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Electrochemical detection of Cd^{2+} ions in aqueous samples at nanoelectrodes

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Contamination from heavy metals has been a potent threat to the environment, and its detrimental effects are felt globally. They bio-accumulate through the food chain, thus leaving humans highly vulnerable to overwhelming health hazards. Most traditional metal-detecting analytical instruments necessitate extensive sample pre-treatment processes, consequently, change metal speciation, one of the most critical factors for evaluating metal toxicity. Furthermore, they are cumbersome, require expensive instruments that are less user-friendly, restricting real-time metal monitoring. As a result, the development of a low-cost, portable, and reliable sensor capable of delivering precise information on metal speciation will significantly assist in the efficient implementation of metal mitigation systems. In this study, we utilize ion transfer between two immiscible electrolyte solutions (ITIES) to design a Cd^{2+} sensor. The chemistry at ITIES is governed by Gibbs's free energy of transfer for an ion at the interface of two immiscible solvents. A potentiostat is used to supply the energy required to overcome the energy barrier in the form of potential energy, and the resulting current is measured. ITIES is less complicated as it does not involve electron transfer; hence more attractive over other redox-based electrochemical techniques. A suitable ionophore, which lowers the energy barrier and increases the selectivity, can be added to the organic phase, facilitating the transfer of ions at lower potentials. Our electrode is a borosilicate glass electrode with an inner radius of 300 nm. It follows a hemispherical diffusion regime, owing to its nanoscale interface that allows fast kinetic measurements. An ionophore- 1-10 phenanthroline was used to facilitate the Cd^{2+} transfer across the nano-interface. We performed ITIES based cyclic voltammetry and amperometry experiments with our nanosensor in various matrices, including simple electrolytes like KCl and complicated buffer solutions such as artificial seawater and artificial cerebellum fluid. We also tested the strength of our ionophore against other standard ligands such as Ethylenediamine tetraacetic acid, Nitrilotriacetic acid and Dimercaptosuccinic acid etc. We found out that our electrode shows excellent stability and can withstand the complex matrices without fouling, an attractive feature of an exemplary sensor. We tested our sensor with Cd^{2+} dissolved in a water sample collected from Indian River Lagoon, Melbourne, FL; thus, we showcase our sensor's power as an environmental monitoring tool. To the best of our knowledge, this is the first time reporting a glass electrode with a sub-nano-meter scale for Cd^{2+} detection in a natural environmental sample using ITIES. Our ultra-small electrode will enable us to study the kinetics of ion transfer across ITIES; thus, allowing us to modify the sensor to enhance the sensitivity and selectivity.

Keywords: Cd^{2+}, Electrochemistry, ITIES, Nanosensor, Pollution

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