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Crown ether-based structures for sensitive electrochemical detection

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Abstract

N-(2-Hydroxypropyl)methacrylamide-co-*N*-acryloxysuccinimide with 2-aminomethyl-18-crown-6 (p(HPMA-NAS-18C6)) graft copolymer deposited on the gold (Au) electrode is able to bind heavy metal cations from aqueous solutions. The binding of the lead(II) cations (Pb^{2+}) is monitored by quartz crystal microbalance, cyclic voltammetry, and anodic stripping voltammetry. Electrochemical studies have demonstrated that the presence of p(HPMA-NAS-18C8) on the Au electrode surface resulted in the shift of Pb oxidation wave to less negative potentials, accompanied by the increase of the oxidation peak magnitude. The p(HPMA-NAS-18C6)-modified electrode could sensitively detect Pb^{2+} cations in a range from 10 ppb to 4.39 ppm with a low detection limit of 0.17 ppb.

Keywords

Hydrophilic copolymer, crown ether, stripping voltammetry, lead detection

Introduction

The crown ethers and their applications have been widely described in the literature[1–3] due to their remarkable ability to form strong complexes with metal and organic cations.[4]

Different crown ether-based structures have been exploited for constructing chemically modified electrodes, which offer the possibility of selective complexation of a cation.[5–8] In a previous article,[9] we reported the application of a siloxane–crown ether polyamide in the electrochemical detection of lead (Pb) at parts per billion (ppb) levels. Heavy metal contaminations constitute a severe threat to human health and environment, and Pb is a general metabolic poison and enzyme inhibitor, which can cause mental retardation and semipermanent brain damage in young children. Pb has the ability to replace calcium in bone to form sites for long-term replacement. Because of the increased industrial use of Pb and its serious hazardous effect to human health, the development of new sensitive methods for quantifying trace amount of the Pb is required.

Electrochemical method such as stripping voltammetry (SV) for the determination of heavy metal ions is one of the most favorable techniques, because of its low cost, high sensitivity, easy operation, and ability of analyzing element speciation.[10–12] SV comprises a variety of electrochemical approaches, having a step of pre-concentration onto the electrode surface prior to the voltammetric measurements. The major advantage of SV compared with direct voltammetric measurement and other analytical techniques is the pre-concentration factor.

Recently, a highly performant copolymer with active pendant crown ether units was synthesized.[13] This graft copolymer, with a controlled uniform content, was obtained by reacting the succinimide rings of *N*-(2-hydroxypropyl)-methacrylamide-co-*N*-acryloxysuccinimide copolymer p(HPMA-NAS), with 2-aminomethyl-18-crown-6 (18c6). The resulting polymer noted as p(HPMA-NAS-18C6) is a nontoxic, water soluble, and biocompatible polymer, which brings a high number of active pendant crown ether functionalities. In the present article, the capability of p(HPMA-NAS-18C6) graft copolymer to bind lead cations (Pb^{2+}) from aqueous solution and to effectively improve its reoxidation was investigated. A novel and efficient modified electrode for the voltammetric determination of Pb^{2+} in aqueous solutions was developed.

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