

DEVELOPMENT OF METAL – ORGANIC FRAMEWORKS, SURFACE ABSORBENT OF BIOLOGICAL POLLUTANTS, INCLUDING HEAVY METALS

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ABSTRACT

The global level of environmental pollution with metals has increased greatly in the last two centuries. The presence of some heavy metals in aquatic ecosystems is a constant threat to the health of human societies. Many of these metals, such as chromium (Cr), copper (Cu), iron (Fe) and cobalt (Co) are essential for plants, living organisms and the human body. While large amounts of these metals are toxic and dangerous for living cells. Porous coordination polymers or metal-organic frameworks (MOFs) are a new class of crystalline and microporous materials that include inorganic secondary structural units connected by organic parts in the form of three-dimensional arrays through coordination bonds. Evaluation of the relationship between the structure and performance of metal-organic frameworks is an interesting topic discussed in this work. The metal-organic framework, $\{[\text{Zn}_2(\text{OH})(\text{AZPY})(\text{BDC})_{1.5}]\cdot\text{H}_2\text{O}\}_n$ was successfully chemically saturated. The surface adsorption efficiency of the considered framework for some heavy metal ions was investigated in order to investigate the effect of the type of functional groups in different pillars in the adsorption process. The results showed that the framework with the Omid factor group showed a better result.

Keywords: Environmental pollution of aquatic ecosystem, Porous coordination polymer of metal-organic frameworks, Surface adsorption of heavy metals removal

INTRODUCTION

The global level of environmental pollution with metals has increased greatly in the last two centuries. The presence of some heavy metals in aquatic ecosystems is a constant threat to the health of human societies. Many of these metals such as chromium (Cr), copper (Cu), iron (Fe) and cobalt (Co) are essential for plants, living organisms and the human body [1]. While large amounts of these metals are toxic and dangerous for

living cells. Minor amounts of heavy metals such as cadmium, lead, copper and chromium, which are usually present in contaminated soils, can be harmful to microbes and plants as well [2]. in such a way that they can aggravate the symptoms of iron deficiency and as a result cause their growth to slow down. In addition, heavy metals can combine with sulfhydryl groups of proteins and cause a decrease in enzyme activity. Cadmium and lead show severe toxicity even in low concentration [3]. While determining the exact amount of heavy metal ions in environmental samples is highly desirable, it faces two main problems: 1- the effects of interaction with the background 2- the usual low concentrations of heavy metal ions that may be lower than the limit to recognize many analytical techniques [4].

Porous coordination polymers or metal-metal frameworks (MOF) are a new class of crystalline and microporous materials that include inorganic secondary structural units that are connected by organic parts in the form of three-dimensional arrays through coordination bonds [5].]. This field of research has attracted the attention of many researchers in the last two decades. Metal-organic frameworks have many structural variations and have high pore volumes. So far, many metal-organic frameworks with a surface area greater than 1000 m²/g have been reported [6]. These compounds, having properties such as versatility and inherent flexibility, the possibility of placing chiral centers in organic parts and placing various functional groups in the frameworks, have a superior position compared to other crystalline solids. These frameworks are used in many fields, including gas storage, catalysts, sensors, electrical conductivity, luminescence, and drug release due to their diverse and interesting structures and favorable physical and chemical properties. [7,8] One of the most attractive applications of these frameworks is in the field of trapping heavy metal ions, during this process, heavy metal ions are chelated between the metal ion and the functional group in the ligand in the metal-organic framework. The shape and size of the pores lead to high selectivity, which ultimately causes surface adsorption of the guest. In this article, two topics are discussed. 1: Synthesis of metal-organic frameworks with different functional groups 2: Investigating the effects of different functional groups on the performance and efficiency of surface adsorption [9].

EXPERIMENTAL PART

All materials used, zinc (II) nitrate 6A, 1,4-benzenedicarboxylic acid and AZPY were obtained from Sigma Aldridge. First, we prepare a mixture of 0.045 grams of benzene dicarboxylic acid along with 0.081 grams of salt on nitrate and 0.05 grams of AZPY in 100 ml



of a mixture of water and ethanol solvents in a ratio of 1:1. After mixing in a stirrer for 15 minutes, transfer the resulting mixture to a suitable volumetric flask and put it in the reflux system for 48 hours at a temperature of 80 degrees Celsius.

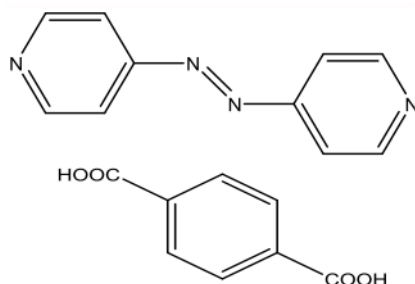


Figure 1 Chemical structure of APY and 1,4-BDC

Then remove the resulting sediment from the reflux system and after washing with solvent put it at 120 degrees Celsius for 2 hours to dry.

After that standard solution (1000mg/L) of ions, Fe(II) Cu(II), Cd(II), Co(II), Pb(II) Cr(III), by dissolving a specific amount of nitrate salts The solid phase extraction of heavy metal ions was carried out with the following steps: First, 100 ml of metal ions solution was added to a 200 ml beaker containing 10 mg of MOF as an adsorbent. The pH value of the solution was adjusted to 8. After stirring the solution for 10 minutes to accelerate the adsorption of analytes on the MOF, the solution was centrifuged at 6000 rpm for 2 minutes. Then the adsorbent was separated from the solution. The analytes adsorbed by the adsorbent were mixed with 200 μ L of The detergent containing 0.4 methyl ethylene diamine tetraacetic acid (EDTA) was separated. To check the adsorption capacity of MOF, 3 mg of the desired framework was added to 15 ml of metal ion solutions at different concentrations in the range of 200-200 ml. added grams per liter and then the pH was adjusted to about 6. The solution was stirred for 15 minutes at room temperature, when the equilibrium point was reached, the adsorbent was separated by a centrifuge and the concentration of the remaining ions in the solution was determined by ICP-OES.

RESULTS AND DISCUSSION

Thermal analysis (TGA) of the synthesized framework can be seen in Figure 2x. In the range of 150-300, no significant weight loss was seen, which indicates that their pores were free of any guest molecules. Above this temperature, the desired framework begins to decompose. The prepared framework is immersed in water and some organic solvents such as ethanol, acetonitrile and dichloromethane for at least 24 hours at room temperature to determine if they are stable in these solvents.

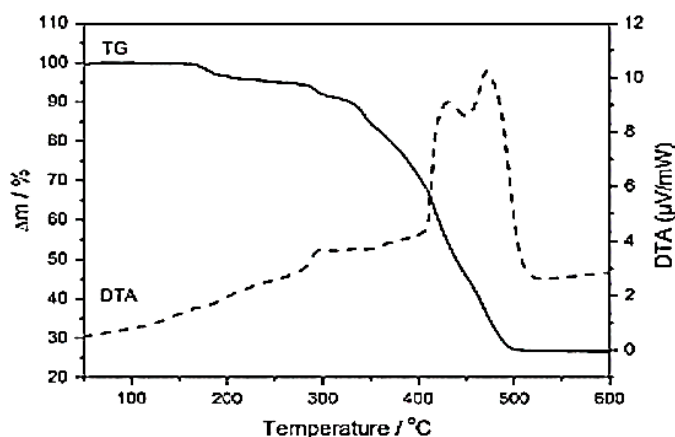


Figure 2. Thermal analysis (TGA)

In infrared spectroscopy (FT-IR) analysis, the bond (C-H) related to AZPY appeared in the region of CM-11504. Among the carboxyl-COO-related ship bonds appeared in the CM-1 region of 1586. In the region CM-1 186 onwards, the presence of zinc element is visible.

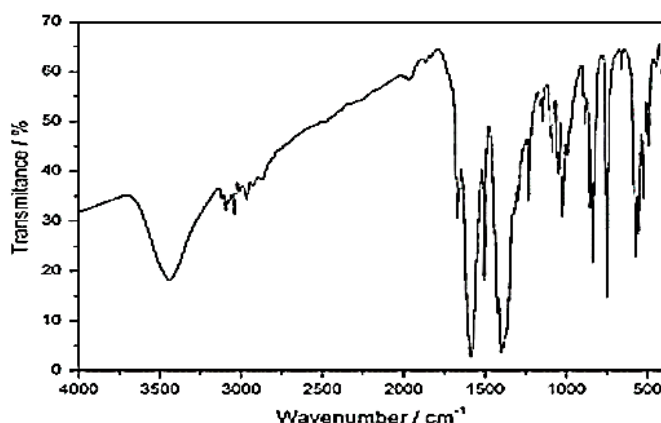


Figure 3. Spectrum analysis (FT-IR)

Wide-angle X-ray scattering (WAXS) experiments showed that the framework structure of the compound was preserved by removing the water molecule upon reheating WAXS. on a sample shows a pattern (Figure 4, curve b), which, despite the line broadening, shows that the structure of the sample closely matches that calculated from the single crystal fraction data (Figure 5, curve a) after heating Up to 250 °C, the WAXS pattern of the material showed that it was still crystalline (Figure 4, curve c) and retained the same diffraction lines as the sample. Before heating (Figure 4, curve b), although the peaks shifted to a lower degree of observation The shift of the diffraction lines showed an increase in the unit cell parameter upon heating. At 250 °C this may be caused by small structural changes, for example, the rotation of the phenyl rings of the 1,4-BDC ligand, which during Removal of water without loss of crystalline state are located in the channel.

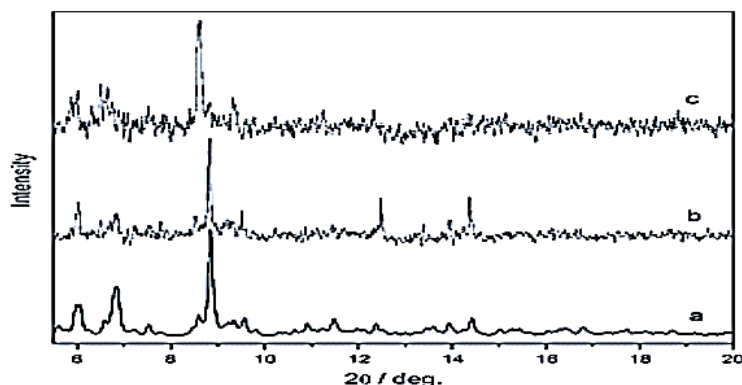


Figure 4. X-ray analysis

To obtain the highest sensitivity and precision, the equilibrium time of the adsorption process must be determined. For this purpose, subsequent experiments were performed to change the extraction time by changing the time in the range of 2-20 minutes. It was observed that there is an increase in the extraction efficiency with an increase in the extraction time from 2-10 minutes, while no improvement in the efficiency was observed with a further increase in the time. Therefore, the time of 10 minutes was used for further experiments. This fast absorption process can be attributed to the short diffusion path of metal ions and the high porosity and surface area of the Fler-Al framework, which cause the equilibrium to be reached in a shorter contact time. The effect of adsorption time was also investigated and it was found that after 2 minutes, no significant change in efficiency and adsorption occurs. (Figure 5)

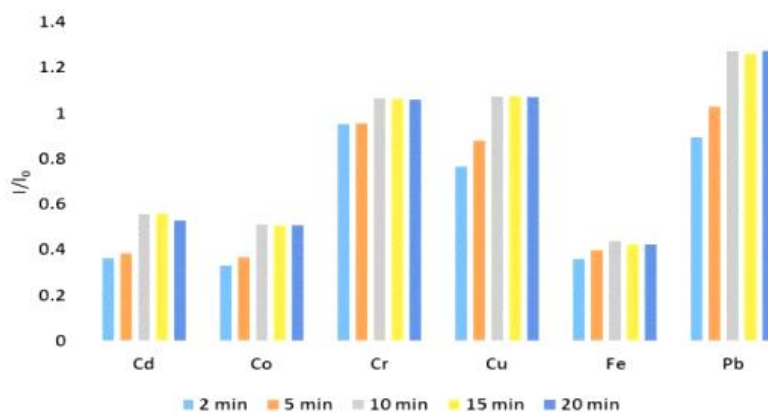


Figure 5. Effect of time on extraction efficiency

CONCLUSION

Here, we investigated the adsorption behavior of metal-organic frameworks that have different functional groups in their pillar structure for the adsorption of some heavy metal ions. For this purpose, the centered framework was synthesized using a chemical method so that their differences are in the type of functional group (imine or amide) and quinyll or

naphthalene group in their pillar structure. The results showed that the presence of amide and quinyl groups in the pillar makes it more inclined to absorb metal ions compared to the framework with imine and naphthalene groups. This can be attributed to the basicity of the Omid group compared to the imine group, which leads to the interaction of metal cations with the coordination sites in the framework. On the other hand, the increase of electron resonance in the functional groups by the naphthalene group compared to quinyl decreases the absorption ability of the considered framework.

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