ g L<sup>-1</sup> with coefficients of determination (R<sup>2</sup>) ranging from 0.995 to 0.998. The limits of detection (LODs) based on definition of 3S<sub>b</sub>/m (where, S<sub>b</sub> is the standard deviation of three replicate blank measurements, and m is the slope of the calibration curve) were between 0.05-0.2  $\mu$ g L<sup>-1</sup>. The preconcentration factors (PFs), calculated as the ratio of the slopes of the preconcentration and direct calibration equations were found to be in the range of 40–350. The precision of the proposed method was evaluated in terms of repeatability and RSDs% < 5.3 (n = 5) were obtained at a concentration level of 20  $\mu$ g L<sup>-1</sup>. The ER% was calculated according to the following equation:

$$ER = \frac{C_f \mathscr{W}_f}{C_0 \mathscr{W}_0} \times 100$$

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Where,  $C_f$  and  $C_0$  are the concentration of analyte in the eluent phase (after preconcentration) and the initial concentration of analyte in the sample solution, respectively, and  $V_f$  and  $V_0$  are eluent and sample solution volumes, respectively.

Table 1. Figures of merit of the proposed method for extraction of the

target metal ions							
Analyte	$^{a}LDR$ (µg $L^{-1}$ )	$R^2$	$^{b}LOD$ (µg L <sup>-1</sup> )	°РF	ER (%)	$^{d}$ RSD (%) (n = 5)	
$\mathrm{Cd}^{+2}$	0.5-200	0.998	0.2	84	17	3.3	
Co <sup>+2</sup>	0.5-200	0.995	0.2	40	8	3.8	
Cr <sup>+3</sup>	0.2-200	0.998	0.05	230	46	2.3	
Cu <sup>+2</sup>	0.2-200	0.996	0.05	270	54	4.8	
$Pb^{+2}$	0.5-200	0.997	0.2	350	70	5.3	
Fe <sup>+2</sup>	0.3-200	0.996	0.1	90	18	3.1	

<sup>a</sup>Linear dynamic range. <sup>b</sup>Limit of detection. <sup>c</sup>Preconcentration factor. <sup>d</sup>Data were calculated based on the extraction of a 20  $\mu$ g L<sup>-1</sup> sample for each analyte.

#### 3.4. Determination of the metal ions in real samples

In order to investigate the reliability and analytical performance of the proposed method for determination of metal ions in real samples, the proposed method was verified by analyzing 100 ml of some real water samples such as tap water, and mineral water before and after spiking with known amounts of the target metal ions. The obtained results are summarized in Table 2. As can be seen, the relative recoveries of the target metal ions ranged from 92% to 110% and acceptable repeatability are indicating good performance of the proposed method to apply to real samples.

	$Cd^{+2}$	Co <sup>+2</sup>	Cr <sup>+3</sup>	$Cu^{+2}$	$Fe^{+2}$	$Pb^{+2}$	
	Found $\pm$ SD	Found $\pm$ SD	Found $\pm$ SD	Found $\pm$ SD	Found $\pm$ SD	Found $\pm$ SD	
			Tap water				
Non spiked	<lod< td=""><td><lod< td=""><td><math>0.3_0 \pm 0.0_2</math></td><td><math>0.4_5 \pm 0.0_1</math></td><td><math>1.1_0 \pm 0.0_4</math></td><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td><math>0.3_0 \pm 0.0_2</math></td><td><math>0.4_5 \pm 0.0_1</math></td><td><math>1.1_0 \pm 0.0_4</math></td><td><lod< td=""></lod<></td></lod<>	$0.3_0 \pm 0.0_2$	$0.4_5 \pm 0.0_1$	$1.1_0 \pm 0.0_4$	<lod< td=""></lod<>	
Added (5 $\mu$ g L <sup>-1</sup> )	$5.3 \pm 0.1_1$	$5.1 \pm 0.1_3$	$5.4_7 \pm 0.1_1$	$5.4_3 \pm 0.0_8$	$6.3_1 \pm 0.1_3$	$4.8_9 \pm 0.0_7$	
Recovery%	106	102	103	99	104	98	
Added (10 $\mu$ g L <sup>-1</sup> )	$9.4_1 \pm 0.3_9$	$10.1_6 \pm 0.2_4$	$10.2_0 \pm 0.0_9$	$10.4_0 \pm 0.3_8$	$10.7_5 \pm 0.2_5$	$9.3_6 \pm 0.3_5$	
Recovery%	94	102	99	99	96	93	
Mineral water							
Non spiked	<lod< td=""><td><lod< td=""><td><loq< td=""><td><math>0.5_4 \pm 0.0_2</math></td><td><math>1.0_1 \pm 0.0_5</math></td><td><lod< td=""></lod<></td></loq<></td></lod<></td></lod<>	<lod< td=""><td><loq< td=""><td><math>0.5_4 \pm 0.0_2</math></td><td><math>1.0_1 \pm 0.0_5</math></td><td><lod< td=""></lod<></td></loq<></td></lod<>	<loq< td=""><td><math>0.5_4 \pm 0.0_2</math></td><td><math>1.0_1 \pm 0.0_5</math></td><td><lod< td=""></lod<></td></loq<>	$0.5_4 \pm 0.0_2$	$1.0_1 \pm 0.0_5$	<lod< td=""></lod<>	
Added (5 $\mu$ g L <sup>-1</sup> )	$4.6_4 \pm 0.2_1$	$4.6 \pm 0.1_0$	$5.1_2 \pm 0.2_0$	$6.0_5 \pm 0.1_8$	$6.4_4 \pm 0.0_9$	$5.1_4 \pm 0.2_7$	
Recovery%	92	92	102	110	109	102	
Added (10 $\mu$ g L <sup>-1</sup> )	$10.1 \pm 0.3_4$	$10.2_4 \pm 0.1_7$	$9.6_3 \pm 0.1_1$	$11.0_5 \pm 0.2_5$	$11.8_7 \pm 0.1_0$	$9.4_3 \pm 0.3_6$	
Recovery%	101	102	96	105	108	94	
Mineral water							
Non spiked	<lod< td=""><td><lod< td=""><td><lod< td=""><td><math>0.6_1 \pm 0.0_6</math></td><td><math>0.8 \pm 0.0_4</math></td><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><math>0.6_1 \pm 0.0_6</math></td><td><math>0.8 \pm 0.0_4</math></td><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td><math>0.6_1 \pm 0.0_6</math></td><td><math>0.8 \pm 0.0_4</math></td><td><lod< td=""></lod<></td></lod<>	$0.6_1 \pm 0.0_6$	$0.8 \pm 0.0_4$	<lod< td=""></lod<>	
Added (5 $\mu$ g L <sup>-1</sup> )	$5.1_2 \pm 0.0_7$	$4.8 \pm 0.2_1$	$5.3_1 \pm 0.1_7$	$6.3_3 \pm 0.3_3$	$5.8_7 \pm 0.1_0$	$4.8 \pm 0.2_2$	
Recovery%	102	96	106	110	101	96	
Added (10 $\mu$ g L <sup>-1</sup> )	$9.8_4 \pm 0.4_3$	9.6±0.12	$10.2 \pm 0.2_8$	$10.9 \pm 0.1_3$	$11.5\pm0.0_8$	$9.7_6 \pm 0.3_5$	
Recovery%	98	96	102	103	107	97	

 Table 2. Analytical results for extraction and determination of target metal ions in real samples

#### 3.5. Evaluation of adsorption capacity of the MOFs

Forasmuch as the MOFs have porous structure, it was expected that they have high adsorption capacity of metal ions. For investigation of their maximum adsorption capacities, the equilibrium adsorption experiments mentioned in the experimental section were performed at different concentrations of the metal ions and the obtained results were evaluated by Langmuir adsorption isotherm. With regard to the maximum adsorption capacities ( $Q_m$ ) of the MOFs listed in Table 3,

it can be seen that all the MOFs demonstrate high and nearly same maximum adsorption capacities for each of the metal ions. This observation is in compliance with their high porosity and approximately same free spaces (33%, 30%, 32% and 30% for TMU-6, TMU-21, TMU-23 and TMU-24, respectively).

#### 3.6. Comparison of the adsorption behavior of the MOFs

In this work, our purpose was evaluation of the role of functional groups being on the pillar of the MOFs as well as their pore size on adsorption of metal ions. Accordingly, four isoreticular zinc(II)-based MOFs were selected while two of them (TMU-6 and TMU-21) had amide group on their pillars and the other pair (TMU-23 and TMU-24) contained imine group. On the other hand, TMU-6 and TMU-23 contain one phenyl ring and TMU-21 and TMU-24 had two phenyl rings in their pillar structures (Scheme 1). This selection allowed to evaluate the effect of both type of the functional groups and number of phenyl rings in pillars of the MOFs on metal ions adsorption.

For comparison of adsorption behavior of four isoreticular MOFs with different pillars, their extraction recoveries (ER%) and maximum adsorption capacities (Q<sub>m</sub>) were calculated and listed in Table 3. Comparing the ER% of four MOFs studied for metal ions adsorption, it can be seen that MOFs with amide group (TMU-23 and TMU-24) show higher efficiency (greater ER%) for metal ion adsorption rather than MOFs with imine group (TMU-6 and TMU-21). On the other hand, the MOFs which contain phenyl group in their pillar structure to some extent have more ER% than MOFs with naphthyl group in their pillars (TMU-23 toward TMU-24 and TMU-6 toward TMU-21).

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Furthermore, as comparing the values of  $Q_m$  obtained for four MOFs (see Table 3), it can be found that all the MOFs provides nearly similar adsorption capacity for each of the metal ions while this result is not similar to the result of the comparison of the ERs%.

Since the free spaces in all the MOFs are approximately equal (33%, 30%, 32% and 30% for TMU-6, TMU-21, TMU-23 and TMU-24, respectively), it can be concluded that at high concentrations of metal ions free space of the MOFs is determinative of their adsorption rate. However, at low concentrations of metal ions, the interaction of the free coordination sites (amide or imine groups) of the MOFs with metal ions has the major role in the adsorption efficiency. The amide group having more basicity with two coordination sites (O and N) demonstrates greater extraction efficiency than the imine group with lower basicity and one coordination site (N). On the other hand, it seems having naphthyl group in pillar structure could decline the charge density of the coordination sites (in amide or imine groups) by increasing the resonance path length in phenyl rings that results to decrease in the adsorption efficiency (ER%, that is a measure of adsorption efficiency).

**Table 3.** Comparison of extraction recoveries (ER) and maximum adsorption capacities  $(Q_m)$  of four MOFs for the target metal ions.

MOF		$\mathrm{Cd}^{+2}$	Co <sup>+2</sup>	Cr <sup>+3</sup>	$\mathrm{Cu}^{+2}$	Fe <sup>+2</sup>	$Pb^{+2}$
TMU-6	ER	13	7	12	15	12	21
	$Q_{m}$	47	54	118	60	61	230
TMU-21	ER	11	4	9	14	10	18
	$Q_{m}$	49	55	121	60	67	221
TMU-23	ER	17	8	46	54	18	67
	$Q_{m}$	55	47	108	65	64	267
TMU-24	ER	14	8	38	43	15	56

$Q_m$	51	49	115	63	65	256
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By comparing ERs% of TMU-23 and TMU-5 (the azine-decorated MOF studied in details in our previous work [41] for extraction of  $Pb^{+2}$  ions, it can be found that TMU-23 shows much more ER% than TMU-5, nearly twice the ER% of TMU-5, while ERs% of these two MOFs for the other ions studied were almost same. From this observation it can be concluded that  $Pb^{+2}$  ions have more tendency to the amide groups rather than azine groups while the other metal ions studied here (Co<sup>+2</sup>, Cd<sup>+2</sup>, Cu<sup>+2</sup>, Cr<sup>+3</sup>) have approximately similar tendency to both functional groups (amide and azine). Due to the high attraction force of Pb ions towards the aromatic ring as well as the the amide functional groups, the ER is enhanced. [45]

#### 3.7. Theoretical calculations

To analyze the trend obtained for the cations interaction with different ligands, we first analyze the MEP plots of the isolated ligands. Figure S14 shows the MEP isosurfaces on the 0.001 atomic unit electron density isosurface of these molecules, where positive and negative regions are indicative of a nucleophilic and electrophilic site, respectively. Table 4 shows the calculated most negative MEP values with these ligands. As evident from Figure S14, the negative MEP regions are mainly associated with the nitrogen or oxygen atoms, which indicate the potential of these sites to an electrophilic attack. More especially, the most negative MEP in TMU-23 and TMU-24 is mainly associated with the oxygen atom of amide group, with the values of -29.5 and -28.5 kcal/mol, respectively. All these ligands are also characterized by a distinct negative area,

associated with the nitrogen atom of pyridine nitrogen. The absolute MEP value at the nitrogen/oxygen atoms of these ligands decraeses as TMU-23 > TMU-24 > TMU-6 > TMU-21. Note that this is almost consistent with the results obtained for the adsorption of the target cations. In particular, the MEP analysis also properly predicts that TMU-21 should have the weakest interaction with the cation species. This finding is also verfied by the calculated Mulliken atomic charges on the oxygen or nitrogen atoms (Table 4). This indicates that the electrostatic effects should be mainly responsible for the formation of theses cation-ligand complexes.

Figure 4 presents the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the free ligands. It is seen that in all cases, the HOMO is mainly localized over the phenyl or naphtyl group and has a  $\pi$  character. This is in accordance with the prediction of the MEP analysis as noted above, and reveals the potential of these regions to interact with the cation species. As expected, the energy of the HOMO of TMU-21 and TMU-6 is more negative than those of TMU-23 and TMU-24 (Figure 4), which is in agreement with the lower tendency of the former ligands to interact with the cations considered here. Note that in the HOMO of TMU-21 and TMU-6, there are some important contributions from the pyridine groups, which is due to resonance effects within these molecules. Such resonance effects should be responsible for the stabilization of the HOMO state of these ligands and hence their lower potential to interact with the cation species. Moreover, by comparing the HOMO energies of the ligands of TMU-6 and TMU-21 as well TMU-23 and TMU-24 (Figure 4), it can be found that the HOMO of TMU-21 and TMU-24 ligands have more negative energies than those of TMU-6 and TMU-23, respectively, indicating more resonance effect of naphthyl group respect to phenyl group; that this is consistent with the obtained experimental results.

On the other hand, the LUMO state of these free ligands is delocalized over the entire molecular framework and has a  $\pi^*$  character. As evident from Figure 4, the energies of these LUMOs increase (in absolute value) as TMU-6 > TMU-21 > TMU-23 > TMU-24. As seen, the LUMO of TMU-6 and TMU-21 exhibits a more pronounced delocalization on the central phenyl or naphthyl group than TMU-23 and TMU-24 ligands. These results suggest that the different electronic structure of these ligands should be responsible for the observed adsorption efficiency of the MOFs towards the considered heavy metal ions.

**Table 4**. The calculated most negative MEP value ( $V_{S,min}$ ) and Mulliken atomic charge (Q) over nitrogen or oxygen atom of the isolated ligands

Ligands	V <sub>S,min</sub> (kcal/mol)	Q (e)
TMU-6	-16.7	-0.157
TMU-21	-13.8	-0.109
TMU-23	-29.5	-0.561
TMU-24	-28.5	-0.550



Figure 4. The frontier molecular orbitals (isovalue=0.02 atomic unit) and their energies (in atomic unit) of the free ligands

## 4. Conclusions

Here, we examined adsorption behavior of some MOFs having different functional groups in their pillar structures for adsorption of some heavy metal ions. For this purpose, four isoreticular zinc(II)-based MOFs were selected and synthesized by mechanochemical method such that their differences were in type of the functional group (imine or amide) and being phenyl or naphthyl group in their pillar structures. It was found that being of amide and phenyl groups in the pillars causes to its more tendency to adsorption of metal ions compared to the MOF with imine and naphthyl groups. This can be attributed to more basicity of the amide group respect to the imine group that results to the more strength interaction of metal ions with the MOFs coordination sites. On the other hand, the more resonance of electron density of the functional groups by the naphthyl group compared to the phenyl causes to decline of the adsorption ability of the MOFs.

The evaluation of the adsorption behavior of the metal ions by four MOFs at high concentrations, found that all four MOFs having almost same free space show similar  $Q_m$  for each of the metal ions. Moreover, some theoretical studies were desighed and performed to verify the experimental results. According to the DFT calculations, the absolute MEP values at the nitrogen/oxygen atoms of the ligands corresponding to the MOFs decreased as TMU-23 > TMU-24 > TMU-6 > TMU-21, indicating decrease in the charge density of the related functional groups. This also reveals that the electrostatic interactions between the functional groups of the MOFs and the metal ions is mainly responsible for the metal ion adsorption on MOFs. Furthermore, from frontier molecular orbital analysis, it was found that the lower tendency of TMU-6 and TMU-21 ligands to adsorb the metal cations can be attributed to the resonance effects within these molecules. This means that the electronic structure of the ligands is responsible for the different adsorption pattern of the MOFs towards the considered heavy metal ions. Eventually, it can be said that TMU-23 with proper functional groups, high porosity and good water stability,

providing high adsorption efficiency can be the promising material for application in extraction

and removal of metal ions from water samples especially for Pb<sup>+2</sup> ions.

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## Functional group effect of Isoreticular metal-organic frameworks on

### heavy metal ion adsorption

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We examined adsorption behavior of some MOFs having different functional groups in their pillar structures for adsorption of some heavy metal ions.