

Ion-selective adsorption of lead by a two-dimensional terbium oxalate framework

T. Nankawa¹⁾, Y. Sekine²⁾, T. Yamada³⁾

1): Interfacial Reaction Field Chemistry Gr, JAEA 2): Mater. Sci. Res. Center. 3): Univ. Tokyo

Clean water resources are becoming increasingly limited, and advances in toxic ion removal technology are essential for dealing with the global water shortage crisis. In particular, lead (Pb) poses a major threat to human health because it accumulates in the body. Pb poisoning occurs mainly by ingestion of water contaminated with Pb. Sorption using adsorbent materials, such as activated carbon, zeolites has been used to remove toxic ions from water. However, the ion selectivity and absorption capacity of these materials still need to be improved to clean up water more effectively.

In this study, we synthesized a metal-organic framework (MOF) consisting of terbium (Tb) and oxalate by a one-pot hydrothermal method to obtain an ammonium ion contained Tb oxalate framework (TOF-NH₄). The ion absorptivity of the TOF was investigated by sorption tests. According to the results, ionic radius affects adsorption of each ion. And the crystal structure of the TOFs provided useful insights into the ionic radius recognition by the adsorbent.¹

The ion absorptivity of TOF-NH₄ was examined by using a mixed-ion solution containing Pb²⁺, Cd²⁺, Mn²⁺, Co²⁺, Ni²⁺, Cu²⁺, Na⁺, K⁺, Mg²⁺, and Ca²⁺, which are common hazardous or environmentally abundant ions, at concentrations of 0.1 mmol L⁻¹. The removal efficiency value for each metal (R_{eff} (%)) was estimated as

$$R_{\text{eff}} (\%) = (C_i - C_t) / C_i \times 100 \quad (1)$$

where C_i and C_t (mg L⁻¹) are the concentrations of each ion in the aqueous solution initially and after reaction for time t (min). The R_{eff} values for Pb²⁺, Ca²⁺, and Cd²⁺ were 99.9%, 99.0%, and 68% at 40 min, respectively, and those for the other metals were less than 10% (**Figure 1(a)**). We also examined the ionic selectivity of TOF-NH₄ by using a mixed solution containing Pb²⁺ and Ca²⁺ at concentrations of 25 mmol L⁻¹. After the reaction in the mixed solution, the concentrations of Pb²⁺ and Ca²⁺ adsorbed in TOF-NH₄ were measured. To clarify the Pb selectivity of TOF, we calculated the ionic ratio of Pb over Ca. The value of Pb/Ca was 4.06, indicating that Pb²⁺ was selectively adsorbed approximately four-fold more than Ca²⁺ (**Figure 1(b)**).

The values of the distribution coefficient (K_d) and the maximum sorption capacity (Q_{max}) are also important properties for an adsorbent in addition to ion selectivity. The value of Q_{max} of TOF-NH₄ for Pb²⁺ was estimated to be 276 mg g⁻¹ and the K_d values of TOF-NH₄ for Pb²⁺ adsorption was also estimated to be 6.7×10^4 cm³ g⁻¹. In general, a material with a K_d value above 10^4 (m³ g⁻¹) is considered to be an excellent adsorbent. The Q_{max} value (276 mg g⁻¹) of TOF-NH₄ for Pb²⁺ was higher than those of conventional adsorbents. We also confirmed TOF-NH₄ is reusable. These results indicate that the TOF is an excellent Pb reusable

adsorbent with high Pb selectivity and high K_d and Q_{max} values.

TOF-NH₄ showed structural changes caused by sorption of Pb²⁺ in the framework (Figure 2). The Powder X-ray diffraction pattern of TOF-NH₄ after adsorption of Pb²⁺, which is referred as TOF-Pb was completely different from the initial pattern. Structural analysis showed that TOF-Pb had an adsorption structure of hydrated Pb²⁺ on the Tb oxalate framework. The structure consists of a 2D structure with the layer distance, which is similar in the size of hydrated Pb²⁺. The result suggested that the high Pb selectivity of the TOF is due to the similarity of the interlayer distance of the 2D sheet structure to the ionic size of hydrated Pb²⁺. This idea is supported by the observation that Pb²⁺, Cd²⁺, and Ca²⁺ were selectively adsorbed from the mixed solution, meaning larger ions tend to be adsorbed more selectively. In a previous study, we also confirmed that the interlayer distance of TOF could be changed by changing the host metal ion.² Thus, our findings not only demonstrated the usefulness of the TOF as a Pb-selective adsorbent, but also provide important insights into a strategy for developing materials with high ion selectivity.

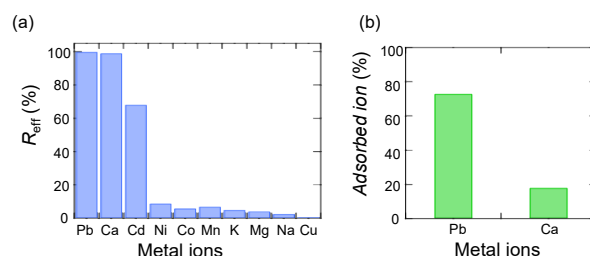


Figure 1 (a) R_{eff} of TOF-NH₄ in a mixed-ion solution. (b) ion absorptivity in TOF-NH₄ using mixed solution containing Pb²⁺ and Ca²⁺ at concentrations of 25 mmol L⁻¹

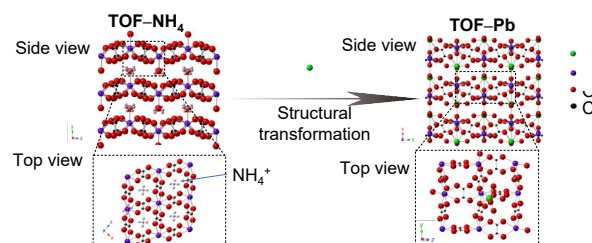


Figure 2 Schematics of 2D square grid sheets of TOF-NH₄ and TOF-Pb.

References

- [1] T. Nankawa *et al.*, Bull. Chem. Soc. Japan. **95**, 825 (2022).
- [2] T. Nankawa *et al.*, U.S. Patent application number 15/680,397 (2017).