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Assessing the Binding Performance of Amyloid−Carbon Membranes toward Heavy Metal Ions

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Supporting Information

ABSTRACT: Amyloid−carbon hybrid membranes have exceptional performance in removing heavy metal ions from water because of the presence of multiple binding sites on the amyloid fibrils, but the binding process is still not fully understood. To understand the mechanisms of amyloid−metal ion binding, we perform adsorption isotherms on a model system given by β-lactoglobulin amyloid fibrils and four representative heavy metal ions: chromium (Cr), nickel (Ni), silver (Ag), and platinum (Pt). Furthermore, to get a comprehensive thermodynamic picture of the binding process between amino acid residues and heavy metals, we here use isothermal titration calorimetry on native β-lactoglobulin monomers and amyloid fibrils exposed to the two model metal ions, that is, silver and chromium. A conclusive thermodynamic insight on the binding process emerges by direct measurements of enthalpy and entropy changes, association binding constant, and average number of binding sites of the protein monomer and amyloid fibril. As a result of the strong amyloid binding affinity between amino acids and metal ions, when the protein is converted into amyloid fibrils and assembled into membranes, the resulting amyloid-activated carbon hybrids remove all the tested heavy metals with efficiencies beyond 99%. Importantly, the efficiency remains stable during several consecutive cycles, demonstrating a high adsorption capacity and a long lifetime and reusability of the membranes. The recovery of adsorbed precious metal ions converted into elemental metals is shown to be a general feature of these membranes, with platinum and silver successfully recovered from saturated hybrid membranes by a simple thermal reduction. The separation performance, evaluated on real electroplating industrial wastewater containing chromium and nickel, is found to exceed 99% at a permeability as high as 2.92×10^{-16} m^2, that is, at least 4 orders of magnitude higher than typical nanofiltration membranes, conclusively validating the technology under stringent real conditions.