Study on Treatment of Uranium-Containing Wastewater by Biosorption

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Abstract. This paper is going to introduce the research status of the treatment of uranium-containing wastewater by biosorption; the definition and advantages of biosorption technology and the types of biosorbents; the effects of pH, temperature and coexisting ions on the adsorption efficiency of biosorption; and the mechanism of biosorption of metals: precipitation, cell enrichment, oxidation and reduction, and enzymatic action. Finally, it provides a direction for further research in the future.

1. Introduction
A large number of low-concentration uranium-containing wastewater can be produced by uranium mining and smelting, and the direct discharge of low-concentration uranium-containing wastewater can a serious impact on the water body[1]. Uranium not only has radioactivity, but also has dynamic biological and chemical toxicity, which will have a very serious impact on human beings[2]. Therefore, it is of great significance to effectively treat low concentration uranium-containing radioactive wastewater from uranium mining and smelting. With the rapid development of China's nuclear industry, the demand for uranium is increasing year by year. The sustainable development of uranium mining and smelting has become a strategic issue[3]. According to the Regulations on Radiation Protection of Uranium Processing and Fuel Manufacturing Facilities issued by China (EJ 1056-2005)[4], the concentration of uranium in wastewater from the total discharge of radioactive hazardous substance uranium from industrial sewage is not allowed to exceed 50 ug/L. However, the mass concentration of uranium in waste water discharged by uranium mining and smelting units is generally about 5 mg/L[5], which is much higher than the national standard. The traditional methods to remove uranium from wastewater include chemical precipitation, ion exchange, adsorption and membrane separation[6]. Biosorption has attracted wide attention because of its simple operation and fast adsorption rate. It has been rapidly developed in the field of low concentration uranium wastewater treatment, and is one of the most promising treatment technologies in this field[7,8].

2. Preface

2.1. Definition of biosorption method
Biosorption method, also known as contact stabilization method or adsorption regeneration method, belongs to activated sludge process[9]. It refers to the method of separating heavy metal ions from water by means of surface complexation, ion exchange, electrostatic adsorption, redox, enzymatic action and so on[10].
2.2. Types of Biosorbents
Biosorbents play a key role in biosorption. Biosorbents can be divided into microorganisms, animals and plants, as well as various derivative and modified products of animals and plants according to their sources. Microorganisms include bacteria, fungi, algae and so on. Plants also include sawdust, crop straw and leaves. It can be said that since the development of biosorption technology, most substances from natural sources can be used as biosorbents for organisms modified by various physical, chemical and biological technologies. The specific classification is shown in Table 1.

| Biosorbent                    | Give an example                                                                 |
|-------------------------------|-------------------------------------------------------------------------------|
| Plants and their derivatives  | sweet sorghum, weeds, straw, earthworms, animal feathers, chitin, chitosan,   |
|                               | cellulose, lignin, starch, etc.                                               |
| algae                         | Green algae, giant algae, microalgae (such as Cyanophyta, Chlorophyta,       |
|                               | Chlorophyta, Rhodophyta, etc.                                                 |
| Natural resource residues     | Wheat straw, masson pine sawdust, masson pine pollen, fir bark, sycamore leaves, |
|                               | peat and various plant residues, etc.                                         |
| Crop waste                    | Wheat husk, sugar beet residue, pods, peanut hulls, rice husks, various kinds of fruit and vegetable waste, etc. |
| Factory waste                 | Sludge (such as activated sludge, anaerobic sludge, aerobic granular sludge), | waste mycelium of fermentation industry (such as brewery, citric acid plant), etc. |
| Bacteria                      | Escherichia coli, Streptomyces, Citrobacter, Acinetobacter, Pseudomonas,      |
|                               | Cladosporium, Bacillus licheniformis, etc.                                    |
| Fungus                        | Aspergillus niger, Rhizopus oligorhizopus, Penicillium digitatum, Saccharomyces cerevisiae, Mucor, Trichoderma, etc. |
| New adsorbent                 | Various kinds of physical, chemical and biological adsorbents, immobilized    |
|                               | biological adsorbents, biologically modified genetic engineering microorganisms, |
|                               | plants, mixed biomaterials, etc.                                              |

2.3. Advantages of Biosorption
On the contrast, compared with conventional heavy metal removal methods, the advantages of biosorption process include[11]: (1) adsorbents are cheap and abundant natural renewable biomaterials, such as corn straw and rice straw; (2) biosorption process has fast adsorption rate, which can treat a large amount of wastewater at high recovery rate; (3) It has high selectivity in the removal and recovery of specific heavy metals, and does not adsorb or weakly adsorb a large number of light metal ions such as K\(^+\), Na\(^+\), Ca\(^{2+}\), Mg\(^{2+}\); (4) It can treat mixed wastewater containing various heavy metals with high affinity, and in many cases it can reduce residual metals to less than 1 ppb; (5) It can operate under various physical and chemical conditions, including (different) temperature, pH value and coexistence conditions of other ions; (6) There is no need for additional treatment and capital investment is relatively low. Under the condition of low cost operation, the quantity of hazardous waste produced can be greatly reduced.

3. Influencing factors of uranium adsorption by biomaterials
The adsorption effect of biosorption materials on uranium is affected by many factors, such as solution pH value, adsorption temperature, species and concentration of coexisting ions, contact time and dosage of adsorbents and so on. Therefore, the adsorption performance of biosorption materials on uranium ions is often different under different factors, and the adsorption capacity of different biosorbents is affected differently.

3.1. Effect of pH Value of Solution
For most adsorption processes, the solution pH value is the key factor affecting the adsorption effect. The results show that each adsorbent has an optimal pH value, generally between 4 and 7. Many studies have shown that the adsorption capacity of heavy metal ions generally increases with the increase of pH value, but the relationship between the adsorption capacity of metals and pH value is
not a simple linear function. It is found that at lower pH value, high concentration of H+ competes with uranyl ion for the surface binding sites of adsorbent, thus reducing the adsorption of uranium (VI)\[^{[12]}\]. However, with the increase of pH value, the surface of adsorbent is negatively charged due to dehydrogenation process. Simultaneously, positive ions such as UO2OH\(^+\), (UO2)\(^{2+}\) and (UO2)\(^{3+}\) turn into uranyl complexes and the adsorption capacity of uranium\[^{[13-14]}\] is increased due to the enhanced electrostatic interaction between uranyl complexes and the surface of the adsorbent. While the hydrolysis of uranium ions will be further strengthened by excessive pH value, resulting in the formation of anionic complexes such as (UO2)\(^{3+}\) (OH)\(^{-}\), UO2 (OH)\(^{-}\) or precipitation of UO2(OH)\(^{-}\), which leads to the decrease of the adsorption efficiency of uranium\[^{[15]}\].

3.2. Effect of Temperature
Because the active absorption of metal ions to active organisms is a process of energy metabolism, adsorbents are often very sensitive to temperature. Shao Ling\[^{[16]}\] and others used APTES modified sludge-based carbon to study the adsorption of Pb (II) in water. When the experimental adsorption temperature increased from 25 °C to 45 °C, the adsorption capacity of Pb (II) increased with the increase of equilibrium concentration and eventually was tending to be stable. The adsorption capacity increased by about 67%. At the same time, the increased heat can also provide energy for the active transport of metal ions, thus increasing the adsorption capacity. However, other studies have shown that the adsorption of uranium by some biomaterials is an active exothermic process. Excessive temperature can inhibit the adsorption.

3.3. The influence of coexisting ions
When there are other metal ions in the adsorption system, the adsorption of main ions is generally inhibited. These coexisting ions will inevitably compete with the main ions for the limited negative functional groups on the adsorption materials, resulting in the reduction of the adsorption capacity of the main uranium ions. Han Runping, Zou Weihua and others used rice husks as adsorbents to study the adsorption competition between binary mixed solutions. It was found that the maximum adsorption capacity of grain hull for Cu\(^{2+}\) and Pb\(^{2+}\) was 1.46 mg/g and 12.5 mg/g, respectively. The presence of one metal ion can significantly reduce the adsorption of hull to another metal ion. The experimental results of single system and mixed system show that the adsorption capacity of hull to heavy metal ions in single system is greater than that in mixed system\[^{[17]}\].

4. Mechanism of Biosorption of Metals

4.1. Sedimentation
Precipitation refers to the process by which organisms produce certain substances, which can react with metals in solution to form insoluble metal compounds and cause precipitation. Sulfate-reducing bacteria living in Lake sediments, marshes and anoxic soils can produce hydrogen sulfide and react with heavy metal ions to form sulfide deposits. Ohnuki et al. found that uranium was deposited on the surface of Saccharomyces cerevisiae cells with needle-like fibrous layers. Resins about 0.2 um produced by plants were also good adsorption and precipitation materials. Lu Yan\[^{[19]}\] et al. used three "717" resin adsorption towers to adsorb 100 mg/L uranium-containing waste water. The reaction formula of "717" resin to adsorb uranium (1) is:

\[
4R-\text{CH}_2N(\text{CH}_3)_3\text{Cl}+\text{UO}_2(\text{CO}_3)_3^{4+}\rightleftharpoons [R-\text{CH}_2N(\text{CH}_3)_3]\text{UO}_2(\text{CO}_3)_3+4\text{Cl}^-
\]  

(1)

At last, the volume of uranium in the treated wastewater is 40 μg/L, and the adsorption efficiency is over 99.9%. Finally, the resin adsorption column in series and the precipitation process of calcium hydroxide-calcium chloride are determined. The experimental wastewater has good treatment effect and meets the treatment needs of uranium-containing wastewater.
4.2. Cell Enrichment (Bioaccumulation)

The kinetics study shows that the absorption of soluble heavy metals by algae cells is mainly composed of two stages\cite{20}. The first stage is the physical and chemical interaction on the cell surface, which causes the adsorption of metal ions and functional groups on the cell wall. Metal ions are passively adsorbed on the cell surface, and the reaction time is very short, without any metabolic process and energy supply. This process is called biosorption. The other stage: Metal ions on the surface of cells bind, deposit or crystallize to some enzymes on the plasma membrane (such as membrane transferase, hydrolase, etc.) and then are transferred to the cells actively. This process is related to metabolic activity, slow and irreversible, so it is defined as bioaccumulation. More specific processes are still being explored, not excluding other ways of absorption\cite{21}.

Shaik Basha and Murthy Z V P\cite{22} examined the kinetic and equilibrium models of the adsorption of Cr\textsuperscript{6+} by chemically modified brown algae. The experiments showed that the adsorption process was rapid and the maximum adsorption amount could be achieved within 2 hours. Metals can also be deposited on cell walls or inside cells by nucleation in the form of phosphate, sulfate, carbonate or hydroxide.

4.3. Oxidation and reduction

The valence of metals would increases or decreases in order to fix uranyl ions. Although oxidation and reduction usually require the action of active microorganisms, oxidation and reduction of certain metals can also actively occur in the chemical active units of microbial cell walls. The H2S produced by acid reducing bacteria under anaerobic conditions can react with metal ions, creating metal sulfide precipitation, thus removing metal ions from wastewater\cite{23}. Parajuli\cite{24} et al. used persimmon peel to selectively adsorb from chloride solution. It was found that polyphenol functional groups in tannin structure of persimmon peel could reduce Au\textsuperscript{3+} to Au\textsuperscript{0}\cite{25-26}.

4.4. Enzymatic mechanism

Both inactive and active organisms can absorb heavy metals. Metal uptake by active cells may be related to the activity of some enzymes in cells. Ulberg\cite{27} et al. studied the adsorption of ionic and colloidal gold by Bacillus spp. and found that the accumulation of gold was related to the functional groups of proteins and carbohydrates on the cell surface.

5. Prospects for future research

Biosorption has attracted considerable attention in recent years in the field of mineral resources recovery and uranium-containing wastewater treatment due to its extensive and cheap raw materials, which can achieve the effect of waste treatment. Currently, the research progress in the field of biosorbents in our country is still relatively slow, and the specific adsorption mechanism is still not clear. Biosorbents in vivo are more susceptible to environmental factors and cannot meet the conditions of their effective action.

Therefore, further studies on the adsorption behavior of uranium by biosorbent materials and their development and application are needed, which can be carried out in the following aspects:

1. The surface complexation model is used to study the composition of uranium complexes on the surface of materials. The adsorption mechanism is explained according to the types of uranium complexes.

2. The binding of uranium with functional groups on the surface of materials was studied by means of EXAFS, XPS, RS, TRLFS and EYIR spectroscopy. Furthermore, the morphology and microstructure of uranium adsorbed on the molecular level are revealed.

3. The adsorption mechanism is studied by theoretical calculation, such as the physical and chemical interaction between nuclides and adsorbents by density functional theory calculation; the adsorption performance of physical adsorption or chemical adsorption can be determined by theoretical calculation of the binding energy between uranium and different functional groups, and the interaction mechanism between uranium and materials can be obtained.
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