Metal-Organic Frameworks for Removing Radioactive Wastes in Water

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Abstract. Humans only got a limited number of natural resources to survive and exploit. Water, as one of the limited natural resources, has been polluted because of human rapid development in many fields of industries. Nuclear wastes, as one of the pollutants, bring serious or in-reversible harm not only to the environment but also to human health. Metal-organic frameworks (MOFs) materials could be applied to various kinds of areas and also got a huge potential in the treatment of wastewater with radioactive wastes. This article mainly talks about the research progress of MOF material used in the field of radioactive wastewater treatment and introduces the preparation and characteristics of MOF-5, HKUST-1/KCoFC, and UiO66-COOH materials. Additionally, factors including solid-liquid ratio, initial concentration, reacting time, and pH value that affect the adsorption capacity on U(VI), Cs, and Sr are analyzed. Some research on MOFs materials used to remove different kinds of radioactive substances is also highlighted. Finally, some problems that still exist are raised, and expectations and directions for future development in this field are provided.

Keywords: Metal-organic frameworks; radioactive wastewater treatment; U(VI); Cs⁺; Sr²⁺.

1. Introduction

Water, as one of the most important resources for people’s life, seems to be abundant because the surface area of the planet we’re living on is covered by water resources. But only a small amount of them could be used for human survival purposes, and especially in nowadays situation of explosive population growth, the demands on this source will only increase and let it become more and more valuable. However, with the rapid development of global industry and economy, various kinds of environmental problems such as global warming, acid rain, and reduction in biodiversity have been brought to people’s attention, and also, those problems include the pollution of water. All these factors make the problem of water scarcity more serious than before, so the treatment and recycling of water are considered one of the most efficient ways to dealing the problem of water pollution and water scarcity until now [1].

Many industries contribute to the pollution of water, including textiles, leather, paper, printing, dye, plastic, chemical manufacturing, coal mining, and also, the nuclear energy industry [2]. Compare to those carbon-based fossil fuels which are continuing to decline, nuclear energy has many merits: it won’t create polluted gases in the atmosphere, it won’t create carbon dioxide which causes global warming, and it has a much higher energy density than those carbon-based fuels, and the metal sources used for nuclear energy store in Earth are enough for a human to use for thousands of years if people could utilize them effectively [3]. But those nuclear power plants also produce tons of radioactive wastes that may cause air and water pollution if they haven’t been treated properly, and that may cause in-reversible damage to the environment and also human health. So, how to exploit nuclear energy productively and treat nuclear waste water appropriately is the challenge that every country in the world that wanted to utilize nuclear power widely needs to face [3].

Metal-organic frameworks (MOFs) are known as coordination polymers, the lattices of which are composed of secondary building units and organic linkers [4]. The MOFs material could be synthesized by one organic ligand with different metal sources such as Zn, Cu, Mn, a lanthanide metal, and alkali metals, or by many kinds of organic ligands, such as carboxylate-based and azolate-based, and one metal source [5]. Figure. 1 shows the structure of some inorganic secondary building units and organic linkers [3]. As a new crystalline material, MOF material got a great potential application
value in many areas because of its high porosity, adjustable shape and size of holes, and large surface area [2]. In recent years, there are many reports of the application of MOFs material in radioactive wastewater treatment. Various kinds of MIL-100 have been used and researched on the adsorption capacity on U(VI). UiO-66-AO has been reported to have a great potential for removing Eu(III) in radioactive water. And magnetic Fe3O4@ZIF-8 has been reported to be highly efficient in removing both U(VI) and Eu(III) (up to 75%), and so many other than these [3,6].

![Inorganic secondary building units (A) and organic linkers (B) [3].](image)

2. MOFs Materials for Treatment of Radioactive Wastewater

Now scientists have already figured out many types of MOF materials and apply them to solving real-life situations, and of course including the MOF materials that could be used for radioactive wastewater treatment. The following part of the essay is going to talk about some MOF materials like MOF-5 that could be used to remove U(VI) in wastewater, HKUST-1/KCoFC composite material that could be used to remove Cs⁺, and UiO66-COOH that could be used to remove Sr²⁺, and some factors including the solid-liquid ratio, the initial concentration of radioactive substances, the reacting time, and the pH value that might affect the adsorption capacity of these materials [6,7,8].
2.1 Preparation and Adsorption of MOF-5 Material for U(VI)

2.1.1 Preparation of MOF-5

The MOF-5 was generally prepared by solvothermal methods. Let Zn(NO$_3$)$_2$·6H$_2$O, C$_{10}$H$_{10}$O$_4$, and polyvinyl pyrrolidone(PVP) dissolve in the solvent dimethyl formamide(DMF) and anhydrous ethanol; then put this mixture into an autoclave made by stainless steel and lined with Teflon, and keep it for three hours at a temperature up to 140 celsius; after cold down the mixture to the room temperature, collect the white product by using the methods of centrifugation, use DMF and CHCl$_3$ to wash it, and finally dry it in a temperature of 120 Celsius [6].

Whether the MOF-5 material has been successively produced could be tested by using Fourier transform infrared spectroscopy (FT-IR) [6]. The images of the scanning electron microscope (SEM) and transmission electron microscope (TEM) not only show the surface and its porous structure but also display the property of mutual growth of this crystal [6]. MOF-5 has four diffraction peaks around 6.8, 9.6, 13.6, and 15.3 degrees in its X-ray diffraction (XRD) diagram, corresponding to the characteristic diffraction of 200, 220, 400, and 420 [6]. The formation of the 420 peaks is because the structure of this material has changed after absorbing water, and the high definition and high resolution of peaks indicate the high degree of crystallinity of MOF-5 [6]. The X-ray photoelectron spectroscopy (XPS) that is used to study the chemical state and constituent elements of MOF-5 reveals that carbon, oxygen, and zinc are evenly distributed on the whole surface of MOF-5, and the C 1s XPS spectrum could be divided into three parts, including C-C functional group (65.02%), C-O functional group (13.65%), and C=O functional group (21.33%), which means that these functional group could provide enough reacting sites during the bonding process of MOF-5 and U(VI) [6].

2.1.2 Effect of the solid-liquid ratio on the adsorption of MOF-5

Based on the limitation of the number of active sites, functional groups, and contactable area of MOFs material, the solid-liquid ratio will be one of the important factors that affect the adsorption ability of MOFs material, and so it will be important for scientists to determine the best solid-liquid ratio [6]. Figure 2 shows the data of the sorption rate and the adsorption quantity when matching the equilibrium ($q_e$) [6]. As shown in the diagram, the removal rate of U(VI) increase rapidly from approximately 40% to 75% as the solid-liquid ratio increase from 0.06g/L to 0.15g/L; for the solid-liquid ratio from 0.15g/L to 0.3g/L where the speed of increase in sorption rate gets slower, the sorption rate increase to 84.4g/L; apparently, with solid-liquid ratio high than 0.3g/L, the rise in sorption rate is not obvious and stay below 90% [6]. On the contrary, the adsorption quantity is inversely proportional to the solid-liquid ratio [6]. These phenomena might be explained by the competition on active sites: the sorption rate increase sharply because more adsorption sites could be used to bond with U(VI) in a low solid-liquid ratio, but as the ratio is greater than 0.15m/L, the competition of active sites and the aggregation of solids partials low down the binding sites; the $q_e$ might decrease because of the competition of adsorption sites as the solid-liquid ratio increase [6].

![Fig. 2 The effect of the solid-liquid ratio of MOF-5 on the adsorption of U(VI) [6].](image-url)
2.1.3 Effect of pH value and ionic strength on the adsorption ability of MOF-5

Figure 3a shows the impact of pH value on the sorption of U(VI) at different concentrations of NaNO₃, Figure 3b shows the Zeta potential of MOF-5 material in different pH values, and Figure 3c shows the species distribution of U(VI) in aqueous solution [6]. In Figure 3a, the sorption rate increases quickly as the pH value increase from approximately 4.6 to 7.0 and keep at a high rate for pH greater than 7.0. That is because the MOF-5 tend to be negatively charged when the pH value is bigger than 4.6 as shown in Figure 3b, and most of the U(VI) exist as positive ions when the pH value is smaller than 7.0, so the electrostatic attraction force between these charged sources pulls them together and increase the sorption rate [6]. Additionally, according to Figure 3a, the effect of ionic strength on the sorption rate is not significant since there are not many differences between different concentrations of NaNO₃.

![Fig. 3](image-url) (a) The impact of the adsorption rate of MOF-5 on U(VI) in different concentrations of NaNO₃; (b) The Zeta potential of MOF-5 at different pH values [6].

2.2 Preparation and Adsorption of HKUST-1/KCoFC composite material for Cs⁺

2.2.1 Preparation of HKUST-1/KCoFC composite material

Let Cu(NO₃)₂·3H₂O dissolved in deionized water and trimesic acid C₉H₆O₆ dissolved in ethanol, then vibrate it by ultrasound for 15 minutes and mixed it with the solution of copper nitrate [7].
Stirring the mixture for 1 hour and put it into the reactor to react for 12 hours under the temperature of 1200 Celsius, then filtrate it to get a blue powder [7]. Finally, wash it with deionized water and ethanol and dry it in a vacuum for a night under the temperature of 1500 Celsius, then the product will be the HKUST-1 [7]. Put HKUST-1 to Co(NO\textsubscript{3})\textsubscript{2} 6H\textsubscript{2}O solution and stir it magnetically for 3 hours, then filtrate the products, wash it for times using deionized water, and dry it in a vacuum for 12 hours at 900 Celsius [7]. Repeat the above step, but change the Co(NO\textsubscript{3})\textsubscript{2} 6H\textsubscript{2}O to K\textsubscript{4}Fe(CN)\textsubscript{6} 3H\textsubscript{2}O, and the detergent will be both deionized water and acetone [7]. The final product will be the HOUST-1/KCoFC composite material.

Also, the product is HKUST-1/KCoFC could be tested by using FT-IR. When the stretching vibration peak of C≡N bond, the symmetric vibration peak of COO-, and the stretching vibration and bending vibration peaks of Fe-C bond exist, the products are the sample of HKUST-1/KCoFC [7]. In the graph of SEM, the surface of HKUST-1/KCoFC is much more coarse compare to HKUST-1 since the composite material has KCoFC particles distribute in its surface [7]. That’s because the pore size of this synthesised material is about 1nm, so the KCoFC particles could only stay on the surface of the “carrier” but not go inside the material [7]. By using the XRD to scanning the composite material, it is observed that there is no difference between the position and relative intensity of diffracted rays of HKUST-1/KCoFC and pure HKUST-1, which means that the crystal structure of HKUST-1 was preserved even after the KCoFC is introduced [7].

2.2.2 The effects of time on Cs\textsuperscript{+} adsorption capacity

Figure 4 shows the relationship between adsorption time and the adsorption capacity of HKUST-1/KCoFC composite material in the Cs\textsuperscript{+} solution with a concentration of 200 mg/L pH value of 6 [7]. In the diagram, the adsorption quantity of this material rises sharply in the first 60 minutes, then the speed gets slow down and stops after about 6 hours with a capacity of 44.2 mg/g. That may be because the KCoFC materials are uniformly distributed on the surface of HKUST-1, and many adsorption sites are available to adsorb Cs\textsuperscript{+} at the beginning; although the available sites decrease as time passed, the porous and the large surface area of HKUST-1 keep the material to adsorb, so only stop in increase adsorption quantity after 6 hours [7].

![Fig. 4](image-url)

2.2.3 The effect of pH value on the adsorption capacity

Figure 5 shows the effect of pH value on the adsorption capacity of Cs\textsuperscript{+} of the composite material under the condition of 200 mg/L for the concentration of Cs solution, 1g/L for adsorbent, and 8 hours for reaction time [7]. As shown in the diagram, the adsorption quantity reaches the highest (49 mg/g) when the pH value is 8. The sorption quantity increase as the pH value increases because the competition between H\textsuperscript{+} and Cs\textsuperscript{+} to exchange K\textsuperscript{+} decrease as the pH value increase, and also, the electrostatic force between the adsorption surface and Cs\textsuperscript{+} will affect the adsorption quantity when the pH value is comparatively high [7].
2.3 Preparation and Adsorption of UiO66-COOH for Sr\(^{2+}\)

2.3.1 Preparation of UiO66-COOH

Dissolve ZrCl\(_4\) and metatricarboxylic acid (C\(_9\)H\(_6\)O\(_6\)) in deionized water, vibrate it by using ultrasound for 10 minutes to let them dissolve completely in the solution, and put this mixture into a Teflon reactor to react for 1 day under the condition of 100 Celsius in a vacuum drying oven [8]. Let the reactor cool down naturally to room temperature and wash the products with pure ethanol and deionized water many times, then dry the products for 12 hours in a vacuum environment at 80 Celsius after centrifugation [8].

Still, the FT-IR spectrum could be used to determine whether the products are UiO66-COOH: when the stretching vibration peak of the O-H bond, the stretching vibration peak of the free carboxylic C=O bond, the comparatively strong peaks related to the chemical bond of metatricarboxylic acid and COO-, and two relatively broad adsorption bands that represent the formation of Zn-O bond exist, the composite materials are the UiO66-COOH that the laboratory needed[8]. By using SEM for scanning this composite material, it shows that the particle surface has become coarser as compared to other known UiO66MOF material[8].

2.3.2 The effect of the initial concentration of Sr\(^{2+}\) on the adsorption capacity

Figure 6 shows the pattern of adsorption quantity changes with the initial concentration of Sr under the experiments with a pH value of 6, 2g/L of UiO66-COOH, and concentration of Sr\(^{2+}\) that changes from 100 mg/L to 800 mg/L at room temperature [8]. The adsorption quantity increases promptly at the beginning as the Sr\(^{2+}\) concentration increase, but finally, stay steady after the concentration is higher than 500 mg/L. That’s because the adsorption sites were initially excessive for those Sr\(^{2+}\) ions at low concentration, then as the concentration reaches the saturated points for UiO66-COOH, which as shown in the diagram is approximately about 50mg/g, the adsorption quantity won’t change anymore as the concentration increase [8].
Fig. 6 The effect of Sr\textsuperscript{2+} initial concentration on adsorption quantity [8].

2.3.3 The effect of time on sorption quantity of Sr\textsuperscript{2+}

Figure 7 shows the effect of reacting time on the adsorption quantity of Sr\textsuperscript{2+} at room temperature when the pH value is 6, the adsorbent is 1g/L, and the initial concentration of Sr\textsuperscript{2+} is 200 mg/L [8]. The adsorption quantity increase rapidly at the beginning, gradually decreases in speed as time passed, and stops increasing or reaches the saturated condition (47.91 mg/g) when the reacting time is greater than 180 minutes. That may explain by saying that the adsorption sites were enough for Sr\textsuperscript{2+} ions to exist in the solution at the beginning; then the adsorption sites will decrease as the adsorption take place, so the increase in sorption quantity slows down; the adsorption finally reaches its equilibrium as the material gets saturated, which is when the reacting time is greater than 3 hours [8].

Fig. 7 The relationship between reacting time and adsorption quantity [8].

2.3.4 The effect of pH value on adsorption quantity of Sr\textsuperscript{2+}

Figure 8 reveals how the adsorption quantity changes as the pH value change at room temperature when the initial concentration of Sr\textsuperscript{2+} is 200mg/L, the adsorbent is 1g/L, and the reacting time is 8 hours [8]. The adsorption quantity increases quickly at the beginning but then gets decreases when the pH value is greater than 8 and so the adsorption quantity is highest (49.3 mg/g) when the pH value is 8 [8]. That is because the H\textsuperscript{+} ions will compete with the Sr\textsuperscript{2+} to bond with the UiO66-COOH material, so the more acidic the solution is, there are more H\textsuperscript{+} ions compete with Sr\textsuperscript{2+} [8]. But when the pH value is higher than 8, the electrostatic interaction between the surface of adsorption material and the positive ions that get in will increase as the pH value rises, and so, restrain the sample of UiO66-COOH to adsorb Sr\textsuperscript{2+} ions [8].
3. Application of MOFs Materials in the Treatment of Radioactive Wastewater

There are many types of MOF materials, but not all of them could be used for radioactive wastewater treatment. Types of radioactive waste ions that need to be removed from water include U, Sr, Cs, Co, Cr, Fe, Zn, Mn, and so on, whereas U, Sr, and Cs are the main part of the radioactive substances in nuclear wastewater[9]. Generally, the methods used for treating radioactive wastewater include the chemical precipitation method, ion exchange method, evaporation, membrane technology, and adsorption [9]. Adsorption, as one of them, got the potential to go much farther down the road of radioactive wastewater treatment.

3.1 Other MOFs materials used to remove U(VI) in radioactive water

Feng Yahei et al. used HOUST-1 to separate U(VI) in the wastewater, and they found that when the pH is 6, and the temperature is 25 Celsius, the greatest adsorption quantity of HKUST-1 on U(VI) could reach 784.7mg/g; all these coulomb force, coordination of carboxylic acids, good water dispersion and efficient transportation of mesoporous materials of HKUST-1 play an important role to the high U(VI) adsorption capacity [10].

Bai Zhiqiang et al synthesized an acid-proof MIL-101-(Cr) material and a MIL-101-(Cr) decorated with different amino functional groups and found out that the MIL-101-EDTA got its highest adsorption quantity (350 mg/g) when the pH value is 5.5[10]. Additionally, it got the advantage that the U(VI) adsorbed were easy to be released, recycle and have high selectivity [10].

Yang Weiting et al. used MOF-76(Eu) to detect and remove U(VI) in wastewater, and the experiments show that MOF-76 materials not only have high sensitivity in the detection of U(VI), but also have high selectivity to U(VI) ions when there are many other competing ions in the solution [10]. The highest adsorption quantity(298mg/g) of MOF-76 is when the pH is 3 [10].

3.2 Other MOFs materials used to remove Cs⁺ in radioactive water

Yang Qi et al. found that when the -SO₃H is introduced to the pores of MOFs material, the adsorption capacity on Cs⁺ and Rb⁺ will be highly stimulated [11]. It both got a comparatively high rate of adsorption and the highest adsorption quantity close to 200mg/g, so it is a potential material for the separation of Rb⁺ and Cs⁺ ions [11].

Naeimi et al. produced two kinds of MOFs composite materials with HKUST-1 MOF/KNiFC and MOF/Fe₃O₄/KNiFC and research the adsorption capacity of Cs⁺ ions [11]. The report shows that both of these town kinds of material can reach their highest adsorption quantity (153 mg/g and 109 mg/g
respectively) in 45 minutes when the pH value is 5, and their adsorption capacity is largely unaffected by Na⁺ and K⁺ with low concentration [11].

3.3 Other MOFs materials used to remove Sr²⁺ in radioactive water

GAO et al. synthesized a MOFs material FJSM-InMOF which got an excellent selectivity and adsorption ability to Cs⁺ and Sr²⁺ ions, and experiments show that its highest adsorption quantity on Cs⁺ and Sr²⁺ are 198.63mg/g and 43.83mg/g, which almost got removal rates of 99.83% and 99.63% [11]. FJSM-InMOF has the advantage of high selectivity even under the disturbance of large amounts of K⁺, Ca⁺, Na⁺, and Mg²⁺, and its got a great irradiation property [11].

Mu et al produced two kinds of MOFs materials, MOF-808-SO₄ and MOF-808-C₂O₄, and their highest adsorption quantity on Sr²⁺ is 176.56 mg/g and 206.34 mg/g respectively, which almost remove 99% of Sr²⁺ in solution [11]. These two materials both got a high selectivity and adsorption ability even with coexisting ions of 10 times of concentration, and they are un-reversible on capture Sr²⁺, which means that they got a very strong ability on bonding with Sr²⁺ [11].

People including Aguila also produce MIL-101-SO₃H and take experiments to test its ability to adsorb Cs⁺ and Sr²⁺ [11]. The reports reveal that when the molar ratio of Cs⁺ and Sr²⁺ is 4:1, the pH is 6, the reacting time is 24 hours at room temperature, the removal rate could reach 99.99% and 98.92% respectively, and even under the disturbance of Na⁺ and K⁺, it still got a high selectivity and adsorption capacity [11].

3.4 Other MOFs materials used to remove Co²⁺ in radioactive water

Yuan et al. produced 4 kinds of MOFs material, UiO-66-COOCH₃, UiO-66-CONH₂, UiO-66-CN, and UiO-66-SO₃H, which got the highest adsorption quantity on Co²⁺ of 334.4, 339.7, 274.6, 293.7mg/g respectively under the ideal condition of 35 Celsius for temperature, 8.4 for pH value, 36 hours for reacting time [11].

Yuan et al. produced MIL-101-glycine, MIL-101-diglycine, and MIL-101-triglycine through a series of means and study their capacity for adsorbing Co²⁺ ions [12]. They found out that under the ideal condition of 35 Celsius for temperature, 8.4 for pH value, and 36 hours for reacting time, the highest adsorption quantity on Co²⁺ could reach 185.2, 227.3, and 232.6 mg/g respectively [12].

4. Summary

Because of the high surface area, high porosity, adjustable structure, and versatility, MOFs are good materials for dealing with radioactive wastewater. In this article, the production, properties, and factors that influence the adsorption quantity of MOF-5, HKUST-1/KCoFC, and UiO66-COOH materials are mainly discussed. Based on the study, MOF-5 has a removal capacity of U(VI) (237mg/g) much higher than many other materials, so it will be an excellent alternative for collecting radioactive U(VI) ions. The adsorption capacity on Cs⁺ of HKUST-1/KCoFC (highest sorption quantity of 49mg/g) and Sr²⁺ of UiO66-COOH (highest sorption quantity of 47.91mg/g) is strongly affected by pH value and partially effected by other competing ions, which means that there still need development on these materials or on other materials that have higher capacity on adsorbing Cs⁺. Here also provide various research had been done on the MOFs materials used for removing radioactive substances U(VI), Cs, Sr, and Co.

Although MOFs have some advantages compared to other materials and methods, there still got some issues scientists need to work on. Firstly, the cost of building up MOF materials is too expensive or not affordable for most businesses to use widely for treating wastewater. Secondly, the conditions for making MOFs materials are too rigorous that any small changes may cause the production of a different material or different quantity. Thirdly, the conditions for MOF materials are too strict that some of them may even lose efficacy in a strongly acidic environment. Finally, the adsorb ability and release ability are not balanced for many MOF materials if people wanted to use them in practical
applications. Compared to inorganic adsorbing materials, adsorbing rates for some MOF materials are slow and not so efficient.

References


