The Second International Conference on Mining Engineering and Metallurgical Technology

Experimental study on restoration of polluted groundwater from in situ leaching uranium mining with Sulfate Reducing Bacteria and ZVI-SRB

Hu Kaiguang\textsuperscript{a}, Wang Qingliang\textsuperscript{z}, Tao Ganqiang\textsuperscript{a}, Wang Aihe\textsuperscript{b}, Ding Dexin\textsuperscript{a}\textsuperscript{*}

\textsuperscript{a} Key Discipline Laboratory for National Defence for Biotechnology in Uranium Mining and Hydrometallurgy, University of South China, Hengyang 421001, China
\textsuperscript{b} Hunan city college, Yiyang 410604, China

Abstract

In the case of in situ leaching of uranium, the primitive geochemical environment for groundwater is changed since leachant is injected into the water beaving uranium deposit. This increases the concentration of uranium and results in the groundwater contamination. Microbial reduction technology by Sulfate reducing bacteria and Zero Valent Iron were employed to treat uranium wastewater. The experiments were conducted to evaluate the influence of anion (sulfate and nitrate) on dealing with uranium wastewater. Experimental results show that the utilization of both SRB system and ZVI - SRB system to process uranium wastewater is affected by sulfate ion and nitrate ion. As the concentration of sulfate radical is lower than 4000mg/L, sulfate-reducing bacteria has no influence on precipitated uranium. However, as the concentration of sulfate is more than 6,000 mg/L, uranium removal rate decreases significantly, from 80% to 14.1%. When adding sulfate radical on ZVI - SRB system to process uranium wastewater, its uranium removal rate is higher than SRB system. Low concentration of nitrate contributes to reduction metabolism of SRB. High concentration of nitrate inhibits the growth and metabolism of SRB and affects the treatment efficiency of uranium wastewater. When the concentration of nitrate reaches 1500mg/L, uranium removal rate is less than 0.1%. Nevertheless, as the concentration of nitrate is lower than 1000mg/L, uranium removal rate could reach more than 75%. As existence of nitrate radical, uranium removal rate of SRB by adding ZVI is higher than that without adding.

Key words: sulfate radical; nitrate radical; Sulfate-Reducing Bacteria (SRB); Zero Valent Iron (ZVI); In situ leaching of uranium

Supported by the National Natural Science Foundation of China (50774047). Hunan province(09JJ6081)、(2010GK2025)
1. Background

With the development of uranium mining and metallurgy industry, the groundwater treatment in uranium mine of acid in-situ leaching in China has become an important task for environmental workers. Nowadays, physical and chemical methods are main methods to treat uranium wastewater. However, because of high costs of these methods and easily resultant secondary pollution, their use is very limit.

The utilization of micro-organisms repairing technology on uranium wastewater has attracted the attention of many scholars at home and abroad (1-4). Zero-valent Iron (ZVI), being a kind of environmentally friendly material, has reductive ability and is used to treat heavy metals wastewater and organic polluted wastewater by many scholars (5-6). Currently, the utilization of bioremediation technology to govern wastewater containing uranium is a hot research area by adding sulfate-reducing bacteria (SBR) and zero-valent Iron into uranium wastewater. Because ZVI could strengthen the growth and metabolism of SBR and these two can mutually benefit from each other. It helps to jointly transform and precipitate U(IV), SO₄²⁻ and other heavy metal ions in uranium wastewater. The influence of sulfate radical and nitrate radical on microbial reduction of uranium wastewater by ZVI-SRB is discussed in this article.

1.1. Cultivation of bacteria

1.1.1. Component of substrate

Table 1 Components and contents of API substrate

<table>
<thead>
<tr>
<th>Components</th>
<th>Contents</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium lactate</td>
<td>4.0mL/L</td>
</tr>
<tr>
<td>Yeast leaching juice</td>
<td>1.0mL/L</td>
</tr>
<tr>
<td>Vitamin C</td>
<td>0.1g/L</td>
</tr>
<tr>
<td>MgSO₄·7H₂O</td>
<td>0.2g/L</td>
</tr>
<tr>
<td>K₂HPO₄</td>
<td>0.01g/L</td>
</tr>
<tr>
<td>NaCl</td>
<td>10.0g/L</td>
</tr>
<tr>
<td>(NH₄)₂Fe(SO₄)₃·6H₂O</td>
<td>0.2g/L</td>
</tr>
</tbody>
</table>

1.1.2 Domestication, cultivation and enrichment of SRB

The anaerobic sludge in experiment is derived from sewer near Sixth Nuclear Institute of University of South China. Firstly, adding five grams anhydrous sodium sulfate per liter of sludge and shaking culture (120rpm) in 35 °C condition and domesticating a week. And then use API substrate for further
domesticated cultivation. Fresh substrate is replaced once a week. After being trained four weeks, the mixed SRB bacteria for experiment are obtained. Its concentration is 2g/ L (dry weight).

1.2 Wastewater and elemental iron

The uranium wastewater in experiment is come from leaching solution of uranium ore. Its concentration is 1mg / 1ml. Elemental iron is added one-time in the shape of reducing iron powder and its grain size is 80 mesh, purity is 90 percent.

2 Test methods

2.1 Influence of sulfate radical on microbial reduction of uranium wastewater by SRB system and ZVI - SRB system

Take 200mL uranium wastewater in 121°C for sterilization. Then add 300mL substrate into flask and is blown off 5 minute by N₂. After that, add sulfate with the concentration of 2000mg / L, 4000 mg / L, 6000 mg / L, 10000 mg / L respectively. And add uranium wastewater and keep the uranium concentration 40mg / L. Adjust pH and keep it 7.08 and access bacteria. Then keep 35°C constant temperature training. Set up a control group, in which all other conditions are the same except non-vaccination. The processing uranium wastewater method by sulfate radical on ZVI-SRB system is similar in every detail with SRB system. Moreover, add 2g reducibility iron powder and the control group is non-vaccinated and iron powder is not added into the control group.

2.2 Influence of nitrate radical on microbial reduction of uranium wastewater by SRB system and ZVI - SRB system

Take 200mL uranium wastewater in 121°C for sterilization. Then add 300mL substrate into flask and is blown off 5 minute by N₂. After that, add nitrate with the concentration of 200mg / L, 400 mg / L, 1000 mg / L, 1500 mg / L respectively. And add uranium wastewater and keep the uranium concentration 40mg / L. Adjust pH and keep it 7.08 and access bacteria. Then keep 35°C constant temperature training. Set up a control group, in which all other conditions are the same except non-vaccination. The processing uranium wastewater method by nitrate radical on ZVI-SRB system is similar in every detail with SRB system. Moreover, add 2g reducibility iron powder and the control group is non-vaccinated and iron powder is not added into the control group.

3 Results and discussion

3.1 Influence of the initial concentration of sulfate on processing uranium concentration by SRB system and ZVI-SRB system

Figure 1 shows the uranium concentration changes with time in the process of SRB reduction precipitation under different initial concentrations of sulfate. As the initial sulfate concentrations below 4000mg / L in the SRB processing system, the concentration of uranium changes rapidly with time. After 36h treatment, the removal rate of uranium can reach more than 80%. However, as the concentration of sulfate is 10000mg / L, the removal rate of uranium is less than 20% after 72h treatment. Figure 2 shows the uranium concentration changes with time in the process of ZVI-SRB reduction precipitation under different initial concentrations of sulfate.
Deduced by Figure 1 and Figure 2, the reduction trend of ZVI-SRB test is similar to the SRB test. The ultimate removal rate of uranium of ZVI-SRB system is higher than that of SRB system. This is, enzymes are activated and adjusted by ZVI and affinity between enzymes and substrate is strengthened. However, its strengthening effect changes with the concentrations of sulfate. As sulfate concentrations below 4000mg / L, strengthening effect is obvious and uranium variety curves coincide basically. As sulfate
concentrations reach 10000mg / L, the strengthening effect of SRB by ZVI is not obvious and the ultimately removal rate of uranium is only 14.1%.

3.2 Influence of the initial concentration of nitrate radical on processing uranium concentration by SRB system and ZVI-SRB system

Nitrogen is one of prerequisite elements for microbial growth. On the one side, low nitrogen content is detrimental to the growth of microorganism. According to reports, keeping minimum TN (total nitrogen) in 200mg/L in the growth solution can maintain the metabolic activity of anaerobic bacteria. On the other hand, $\text{NH}_4^+$ gives rise to microbe for high content of nitrogen and affects microbial metabolism. Therefore, the amount of nitrogen must be kept in the process of cultivating SRB.

Figure 3 and Figure 4 show the influence of the initial concentration of nitrate radical on uranium concentration processed by SRB system and ZVI-SRB system respectively.

Figure 3  Influence of the concentration of nitrate radical on reduction of uranium by SRB system

Figure 4  Influence of the concentration of nitrate radical on reduction of uranium by ZVI-SRB system
Deduced by Figure 3 and Figure 4, the initial concentration of nitrate has a significant influence on the growth of SRB and in turn affects the removal rate of uranium in wastewater. When the concentration of nitrate is lower than 1000 mg/L, the removal rate of uranium can basically reach more than 75%. However, as the concentration of nitrate reaches 1500 mg/L, the removal rate of uranium decreases significantly. Regardless of inclusion of ZVI or not, the ultimate removal rate of uranium is less than 0.1%. And the ultimate removal rate of uranium by adding ZVI is lower than that without adding. The main reason is that NO_3^- can be reduced to NH_4^+ by ZVI, and has poisoned on SRB. On the other hand, more NH_4^+ are caused by high concentration of nitrate in the process of denitrification, which has a very large poisoning effect on SRB.

4 Conclusions

(1) The concentration of sulfate and nitrate in wastewater has obvious influence on the treatment of uranium wastewater by SRB system.

(2) A certain concentration of sulfate in the wastewater helps to promote reduction and precipitation of uranium in the SRB system. However, H_2S, which is produced by high concentrations of sulfate in the process of metabolism, could inhibit the activity of SRB and in turn affect the removal rate of uranium in the wastewater. Therefore, when the concentration of sulfate is less than 4000 mg/L, the removal rate of uranium reaches 80%. And when the concentration of sulfate reaches 10000 mg/L, the removal rate of uranium is less than 15%. Being sulfate in the uranium wastewater, the ultimately removal rate of uranium in ZVI-SRB joint treatment system is higher than the SRB system.

(3) The concentration of nitrate has a significant influence on the treatment of uranium wastewater by SRB system. When the concentration of nitrate reaches 1000 mg/L, it has little influence on the removal rate of uranium on the SRB system. However, as the concentration of nitrate reaches 1500 mg/L, it affects the removal rate of uranium obviously. Being nitrate in the uranium wastewater, the ultimate removal rate of uranium by adding ZVI is lower than without adding.

References


