Research Group for Interfacial Reaction Field Chemistry

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The research objectives of this group are to explore novel chemical reactions of aqueous species of elements at liquid-solid and liquid-liquid interfaces in order to contribute to environmental chemistry and liquid and waste treatments including valuable metal recovery. In the year of 2016, we studied 1) accumulation of radioactive Cs by Shiitake mushroom from radioactive-Cs-contaminated wood logs [1] and 2) extraction characteristics of diglycolamic acid extractant for rare-earth metal ions [2].

Accumulation of radioactive Cs by Shiitake mushroom from radioactive-Cs-contaminated wood logs

It is known that mushrooms accumulate radioactive Cs from contaminated litters and wood logs. But, there was no available knowledge to prevent accumulation of Cs in fruit bodies (cap and stem) of mushrooms. In this research, we challenged ourselves to reducing Cs accumulation in Shiitake mushroom from contaminated wood log.

We grew Shiitake by inoculating the sawdust spawn (mixtures of saw dust and spawn of Shiitake) in a wood log contaminated with the radioactive Cs from the Fukushima Daiichi Nuclear Power Plant to examine the absorption of radioactive Cs by Shiitake. The concentration of radioactive Cs in the fruit body of Shiitake was about 160 Bq/kg in average, which was almost the same as the Cs concentration, about 160 Bq/kg, in the wood log. In the next step, we prepared the sawdust spawn containing 5 or 10 weight % of vermiculite powder with high sorption capacity for Cs and inoculated it in the wood log to grow Shiitake. The concentration of Cs in the fruit body decreased to about 80 and 60 % of the Cs concentration in the wood log when the vermiculite content was 5 and 10 %, respectively. When zeolite powder was used instead of vermiculite, the Cs concentrations in the fruit body decreased similarly or more. These results show that the vermiculite and zeolite in the sawdust spawn reduced the absorption of radioactive Cs by the fruit body of mushroom. After the harvest of the fruit body cultured from the vermiculite-containing sawdust spawn, the distribution of radioactive Cs in the wood log was analyzed. We found that Cs was accumulated in the sawdust spawn. On the other hand, Cs was not accumulated in the sawdust spawn from which any fruit body did not grow. These results suggest that the Cs dissolved in the water in the wood log migrated along with the water when Shiitake absorbed the water and a fraction of the Cs was adsorbed on the vermiculite before being absorbed by Shiitake.

These results suggest that reduction of accumulation of radioactive Cs by Shiitake may be possible by selecting minerals and adjusting their mixing ratios.

Extraction characteristics of diglycolamic acid extractant for rare-earth metal ions

Liquid–liquid extraction is an effective separation and purification method to selectively recover target metal ions from aqueous solutions containing a variety of metal ions. The extractant plays a key role in the efficiency of extraction and separation. To date, numerous potentially attractive extractants have been developed for efficient extraction of valuable metal ions such as rare-earth (RE) elements. However, the mutual separation of individual RE cations (RE^{3+}) from each other is difficult because of their chemical similarity. In this study, we have developed novel acidic tridentate chelate ligands with a diglycolamic acid (DGAA) framework, which is composed of an amide group and a carboxy group connected by an ether chain. *N*,*N*-dioctyldiglycolamic acid (DODGAA), with a tertiary amide group, provides remarkably high extraction and separation performance for all RE^{3+} compared with typical commercial extractants. Furthermore, DODGAA exhibits high selectivity for heavier RE^{3+}, and high mutual separation ability for light RE^{3+}. On the other hand, *N*-dodecyldiglycolamic acid (C_{12}DGAA), with a secondary amide group, shows the similar extraction behaviour for RE^{3+} compared with DODGAA. However, the extraction performance and separation ability of C_{12}DGAA for RE^{3+} are lower than those of DODGAA because of the weaker basicity of the amide oxygen. The results suggest that the amide group of DGAA-type extractants has a significant influence on the extraction characteristics of the extractants. We found that RE^{3+} transfer with DGAA-type extractants proceeded through a proton-exchange reaction, forming a 1:3 complex, $RE(DGAA)_3$. The extraction equilibrium equation for RE^{3+} transfer using DGAA-type extractants (HL) is represented as follows:

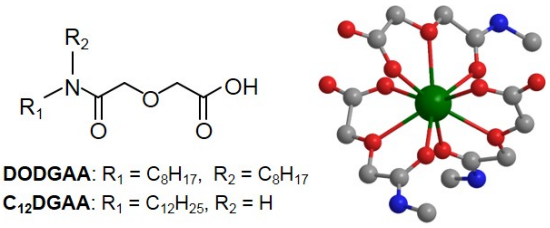

Fig. 1 Crystal structure of $[La(DGAA)_3]$. Green = La^{3+}; red = oxygen; blue = nitrogen; gray = carbon. Hydrogen atoms, alkyl chain, and H_2O molecules are not shown for clarity.

$$RE^{3+} + 3HL_{org} \leftrightarrow RE(L)_{3,org} + 3H^+$$

Furthermore, structural characterization by X-ray diffraction revealed that three DGAA molecules coordinated to the La^{3+} central ion in a tridentate fashion and the La^{3+} primary coordination sphere consisted of three oxygen atoms from the amide group, three oxygen atoms from the ether group, and three oxygen atoms from the carboxy group with average coordination distances of 2.502 Å, 2.649 Å, and 2.481 Å, respectively (Fig. 1).

These findings suggest the molecule incorporating a DGAA framework is a promising tridentate chelate extractant for RE^{3+}.

References

[1] T. Ohnuki et al., Sci. Rep., DOI: 10.1038/srep29866.
[2] K. Shimojo *et al.*, Solvent Extr. Res. Dev., Jpn. **23**, 151 (2016).