

# Application of a terephthalate and pyrazine-based MOF in Cr adsorption

Zahra Rezaee<sup>1</sup>, Faranak Manteghi<sup>1,\*</sup>

<sup>1</sup>Department of Chemistry, Iran University of Science and Technology, Tehran, Iran

\*[f\\_manteghi@iust.ac.ir](mailto:f_manteghi@iust.ac.ir)

## **Abstract:**

In this study, a terephthalate and pyrazine-based metal-organic framework was prepared using the oxygen and nitrogen donor ligands through the hydrothermal method. In the MOF, cobalt and nickel ions were selected as metal nodes which are connected by terephthalate and pyrazine linkers. The as-prepared MOF was utilized as Cr adsorbent in water by ultrasonic method. The MOF capacity towards chromium ion adsorption was obtained about %96 in 50 ppm initial concentration. In order to characterize and determine the morphology of the title MOF, the FT-IR and XRD methods were applied, while the chromium concentration before and after adsorption was determined by the ICP method.

**Keywords:** Terephthalate; Pyrazine; MOF; Chromium Adsorption

## **Introduction**

Today, water contamination becomes as a worldwide challenge due to growing various industrial activities such as food processing, mining, oil, agricultural, textile, leather, pharmaceutical industries and so on [1]. Hexavalent chromium, Cr(VI) is highly toxic and mutagenic when inhaled. Ingestion of chromium(VI) in water has been linked to stomach tumors, moreover, it may cause allergic contact dermatitis (ACD). Chromium is naturally present in the environment in trace amounts, but it is used in rubber and stainless steel manufacturing, chrome plating, dyes for textiles, tanneries, etc. Irrigation water standards for chromium are 0.1 mg/L [2]. Chromium, especially hexavalent chromium, is highly toxic to fish, because it is easily absorbed across the gills, readily enters blood circulation, crosses cell membranes, and bioconcentrates up the food chain. In contrast, the toxicity of trivalent chromium is very low, attributed to poor membrane permeability and little biomagnification [3].

Herein, we investigate the adsorption performance of an MOF, formulated as  $[\text{CoNi}(\mu_3\text{-tp})_2(\mu_2\text{-pyz})_2]$  toward various metallic pollutants.

## Experimental

### *Synthesis of $[\text{CoNi}(\mu_3\text{-tp})_2(\mu_2\text{-pyz})_2]$*

The title MOF was obtained from the mixture of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (1 mmol),  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (1 mmol), terephthalic acid ( $\text{tpH}_2$ ) (2 mmol), pyrazine (pyz) (2 mmol) and  $\text{H}_2\text{O}$  (14 ml). The suspension was stirred and then transferred to a 23 ml teflon-lined stainless steel autoclave to heat up for 48 h. After slow cooling to room temperature, the product was filtered, washed with distilled water and dried in air as reported in literature [4].

The adsorption capacity (AC) and removal efficiency (RE) of heavy metal ions by the title MOF as an adsorbent could be calculated as follows:

$$AC = \frac{V(C_0 - C_i) \times 207}{W_g} \times 1000$$

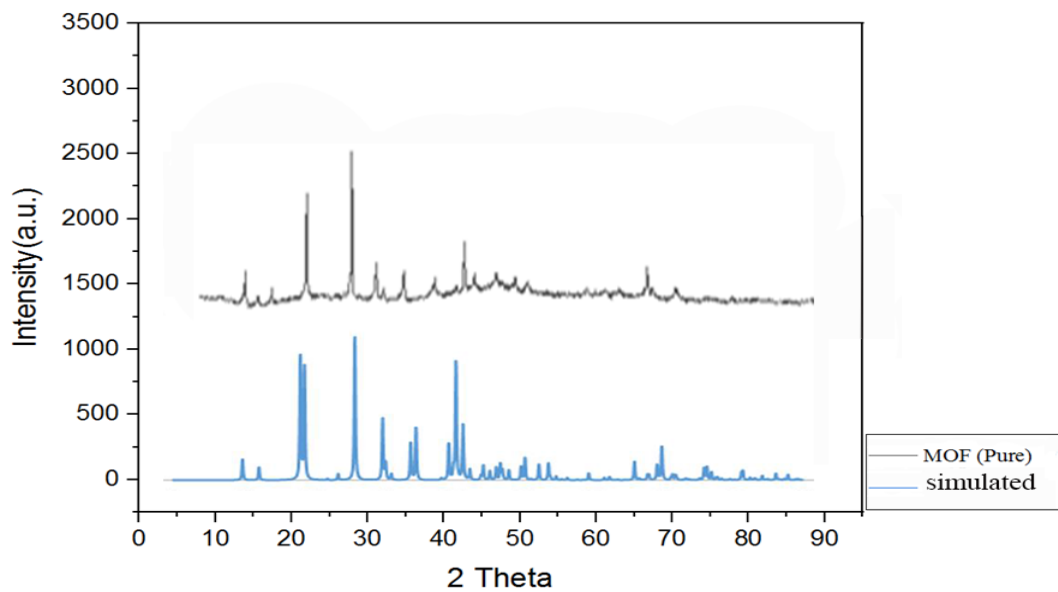
$$RE(\%) = \frac{(C_0 - C_i)}{C_0} \times 100$$

In these equations,  $C_0$  (mol/L) is the initial concentration of heavy metal ions and  $C_i$  (mol/L) is the concentration after a determined adsorption time  $t_i$ , respectively.  $V$  (ml) is the solution volume of heavy metal ions, and  $W_g$  (mg) is the dosage of MOF. When the adsorption reaches to the equilibrium point,  $C_e$  is equal to  $C_i$  and at the same time, AC is equal to  $Q_e$ , namely, equilibrium adsorption amount.

## Results

### *XRD pattern of $[\text{CoNi}(\mu_3\text{-tp})_2(\mu_2\text{-pyz})_2]$*

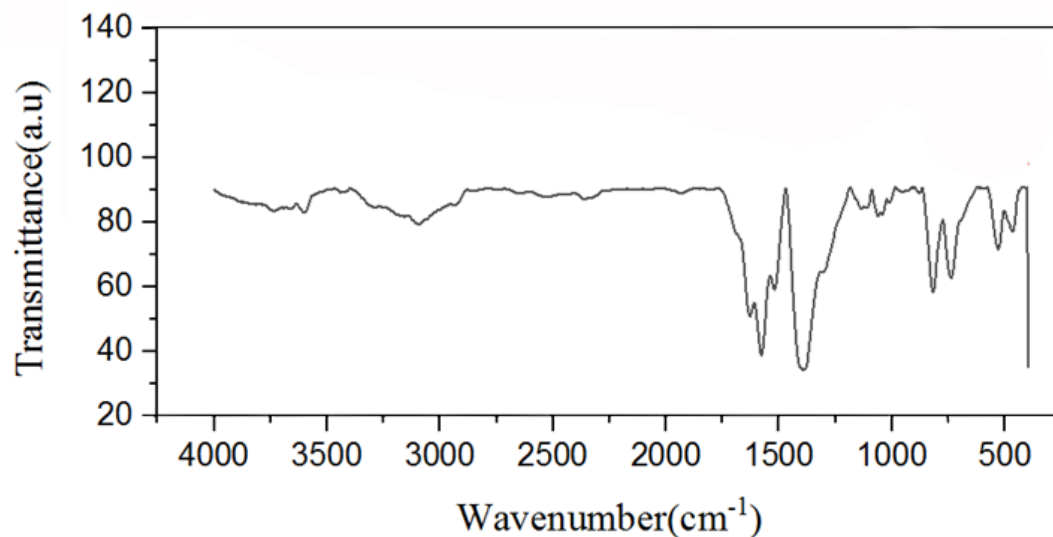
The XRD pattern coincided with the simulated XRD of the similar previously reported MOF [4] confirming the correction of the solvothermal method, as shown in Fig. 1.



**Figure 1** X-ray diffraction pattern of the synthesized MOF (up) and simulated pattern (Down)

### FT-IR spectrum

As shown in Fig. 2, each therephthalate linker joins three  $\text{Co}^{2+}$  and three  $\text{Ni}^{2+}$  centers with two different coordination modes of bidentate and bridging bis-monodentate.



**Figure 2** FT-IR spectra of the synthesized MOF

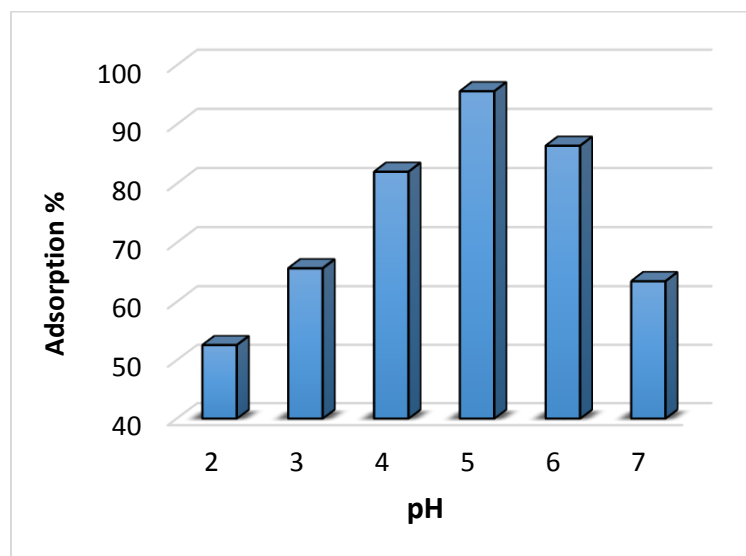
Bridging modes of two tp linkers leads to the formation of planar 10-membered rings of  $\text{Ni}_2\text{Co}_2\text{C}_2\text{O}_4$  units. These 2D planes containing rectangular grids are pillared by pyrazine to create the 3D network.

### Cr adsorption results at different pH

Adsorption of chromium ion on the synthesized MOF in different pH was studied.

#### *Effect of pH*

As mentioned in literature, adsorption process is correlated with the pH. At low pH,  $\text{H}^+$  ions compete with analyte cations to occupy the active sites of adsorbent. On the other hand, at highly basic pH,  $\text{OH}^-$  causes that the analyte precipitate in the solution and incorrect data will be received. Therefore, finding an optimum pH is necessary in the adsorption process. First, a 50 ppm solution of chromium was prepared and then, 0.01 g of adsorbent was added to 50 ml of it in separate flasks. As can be seen in Fig 3, at pH 5 the amount of adsorbed chromium reaches to the maximum value. Consequently, other tests were followed in this pH.



**Figure 3** Diagram of the pH effect on Cr uptake using the title MOF as an adsorbent.

### Conclusion

During this visit, the substrate level of Cr from aqueous solution can be controlled using the title metal-organic framework. The optimum conditions for Cr ion surface

display were as follows, the Cr ion coated by Co/Ni MOF, pH 5, absorbent amount = 0.01g and initial concentration = 50ppm.

## References

- [1] T. Pradeep, Anshup, "Noble metal nanoparticles for water purification: A critical review", *Thin Solid Films* 517 (2009) 6441-6478.
- [2] R.G. Lefavi, R.A. Anderson, R.E. Keith, G.D. Wilson, J.L. McMillan, M.H. Stone, "Efficacy of chromium supplementation in athletes: emphasis on anabolism", *International Journal of Sport Nutrition* 2 (1992) 111-22.
- [3] A.R. Ahmed, A.N. Jha, S.J. Davies, "The efficacy of chromium as a growth enhancer for mirror carp (*Cyprinus carpio* L): an integrated study using biochemical, genetic, and histological responses", *Biological Trace Elements Research* 148 (2012) 187-197.
- [4] Abbasi, A., T. Moradpour, K. Van Hecke, "New interpenetrated mixed (Co/Ni) metal-organic framework for dye removal under mild conditions", *Inorganica Chimica Acta* 430 (2015) 261-267.