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Proceeding Paper

Pb(II) Adsorption by a Calcium Metal-organic Framework †

Mina Aghaee [1] and Faranak Manteghi [1,*]

Department of Chemistry, Iran University of Science and Technology, Tehran, Iran
* Correspondence: f_manteghi@iust.ac.ir

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Abstract: Among the water pollution sources, heavy metals are considered as the most hazardous, because of high toxicity to human health and badly damage the kidneys, brain and nerves as well as causing birth defects. Based on the promising feature of metal-organic frameworks, MOFs, they could act as a favorable candidate for heavy metal removal applications. A calcium-based metal-organic framework was synthesized by the deposition method using benzene-1,2,4,5-tetracarboxylate as linker. After characterization of the MOF performed using XRD, SEM and FTIR analyses, it was applied to efficient adsorption of Pb(II) pollutant ions. The potential of obtained MOF, $[Ca(H_2btec).H_2O]_n$, H_2btec: benzene-1,2,4,5-tetracarboxylic acid was investigated by the adsorption of Pb(II) ions in aqueous solution, separation of the adsorbent by centrifugation and finally measuring the residual Pb(II) ions by ICP-AES method.

Keywords: metal-organic framework; green synthesis; heavy metal; adsorption

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1. Introduction

With developing industrial efforts, decreasing clean water, increasing amount of water pollution and toxic pollution agents became a basic problem of human being. Wastewaters contain inorganic chemicals such as heavy metals which easily pollute the environment. The metals including lead (Pb), arsenic (As), mercury (Hg), chromium (Cr), nickel (Ni), barium (Ba), cadmium (Cd), cobalt (Co), selenium (Se), and vanadium (V) are poisonous even in ppb (parts per billion). These toxic elements inter food and water and even items like toys and damage kidneys, brain, nerves, digestive system. The concentration of lead (Pb^{2+}) in water must not overpass ppb in drinking water. Based on reticulating metal ions and organic carboxylates as linker extended them and allowed the design of structures and increasing absorption in them. In this regard, metal-organic framework (MOF) are attractive due to their exceptional high porosity. Regard to absorption heavy metals is important but green synthesize also valuable. For every materials was synthesized used H_2O as solvent, as well as was used green synthesize method. The application of such green-based adsorbents could decrease heavy metal ions from wastewater [1,2].

2. Experimental Method

2.1. Synthesis of Exprimental $[Ca(H_2btec)\cdot H_2O]_n$

1 mol (0.255g) of benzene-1,2,4,5-tetracarboxylic acid (H_2btec) was dissolved in 20 cc water, then 10 cc ethanol added for 2 min on stirring in room temperature until dissolved absolutely. 2mol (0.47g) $Ca(NO_3)_2$ dissolved in 10 cc water, was mixed these two solutions while stirring at 100 °C, 600 rpm for 2h, the resulting solution was cooled to room temperature. The precipitated white powder was dried in room temperature for 1 day [3].

2.2. Pb(II) Ions Adsorption

In this case, the effect of different parameters such as Pb(II) initial concentration on the absorbance mass and contact time were studied. For the isotherm adsorption survey, all the experiments were at room temperature by adding 10 mg of $[Ca(H_2btec)\cdot H_2O]_n$ to 30 mL of Pb(II) solution with first concentration of 12, 25, 50, and 100 mg l^{-1}. Afterwards, the solution was shaken for 15 min in 100 rpm.

The Pb(II) capacity is an important factor which appoints the adsorption capacity for eliminating specific amounts of contaminants. The following Equations (1) and (2) state the contaminant elimination percentage.

$$\%R = \frac{(c_0 - c_e)}{c_0} \times 100 \tag{1}$$

$$q_t = \frac{(c_O - c_v)v}{m}(\tag{2}$$

In which C_0 (mg l^{-1}) and C_e (mg l^{-1}) are the initial concentration and equivalent concentration of contaminants, respectively. V (ml) introduces as solution volume, m (g) as adsorbent mass and q_e (mg/g) as surface equivalent adsorption capacity.

2.3. Results and Discussion

2.3.1. XRD Pattern

Figure 1 shows the XRD pattern of $[Ca(H_2btec)\cdot H_2O]_n$, exhibits a sharp and highly intense peak at 2θ 26.5°.

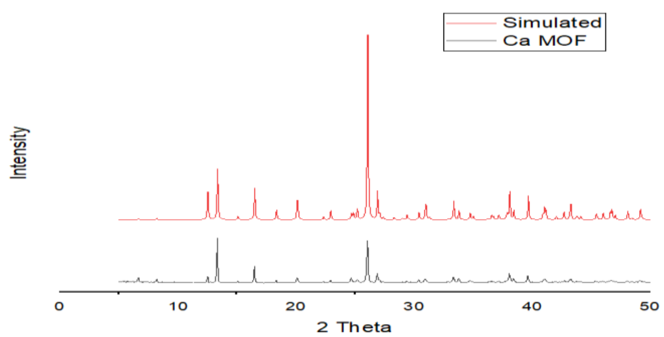


Figure 1. The XRD pattern of $[Ca(H_2btec)\cdot H_2O]_n$.

2.3.2. FTIR Spectrum

The bands at 3500 cm^{-1} and 3650 cm^{-1} are attributed respectively to carboxylic groups and water molecules. The band at 900-690 cm^{-1} is attributed to aromatic ring of linker.

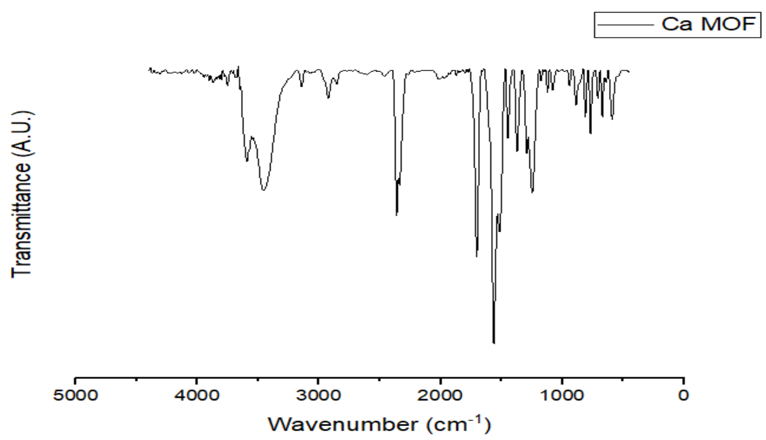


Figure 2. FTIR spectrum of $[Ca(H_2btec)\cdot H_2O]_n$

2.3.3. Scanning Electron Microscopy

The result shown in Figure 3, illustrates rod shapes of the MOF particles, with average size of 1-3 μm.

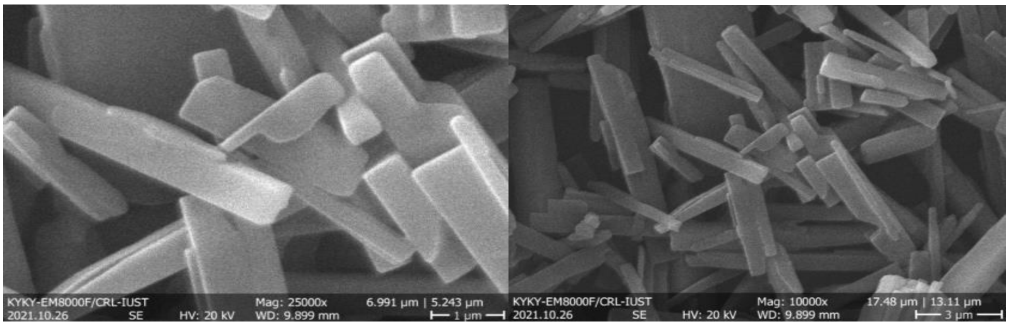


Figure 3. The SEM images of $[Ca(H_2btec)\cdot H_2O]_n$.

2.3.4. Effect of pH and Time on Adsorption

The amount of Pb(II) adsorbed onto $[Ca(H_2btec)\cdot H_2O]_n$ is a function of time and pH. As shown in Figure 4, the best pH is 5, in which more than 95% adsorption is occurred. Moreover, Pb(II) adsorption is increased to 96% mg g^{-1} at 15 min, shown in Figure 5 as the highest adsorption and then it remains constant till 35 min.

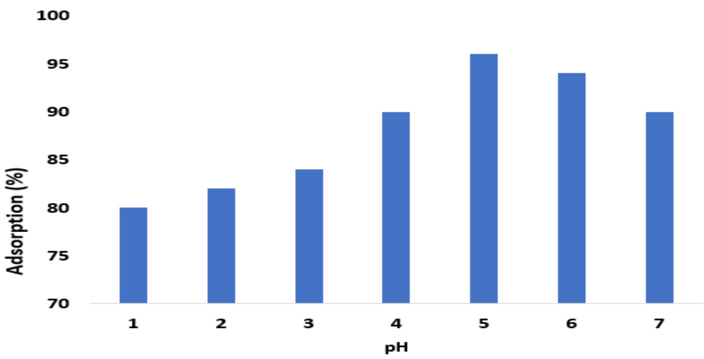


Figure 4. The effect of pH on lead absorption by $[Ca(H_2btec)\cdot H_2O]_n$.

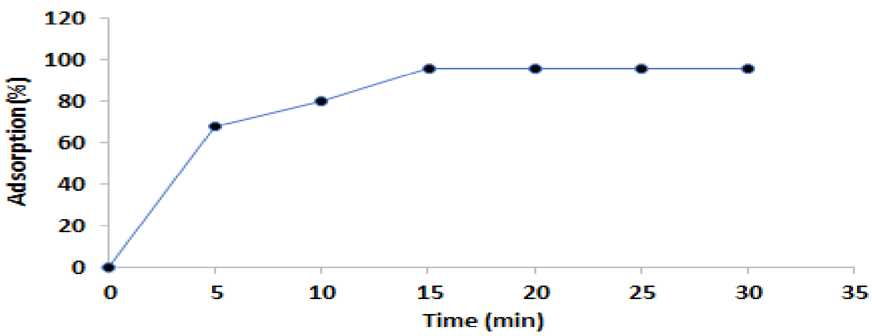


Figure 5. The effect of time on the amount of lead absorption by the $[Ca(H_2btec)\cdot H_2O]_n$.

2.3.5. Adsorption of Metallic Ions

On examining toxic metallic ions including lead, copper, cadmium, chrome and barium, we found out that the title MOF can adsorb the former, most effectively. This can be seen in Figure 6, in which Pb(II) ions is adsorbed near to 100%, much better than the others.

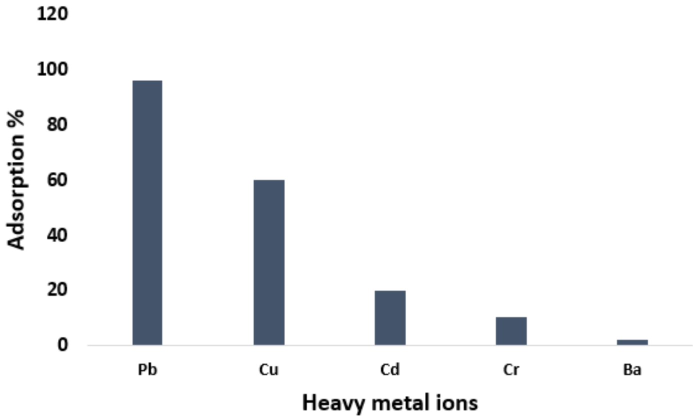
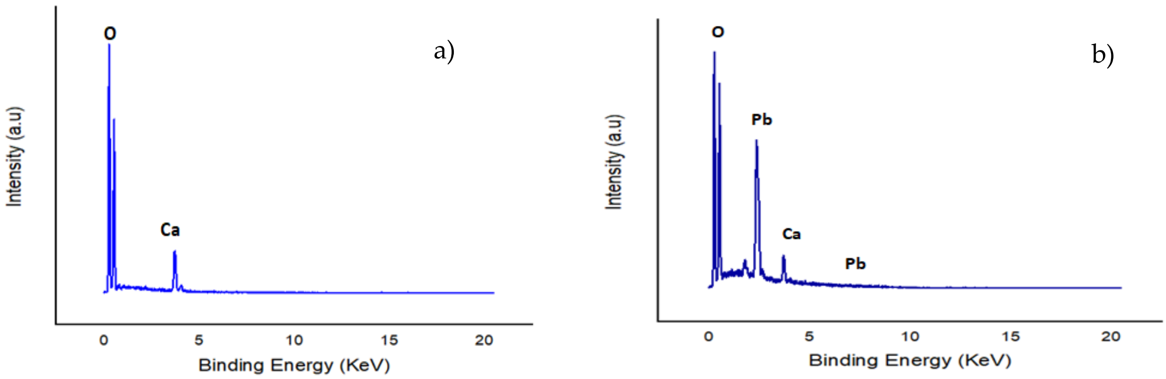


Figure 6. Comparative adsorption of various toxic ions.

2.3.6. Desorption After Adsorption

After adsorption of Pb(II), we tried to desorb it from the adsorbent, for examining whether the structure of MOF has been remained or not. Primarily, we search for lead ions and as shown in Figure 6, EDX results illustrates the presence of the ions in the MOF after adsorption. Afterwards, we desorb the ions by removing them from the MOF in D.I. water by three times of washing in RT, separation and drying the MOF. The XRD pattern of the empty MOF shown in Figure 8 illustrates some peaks similar to the initial MOF. This reveals that the MOF's structure has not been changed after adsorption and desorption of lead ions.



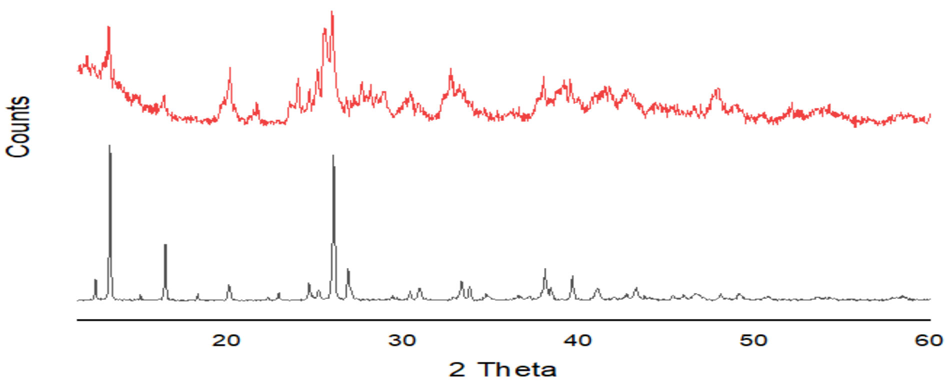


Figure 8. The XRD pattern of $[Ca(H_2btec)H_2O]_n$ before adsorption (black, bottom line) and its XRD pattern after three times of Pb(II) adsorption and desorption (red, top line} .

3. Conclusion

In this work, $[Ca(H_2btec)\cdot H_2O]_n$ has been investigated for the absorption of heavy metals and it has successfully absorbed about 96% of the Pb(II) in water after 15 min. It should be considered that the adsorbent is synthesized in an environmentally friendly approach, and the aim was absorbing a pollutant that is very harmful to the environment. Therefore, this can be research in the way with green chemistry. Finally, we found out that the MOF's structure has been remained well, after three times of washing in aqueous solution.

References

1. Rouhani, F.; Morsali, A. Fast and Selective Heavy Metal Removal by a Novel Metal-Organic Framework Designed with In-Situ Ligand Building Block Fabrication Bearing Free Nitrogen. Chem. A Eur. J. **2018**, *24*, 5529–5537.
2. Zhu, H.; Yuan, J.; Tan, X.; Zhang, W.; Fang, M.; Wang, X. Efficient removal of Pb^{2+} by Tb-MOFs: Identifying the adsorption mechanism through experimental and theoretical investigations. Environ. Sci. Nano **2019**, *6*, 261–272.
3. Shunfu Du, Chunqing Ji, Xuelian Xin, Mu Zhuang, Xuying Yu, Jitao Lu, Yukun Lu, Daofeng Sun, Syntheses, structures and characteristics of four alkaline-earth metal-organic frameworks (MOFs) based on benzene-1,2,4,5-tetracarboxylicacid and its derivative ligand, J. Mol. Struct., 2017, 1130 (15), 565-572. [10.1016/j.molstruc.2016.10.008].

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