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Adsorption of Perfluoroalkyl Substances on Allophane

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Per- and polyfluoroalkyl substances (PFAS) are a serious problem of contamination of aquatic environments due to their persistence and bioaccumulation [1]. There have been few studies on the dynamics of PFAS in soil, and it is essential to understand the adsorption characteristics of PFAS in soil to elucidate their leaching mechanisms, especially into groundwater. On the other hand, allophane, an aluminosilicate typically found in the soil, is thought to contribute to the adsorption of PFAS because of its high specific surface area and surface charge. Perfluorooctanoic acid (PFOA) used in this experiment is present in the environment mainly as anions, dissociating hydrogen ions, and are highly reactive with positive charges. As the soil becomes more acidic, the hydroxyl groups on the surface of allophane become positively charged, increasing their reactivity with anions. The objective of this study was to investigate the mode of retention of PFOA on allophane using Al K-edge XANES spectroscopy.

Synthetic allophane adsorbed with PFOA was analyzed. Allophane was hydrothermally synthesized by mixing reagents at a molar ratio of Si/Al = 1/1. A solution containing PFOA was added to the synthesized allophane and shaken for up to 168 hours. After PFOA adsorption, the allophane was washed and lyophilized, then applied to carbon tape for Al absorption edge XANES measurements. Aluminum acetate, aluminum fluoride, and synthesized allophane were used as standard samples. Al K-edge XANES spectra were measured at BL-10, SR Center, Ritsumeikan University. The measurement modes were fluorescence yield mode.

Figure 1 shows the Al K-edge XANES spectra of PFOA-adsorbed allophane. The standard compound of Al-acetate shows an absorption edge at 1569 eV and a broad peak at 1583 eV. Al-fluoride shows an absorption edge at 1571 eV and peaks at 1576 and 1587 eV. Synthetic allophane shows an absorption edge at 1568 eV and a weak peak at 1571 eV. The XANES spectra of PFOA-adsorbed allophane shows no peaks characteristic of aluminum acetate or Al-fluoride and were similar to those of pre-adsorbed allophane. The overall shape of the XANES spectrum did not change as the reaction time between PFOA and allophane increased.

If the shape of the Al XANES spectrum of PFOA-adsorbed allophane is similar to that of the Al-acetate of the standard sample, it is likely that PFOA is chemically bonded to the Al-O on the surface of the allophane and the carboxyl group, the functional group of PFOA. However, the shape of the XANES spectrum of allophane adsorbed with PFOA was similar to that of allophane, not Al-acetate. This suggests that electrostatic interactions on the allophane surface, rather than chemical bonding, are responsible for the adsorption of PFOA on allophane. Further investigations using different analytical techniques are need to understand the mechanism of PFOA retention on allophane.

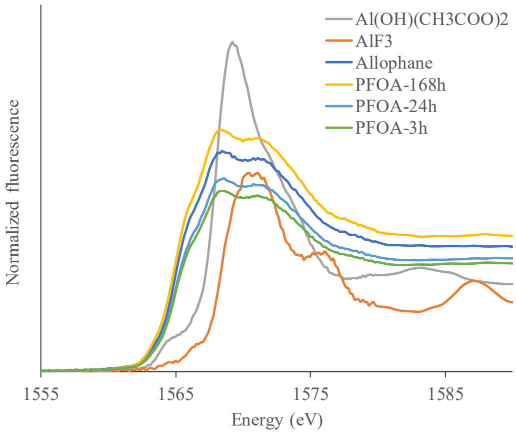

Fig. 1 Al K-edge XANES spectra of PFOA-adsorbed allophane and Al standard compounds.

References

[1] Campos-Pereira, H., Kleja, D.B., Sjöstedt, C., Ahrens, L., Klysubun, W. and Gustafsson, J.P. *Environmental Science & Technology 2020*, 54, 15722.