Design and research of uranium-containing wastewater treatment equipment based on new organometallic framework materials (MOF-808)

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Abstract. With the significant increase in the amount of natural uranium mining in various countries around the world, a large amount of waste rocks are piled up in the tailings pond. If the uranium-containing wastewater is not treated, it will bring serious environmental problems. After related experiments in the laboratory, it is measured that the adsorption rate of high-tech products-MOF-808 material to uranium ions can reach 97% (the optimal pH=7.0, and the optimal dosage is 0.2mg/L). It can be used as a good adsorption material. Based on the high-efficiency selective adsorption of this material to uranium, a set of equipment using MOF-808 was designed in this paper. This device adopts improved intermittent processing, high integration and automation level, and small floor space. According to the desorption characteristics of the material, a simple membrane cleaning method is designed to recover high-concentration uranium-containing cleaning liquid, which greatly reduces the amount of mud and can produce considerable economic benefits. In addition, cleaning and operation can be carried out at the same time, realizing continuous uranium-containing wastewater treatment, which meets the requirements of energy saving and emission reduction, and is beneficial to the construction of green mines.

1. Introduction
With the rapid development of nuclear power and military industry, the world's demand for natural uranium has also begun to rise substantially, forming a new round of uranium development craze. However, the ensuing problem is that the amount and types of radioactive waste water produced in the process of uranium mining are also increasing, and traditional physical and chemical treatment methods have many shortcomings in practical applications, mainly due to complex procedures and production. The amount of mud is relatively large, and the secondary pollutants need to be treated again.

2. Project background and significance
2.1. Development of MOFs materials
In 1706, the first synthetic polymer with a three-dimensional network structure-iron hexacyanoferrate was discovered [1]. In 1958, Kinoshita Y et al. [2] synthesized a bis-adiponitrile cuprous nitrate crystal. The concept of crystallography was put forward in 1971, prompting domestic and foreign researchers to conduct in-depth exploration and research on MOFs materials. In 1995, Yaghi et al. reported for the first time a coordination compound with a two-dimensional structure synthesized from BTC and Co,
and named it MOF. The concept of metal-organic compounds was also proposed for the first time, namely: a new organic-inorganic hybrid supramolecular material self-assembled by organic ligands and metal cations. In 1997, a metal organic framework compound with certain gas adsorption properties at room temperature was discovered. In 1999 [3], the MOF-5 material published by Yaghi's group became a milestone in metal organic framework materials. After 2002, a variety of metal organic framework compounds with different properties began to appear.

In recent years, MOFs have received extensive attention in the field of water treatment. Compared with other traditional adsorbents, MOFs have the characteristics of high porosity, high specific surface area, structural diversity, adjustable pore size, etc [4]. In recent years, it has attracted the attention of a large number of scholars in the field of adsorption and separation [5]. The MOFs reported in the previous period are sensitive to water and are mostly used in harmful gas adsorption and energy gas storage. Later, MOFs with good water stability appeared, and they have been widely used in water restoration such as the removal of heavy metals and organic pollutants [6-9].

3. Adsorption experiment of MOF-808 material

3.1. Simulation of Wastewater from Tailings Pond
Weigh 0.422g UO₂(NO₃)₂ crystal powder and pour it into a 100mL beaker. Pour into 50mL deionized water and stir with a glass stir bar until the solid are completely dissolved. Then pour the solution in the beaker into a 1L volumetric flask and add deionized water to a constant volume. Put it in an ultrasonic cleaner and sonicate for 30 minutes to make the solution in the volumetric flask evenly dispersed. At this time, the concentration of the uranium solution is calculated to be 10 mg/L, and this solution is used as the uranium standard solution. All uranium solutions of various concentrations used in subsequent experiments are obtained by diluting this solution.

3.2. Experimental conditions
In the experiment, we selected the previously determined optimal adsorption pH value, that is, under the conditions of pH=7 and the optimal dosing ratio 0.2mg/g, the adsorbent was added to the conical flask containing the original solution. The connected conical flask is placed in a constant temperature shaking the box to make the adsorbent material and the uranium solution fully contact. By measuring the absorbance value before and after adsorption, the adsorption rate of the material to uranium can be determined.

3.3. Preparation Schemes of MOF-808
Based on the research basis of Yu Chunyue[10] and others. Weigh 0.422g UO₂(NO₃)₂ crystal powder and pour it into a 100mL beaker. Pour into 50mL deionized water and stir with a glass stir bar until the solid are completely dissolved. Then pour the solution in the beaker into a 1L volumetric flask and add deionized water to a constant volume. Put it in an ultrasonic cleaner and sonicate for 30 minutes to make the solution in the volumetric flask evenly dispersed. At this time, the concentration of the uranium solution is calculated to be 10 mg/L, and this solution is used as the uranium standard solution. All uranium solutions of various concentrations used in subsequent experiments are obtained by diluting this solution.

3.4. Experimental results
Use a spectrophotometer to measure the spectrophotometric value of the material after adsorption, and then it is calculated that the adsorption rate of uranium for MOF-808 material under the optimal conditions reaches 97%~98%. Obviously, this material has great application potential for the adsorption of uranium.
4. The process flow of the device

4.1. Figures and description
The overall three-dimensional model of the device is shown in Figure 1, the parts schematic of the model is shown in Table 1:

![Figure 1. Overall device model diagram](image)

Table 1. Components 1

| Serial number | Component name                        |
|---------------|---------------------------------------|
| a             | Inlet pipe                            |
| b             | Pre-treatment pool                    |
| c             | Propeller agitator                    |
| d             | Gate                                  |
| e             | Membrane adsorption system            |
| f             | Slide rail                            |
| g             | Drying room                           |
| h             | Cleaning agent dosing tank            |
| i             | Cleaning fluid collection tank        |
| j             | Initials followed by last name        |
| k             | Check valve or butterfly valve        |
| l             | Initials followed by last name        |

4.2. Operation plans
Step 1: The pre-treated uranium-containing wastewater enters the pre-treatment tank, and under the action of the propeller agitator, the speed of adjusting the pH value of the wastewater is accelerated, and a large amount of wastewater is stored in the pre-treatment tank in advance.

Step 2: Open the open-close gate to make the waste water flow into the treatment tank at a certain water speed.

Step 3: After the wastewater enters the treatment tank, uranium ions are adsorbed from the water to the membrane during the translation and rotation of the operating system. The membrane adsorption
system mounted on the mobile support adopts a roll-up hole design, which not only reduces the fluid resistance, but also allows the material to fully contact the water body.

Step 4: After the wastewater treatment reaches the standard, the concentration of uranium, which is a radioactive hazardous substance in the effluent, is less than 50μg/L, and it is discharged into the municipal pipe network through the drainage pipe.

After that, the gate is reopened to allow the wastewater from the pre-treatment tank to flow in, and the adsorption process is performed again. In this way, the pre-treatment tank water intake can be carried out simultaneously with the adsorption of uranium ions in the treatment tank, which saves a lot of time for adjusting the pH value of wastewater, and the operating system is always in working condition.

4.3. Cleaning plan
When the detector detects that the wastewater treatment rate slows down to a pre-set threshold, it means that the membrane needs to be cleaned. The cleaning process can be divided into the following steps (because the cleaning process of the two MOF membranes is the same, only the cleaning process of one of them is described):

Step 1: After the control room sends out the "start cleaning process" signal. The mobile bracket carries the MOF film back to the end of the slide rail.

Step 2: The retractable spinning clamp carries another cleaned or brand new MOF membrane into the empty slot of the mobile stand. Afterwards, the spinning clamp is aimed at the film to be cleaned, and it is rolled on the round rod to complete the film replacement.

Step 3: The spinning clamp shrinks and enters the drying chamber together with the film. Under the action of the sprayer and the fan, the waste liquid remaining on the film falls back into the treatment tank. At this time, the mobile stand equipped with the new membrane continues to operate, achieving simultaneous cleaning and processing.

Step 4: The spinning clamp carries the film roll to the other end of the drying chamber, and puts the film into the cleaning tank. The cleaning agent dosing tank opens the valves of the methanol zone and the hydrochloric acid zone in turn to allow the cleaning agent to flow into the cleaning tank. After the membrane is soaked in it for a period of time, the desorption process of uranium ions is completed.

Step 5: The valve between the cleaning tank and the uranium liquid collection tank is opened. With the injection of clean water in the dosing tank, the membrane is further cleaned, and the uranium-containing cleaning liquid finally enters the collection tank. The spinning clamp carries the cleaned roll film into the drying chamber again, turns on the fan to dry again, and waits for the next change.

5. Introduction to the main systems

5.1. Membrane adsorption systems
Prepared MOF-808 material is attached to a rolling-blind metal structure, and the selected metal structure needs to be resistant to rust and have good corrosion resistance. The metal structure will adopt a roll-up hole design. On the one hand, it can reduce the fluid resistance of the membrane adsorption system during operation, and on the other hand, it can increase the load on the MOF material.

5.2. Operating systems
The operating system is designed to be active, which treats uranium-containing wastewater intermittently. Two MOF membranes reciprocate in the uranium-containing wastewater to adsorb uranium ions in the wastewater. The membrane adsorption system will treat the uranium ions in the wastewater to below the prescribed standard, discharge, and then treat the next pool of wastewater.
5.3. Water inlet and outlet system

The treated water body is the waste water from the tailings pond with high uranium concentration (5mg/L~10mg/L), which has been conventionally treated by grids and other waste water. The wastewater enters the pre-treatment tank through the inlet pipe, and the pre-treatment tank has the following functions:

a. Adjust pH value: through experiments, the best adsorption pH value of MOF-808 is 7, while the pH value of uranium-containing wastewater itself is 4.8~5.2. The pH value is adjusted by adding drugs;
b. Water storage: In order to make up for the shortcoming of intermittent treatment that requires a long water change time, a large amount of wastewater is stored in the pre-treatment tank in advance, and the water inflow and the adsorption of uranium ions in the treatment tank are carried out at the same time;
c. Adjust the water speed: open the gate. The ideal water inlet speed of the treatment tank can be achieved by adjusting the gate opening.

After the detection system detects that the water quality reaches the standard, most of it is discharged from the lower drainage pipe, and a part is discharged into the feeding pool of the cleaning system for storage.

5.4. Cleaning system

Prepared MOF-808 material is attached to a rolling-blind metal structure, and the selected metal structure needs to be resistant to rust and have good corrosion resistance. The metal structure will adopt a roll-up hole design. On the one hand, it can reduce the fluid resistance of the membrane adsorption system during operation, and on the other hand, it can increase the load on the MOF material.

5.4.1. Spinning clamp

The spinning clamp adopts a retractable design, the main function is to brake and rotate.

5.4.2. Drying room

In order to prevent the residual uranium-containing wastewater on the MOF membrane that needs to be cleaned from directly entering the cleaning tank, reducing the cleaning efficiency and causing harm to the working environment, a drying room is provided between the treatment tank and the cleaning tank.

The drying room is equipped with sprinklers and fans. The sprinkler water is supplied by the treated drainage, the film that is rolled up when spinning clamp is contracted rises to a certain height, and the sprinkler sprays clean water to make the residual liquid on the film fall back into the treatment tank. After that, the fan dried the film. After completing the above process, the spinning clamp moves to the top of cleaning tank and stretches, so that the roll film enters the cleaning tank.

5.4.3. Cleaning tank

The cleaning tank is connected to the feeding tank through a pipeline at one end and the uranium liquid collection tank at the other end. Its working principle is:

a. The three pools can be used to transport water by gravity in order to save energy consumption.
b. The feeding tank is divided into three areas, namely the industrial methanol area, the hydrochloric acid area and the water purification area, which are put into the cleaning tank in order. In addition, the water purification area is connected to the treatment tank. When the water quality reached the standard and needs to be drained, a part of the supernatant is discharged into the water purification area as reserve water for spraying and washing the MOF membrane.
c. The MOF membrane is soaked in methanol and hydrochloric acid successively. After a period of time, uranium ions are desorbed from the membrane and flushed into the uranium liquid collection tank with purified water. The uranium concentration in the collected uranium liquid is relatively high, which has certain economic value.
6. Conclusion
The organometallic framework material MOF-808 has highly efficient selective adsorption to uranium in wastewater, and can be prepared under conventional conditions, and has considerable development prospects in the process of uranium removal. Prepared MOF-808 material has an adsorption rate of 97% for uranium ions, and at the same time it can be attached to a metal material to form a film, and the film is not limited by shape and size. The uranium removal device has a high degree of automation design and a small area. Required automatic control technology and real-time detection system are currently relatively mature, and the management and operation are convenient. The design of the uranium removal process system can be used as a reference for the treatment of heavy metal ion wastewater by other MOFs. However, the high price of the raw materials used to prepare MOF-808 is a problem worth solving in the future.

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