Biosorption of $^{241}$Am by *Rhizopus arrihizus*: preliminary investigation and evaluation

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Abstract

The biosorption of $^{241}$Am from solution by a fungus—*Rhizopus Arrihizus* (*R. arrihizus*), and the effect of experimental conditions on the adsorption were investigated. The preliminary results showed that the biosorption of $^{241}$Am by *R. arrihizus* is very efficient. An average of more than 99% of the total $^{241}$Am was removed by *R. arrihizus* of 1.3g/l (dry weight) from $^{241}$Am solutions of 5.6–111MBq/l (44.3–877.2 µg/l) ($C_0$), with adsorption capacities ($W$) of 4.2–79.4MBq/g biomass (dry weight) (33.2–627.5 µg/g). The biosorption equilibrium was achieved within 1h and the optimum pH ranged from 1 to 3. No significant differences in $^{241}$Am biosorption were observed at 10–45 $^\circ$C, or in solutions containing Au $^{3+}$ or Ag $^{+}$, even 2000 times above $^{241}$Am concentration. The relationship between concentrations and adsorption capacities of $^{241}$Am indicated that the $^{241}$Am biosorption by *R. arrihizus* obeys the Freundlich adsorption equation.

Keywords: Radionuclides; $^{241}$Am; *Rhizopus arrihizus*; Biosorption

1. Introduction

The treatment of radioactive wastewater is one of the important concerns and must be seriously considered in the nuclear industry. As a transuranium element, americium has about 20 radioisotopes or isomers. Among them, $^{241}$Am ($T_{1/2} = 433$ yr, $E_x = 5.468$ MeV, 86.6%; $E_g = 5.443$ MeV, 12.3%; $E_g = 0.0596$ MeV, 35%) is the most important and is generally used as a target material in the nuclear industry. Also, it has widespread use in other fields. For example, most of the fire alarms in hotels, hospitals and other service centers contain $^{241}$Am as source. Unfortunately, $^{241}$Am causes some of the most serious contamination concerns due to its high toxicity and long half-life. If $^{241}$Am gets into a human body, it mainly stays in the skeleton and liver. The maximum permissible dose or concentration for $^{241}$Am in the human body or in water is 11.1kBq ($\sim 8.76 \times 10^{-8}$ g) and 1.48Bq/ml ($\sim 1.17 \times 10^{-6}$ g/l), respectively (Benedict et al., 1981). Due to these reasons, much effort has been invested in the removal and treatment of wastewater containing $^{241}$Am (Nash, 1993). Most studies have focused on the extraction and separation of $^{241}$Am from high-radioactive liquids by chemical reagents (Zhu et al., 1995; Ye et al., 2000). However, few reports were involved in the treatment of low or medium radioactive aqueous solutions containing $^{241}$Am.

Over the past few decades, significant attention has been paid to the removal of heavy metals and degradation of organic chemicals from the wastewater by using biosorption technology for environmental protection (Ross, 1992; Hafez et al., 1997; Bae et al., 2000; Elmen et al., 1997; Reardon et al., 2000; Schorer and Eisele,
2. Experimental

2.1. Reagents and experimental solutions

$^{241}$Am solution in nitrate salt form ($^{241}$Am(NO$_3$)$_3$) was provided by the Institute of Nuclear Physics and Chemistry, CAEP (Mianyang, P. R. China). Stock solutions containing $^{241}$Am of 555 MBq/l (4.38 mg/l) and diluted solutions were prepared by diluting the original solution with redistilled water. All the other chemical regents were of A.P or chromatographic grade and were used without further purification.

All glasswares for the biosorption experiments were routinely rinsed with 0.5 M HNO$_3$ and washed extensively with water to prevent interference by contaminants. The pH of each solution was measured by a digital pH meter and adjusted by the addition of 0.2 M HNO$_3$ or 0.2 M NaOH solution.

2.2. Strains and culture

*Rhizopus arrhizus* (R. arrhizus) was obtained as a gift from the College of Life Science, Sichuan University (Chengdu, P. R. China). Culture medium for growing *R. arrhizus* contained glucose (1%) and (NH$_4$)$_2$SO$_4$ (0.5%) in exudate of potato, and its pH was 6.5. The maintained *R. arrhizus* spores were inoculated in a test tube and incubated for 7 days at 25°C. The spores were eluted by sterile water and were transferred to the culture medium, then cultivated for 57 days at 25°C. The cultured *R. arrhizus* were collected by centrifugation or filtration and were directly applied to the adsorption experiments. In order to calculate the adsorption capacities ($W$), the dry weight of *R. arrhizus* was measured by heating in a stove for 2 h at 100–120°C, and the dry-to-wet-weight ratio was calculated. In this experiment, the dry-to-wet-weight ratio of *R. arrhizus* was 1:7.7.

2.3. Adsorption experiments

To the $^{241}$Am solutions of definite radioactive concentrations in desired pH values, precultured wet *R. arrhizus* were added. The mixture was shaken on a rotary shaker at 200 rpm at room temperature for 2 h, except as otherwise described. Then, the mixture was centrifuged at 3000 rpm for 15 min. The supernatant liquid was removed, and assayed for radioactivity of $^{241}$Am by means of an automatic counter with an NaI well detector.

The results were expressed as adsorption rate ($R$, %) and adsorption capacity ($W$, μg/g or MBq/g dry sorbent). The adsorption rate and adsorption capacity were calculated as

$$ R = (1 - C/C_0)100\% $$

and

$$ W = (C_0 - C)/m $$

where $C_0$ is the initial $^{241}$Am concentration (MBq/l, or μg/l), $C$ is the final $^{241}$Am concentration in the solution, and $m$ is the sorbent concentration in dry form (g/l). The conversion relationship between mass and radioactivity for $^{241}$Am is as follows: 1 mg = 126.54 MBq.

3. Results and discussion

3.1. Effect of pH or acidity on $^{241}$Am adsorption

Many previous reports have shown that pH or acidity was an important factor influencing the biosorption ability of microorganism for heavy metals (Friis and Myers-Keith, 1986; Hafez et al, 1997; Nakajima and Sakaguchi, 1986; Volesky and May-Philips, 1993). As described in Fig.1, the optimum pH for $^{241}$Am adsorption by *R. arrhizus* ranged from 1 to 3. Within this range, the adsorption rate could be up to 99%. When the pH was above 3, the adsorption rate and adsorption rate decreased gradually with increasing acidity. This result may come into existence as hydroxide colloid with pH value. The reason was considered as that americium may come into existence as hydroxide colloid with increasing pH, resulting in the decrease of the adsorption rate. When the acidity increased, the adsorption ability also decreased. This result may be explained as the characteristic variation of various genes on the cell wall at different pH conditions (Kuyucak and Volesky, 1988). When the acidity was more than 0.1 mol/l, the effect of pH on a group of cell wall increased, so that the adsorption rate of $^{241}$Am decreased.
3.2. Effect of contact time on $^{241}$Am adsorption

The effect of contact time on $^{241}$Am adsorption by $R.$ arrhizus is shown in Fig. 2. It can be seen that the $^{241}$Am adsorption was closely related to contact time. The adsorption rate increased rapidly with time and came up to 99% in 1 h. Later, the adsorption rate grew slowly and tended to the equilibrium. Based on this result, the contact time was set up as 2 h for the other adsorption experiments, except as otherwise described.

3.3. Effect of temperature on $^{241}$Am adsorption

As shown in Fig. 3, no significant differences in $^{241}$Am biosorption were observed at 10–45°C. Even until 45°C, the adsorption rate was still up to 98%. This result indicated that the temperature was not a primary factor to influence upon $^{241}$Am adsorption, and that $^{241}$Am adsorption was independent of energy. Since the microorganism is almost in a stagnant state at about 45°C, the result implied that the “dead” microorganism still has a strong ability in the adsorption of $^{241}$Am. This is similar to the results reported by others (Brady and Duncan, 1994; Volesky and May-Philips, 1993; Zhu and Xu, 1998). For convenience, most of the other adsorption experiments were performed at room temperature.

3.4. Effect of $R.$ arrhizus concentration on $^{241}$Am adsorption

The effect of $R.$ arrhizus concentration on $^{241}$Am adsorption is shown in Fig. 4. It can be seen that the $^{241}$Am adsorption by $R.$ arrhizus is exceptionally efficient and the adsorption rate grew slowly with increasing $R.$ arrhizus concentration. Even when the dry fungi concentration was 0.19 g/l, the adsorption rate
was up to 96.7%; until 1.3 g/l, the adsorption rate increased up to 99.5%, then the adsorption tended to the equilibrium. In contrast, the adsorption capacity declined with increasing *R. arrihizus* concentration. For example, when the dry fungi concentration was 0.19 g/l, the adsorption capacity was 28.1 MBq/g (222.1 μg/g). When dry fungi concentration increased to 2.6 g/l, the adsorption capacity dropped to 2.13 MBq/g (16.8 μg/g). This result could be understood by noting that the mass of initial 241Am was fixed while *R. arrihizus* concentration was variable.

3.5. Effect of 241Am concentration on the adsorption

The effect of 241Am concentration on adsorption is shown in Fig. 5. As shown in Fig. 5, within the range of initial 241Am concentration (C₀) of 5.6–111 MBq/l (44.3–877.2 μg/l), the amount of 241Am adsorbed by *R. arrihizus* of 1.3 g/l grew with increasing 241Am concentration, while the adsorption rate remained almost constant with an average value of 99%. It can be seen that the adsorption capacities for 241Am were yet to be saturated even when the 241Am concentration was up to 111 MBq/l, so that the 241Am biosorption process by *R. arrihizus* may be described by a Freundlich isotherm equation:

\[ w = kC^{1/n}_0 \]

where \( k \) and \( n \) are Freundlich constants related to the degree of adsorption capacity and adsorption strength, \( w \) is the metal amount adsorbed per every biological cell, and \( C_0 \) is the metal-ion concentration of the solution. The logarithmic form of the equation should give a right line; thus the constants \( k \) and \( n \) may be evaluated in this way. Taking experimental data from the effect of different 241Am concentrations and according to Freundlich equation for isothermal adsorption, one obtains the result shown in Fig. 6. 241Am adsorption for isothermal equation might be evaluated through a fitting curve:

\[ \log w = 0.981 \log C_0 - 0.11, \text{ its related coefficient: } r = 0.9996. \]

For equation \( w = kC^{1/n}_0 \), where \( k \) (241Am) = 0.78, \( n \) (241Am) = 1.02, we obtained \( w = 0.78C_0^{1/1.02} \).

3.6. Effect of coexistent ions on 241Am adsorption

Considering the wastewater produced from the preparation and recovery process of 241Am fire alarms containing mainly two coexistent ions Au³⁺ and Ag⁺, we must study the effect of Au³⁺ and Ag⁺ on 241Am adsorption by *R. arrihizus*. It can be seen from Table 1 that at C₀ (241Am) = 44.3 μg/l, m (R. arrihizus) = 1.3 g/l, Au³⁺ and Ag⁺ were not found to have a distinct influence on 241Am adsorption, even though the concentrations of Au³⁺, Ag⁺ were 2000 times more than that of 241Am. At this condition, the adsorption rate of 241Am by *R. arrihizus* was still up to 99%. It may be explained that the adsorption amount adsorbed by *R. arrihizus* was far from the saturated state. Although the 241Am adsorption was challenged with Au³⁺ or Ag⁺, no significant differences were observed yet.

Table 1

<table>
<thead>
<tr>
<th></th>
<th>Au³⁺</th>
<th>Ag⁺</th>
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<tbody>
<tr>
<td>C (mg/l)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Adsorption rate (%)</td>
<td>95.9</td>
<td>95.4</td>
</tr>
<tr>
<td>Adsorption rate (%)</td>
<td>99.5</td>
<td>99.4</td>
</tr>
</tbody>
</table>

*a* The adsorption experiments were performed in conditions such as C₀ (241Am) = 5.6 MBq/l, m (R. arrihizus) = 1.3 g/l, and pH = 1.
4. Conclusion

It has been shown in this study that R. arrihizus is an exceptionally efficient biosorbent for $^{241}$Am. The adsorbed $^{241}$Am amount ($w$) could be up to 79.4 MBq/g dry weight (627.5 μg/g) from $^{241}$Am solution of 111 MBq/l (877.2 μg/l) ($C_0$) by R. arrihizus of 1.3 g/l. These preliminary results indicated that the treatment of $^{241}$Am wastewater by R. arrihizus is available. However, it should be further investigated for practical application. The immobilized microorganism and continuous chromatography were considered as a promising way for practical treatment.

References


