XAFS study of antimony adsorption on faceted TiO_2

Chuanyong Jing and Li Yan
Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing, China
cyjing@rcees.ac.cn

Antimony (Sb) contamination poses an emerging environmental risk, whereas its removal remains a contemporary challenge due to the lack of knowledge in its surface chemistry and efficient adsorbent.

In this study, self-assembly {001} TiO_2 was examined for its effectiveness in Sb removal, and the molecular level surface chemistry was studied with X-ray absorption spectroscopy and density functional theory calculations.

The kinetics results show that Sb adsorption followed the pseudo-second order reaction, and the Langmuir adsorption capacity was 200 mg/g for Sb(III) and 156 mg/g for Sb(V). The PZC of TiO_2, which was 6.6 prior to the adsorption experiment, shifted to 4.8 and <0 after adsorption of Sb(III) and Sb(V), respectively, indicating the formation of negatively charged inner-sphere complexes. EXAFS results suggest that Sb(III/V) adsorption exhibited a bidentate binuclear surface complex. The orbital hybridizing of complexes was studied by XANES, molecular orbital theory (MO), and density of states (DOS) calculations. The change in orbital energy derived from orbital hybridizing of adsorbed Sb on surfaces is the driving force underlining the Sb surface chemistry. New bonds between Sb and TiO_2 surface were formed with matched orbital energies. Integrating the molecular and electronic structures into surface complexation modeling reveals the nature of macroscopic Sb adsorption behaviors.

The understanding of Sb surface chemistry enables us to explain why TiO_2 exposed with high-energy {001} facet exhibited favorable Sb adsorption. Our DFT calculations indicated that the surface reconstruction exists on {001} facets in contact with Sb molecules. With respect to the pristine {001} facet with 100% Ti_{5c} and 100% O_{2c} atoms, surface reconstruction reduces the amount of O_{2c} atoms by the formation of O_{2c}-H bond, where H is contributed by the dissociation of $Sb(OH)_3$ or $Sb(OH)_6^-$. Both surface reconstruction and dissociation adsorption of Sb molecules contribute to a favorable adsorption configuration with a low adsorption energy. Therefore, the {001} TiO_2 is capable of immobilizing Sb, and this molecular mechanism may be generalizable and applicable to other metal oxide surfaces.