

Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) Imaging and 3D Reconstruction of Cu in Metal Scavenging Polymers

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We have reported on a novel concept for the extraction of Cu from water, motivated for: remediation of polluted waterways; upcycling waste; and functional anti-biofouling coatings [1-3]. Due to the thin nature (~10nm thick) of the films, characterization to understand Cu distributions and chemical-association is very challenging.

ToF-SIMS was applied to study the distribution of Cu in a variety of these polymer constructs to visualise Cu localization and to assist in identifying the ligands binding copper within the polymers. In 10micron thick mesoporous structures Cu could be imaged in cross-sections and correlated with polymer content. In flat, thin films, ToF-SIMS imaging of the surface was conducted followed by a sequence of surface sputtering with a C₆₀ ion source coupled with sequential imaging. This process enabled 3D reconstruction of Cu distribution in the films with a depth resolution of ~1nm. These analyses have provided unique information on the Cu distribution in these materials as well as the effect of organic layers of polysaccharides that acts as the first stage of biofouling in aqueous environments.

Since ToF-SIMS provides molecular as well as elemental fragments, the Cu association with different organic layers could be identified. Furthermore, information as to the Cu-binding was also given. Cu(II)HO⁺ and Cu(II)CN⁺ were indicative of hydroxide and Schiff-base complexes respectively in different components of the layers. These data and conclusions were supported by other characterization results from Quartz Crystal Microbalance with Dissipation, X-ray Photoelectron Spectroscopy, X-ray Absorption Near Edge Spectroscopy (XANES), and Grazing incidence XANES.

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2. Lindén, J.B., et al., Polyethyleneimine for copper absorption II: kinetics, selectivity and efficiency from seawater. *RSC Advances*, 2015. 5(64): p. 51883-51890.
3. Kaur, S., et al., Unhindered copper uptake by glutaraldehyde-polyethyleneimine coatings in an artificial seawater model system with adsorbed swollen polysaccharides and competing ligand EDTA. *Biofouling*, 2017: p. 1-11.

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