Analytica Chimica Acta. Vol. 1335, 2025, Article number 343423

Enhancement of electrode surface hydrophilicity and selectivity with Nafion-PSS composite for trace heavy metal sensing in electrochemical sensors

Abstract

Background: Effective electrochemical sensing requires optimal signal output value and sensitivity, which often pose a challenge due to their counter-intuitive relationship. In order to enhance both aspects, this study designs a modified screen-printed electrode (Nafion-PSS/SPE) comprising a composite formed by two sulfonate-rich polymers, namely Nafion and poly(sodium 4-styrenesulfonate) (PSS). The Nafion-PSS/SPE was utilized in the electrochemical determination of lead (Pb^{2+}) and cadmium (Cd^{2+}) via square wave anodic stripping voltammetry (SWASV). This innovative approach aims to improve detection limits and overall analytical performance in complex matrices. (84) Results: The addition of hydrophilic PSS positively improves surface wettability of Nafion-PSS/SPE, as confirmed by water contact angle analysis. Despite the improved wettability, the modified sensor maintains a high selectivity towards heavy metal ions. Cyclic voltammetry (CV) reveals a large electrochemically active surface area (ECSA) for cations (0.5646 cm^2) and a relatively low ECSA for anions (0.3221 cm^2). Under optimized conditions, the stripping responses for Pb^{2+} and Cd^{2+} exhibited linearity within the concentration ranges of 0.025–0.7 ppm and 0.0125–0.4 ppm, respectively. The detection limits achieved by the modified sensor are 6.478 ppb (Pb^{2+}) and 5.277 ppb (Cd^{2+}). The enhancement observed can be ascribed to the following factors, including presence of sulfonate ligands (Nafion and PSS), enhanced wettability (PSS), and surface selectivity (Nafion). Furthermore, even in the presence of interfering ions replicating the composition of effluent from the pesticide industry, the Nafion-PSS/SPE showcases remarkable selectivity for the target Pb^{2+} and Cd^{2+} ions. (148) Significance: This work presents a facile screen-printing technique that could be potentially adopted for batch production of heavy metal sensing devices. Besides, by scrutinizing the surface properties of the modified sensor, this work aims to provide insights on how the proposed modification approach can help to improve the sensor's detection performance.

Keywords

Heavy metals; Nafion; Poly(sodium 4-styrenesulfonate); Screen-printed electrode; Stripping voltammetry