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A review of the identification and detection of heavy metal ions in the environment by voltammetry

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ABSTRACT

Currently, environmental pollution by heavy metals is a global problem. Therefore, it is crucial to develop effective detection techniques to determine the levels of heavy metal contamination in various mediums. Voltammetry is a highly sensitive electrochemical method used for the *in situ* detection of heavy metal ions. This study investigates the current trends related to electrode modification, developments in materials, and optimization of the experimental parameters. We discuss the sensing performance of four kinds of nanomaterials capable of inorganic modification (metal nanoparticles, metal oxides, carbonaceous nanomaterials, and their nanocomposites). The impact of several important factors, such as the deposition potential and time, buffer solution types, and pH on the sensitivity, reproducibility, stability, and anti-interference ability of the detection process, especially with regard to the co-detection of several heavy metal ions, was reviewed. We noted that in addition to the application of voltammetry to water-related issues, it is suitable for rapid and simple identification and analyses of heavy metals in polluted soil and other mediums. Thus, it is important to conduct additional research on the application of voltammetry to this area.

1. Introduction

Although trace heavy metal elements are fundamental to living organisms for a normal and healthy life, excessive levels of heavy metal pollution in the environment could cause harm [1–3]. In order to reduce environmental pollution and mitigate the resulting degradation of soil [4] and water resources [5], it is necessary to accurately determine heavy metal concentrations.

Various techniques have been established to detect heavy metal ions (HMIs), including inductively coupled plasma mass spectrometry (ICP-MS) [6], inductively coupled plasma optical emission spectrometry (ICP-OES) [7], inductively coupled plasma atomic emission spectrometry (ICP-AES) [8], flameless atomic absorption spectrophotometry (FAAS) [9] and atomic absorption spectroscopy (AAS) [10]. These are highly sensitive and selective techniques; however, they require relatively expensive instruments, the application of complex operational procedures, and long detection times.

Notably, electrochemical methods have the advantages of low cost, simplicity, high sensitivity, ease of operation, rapid analysis, portability and applicability for field monitoring of environmental samples. However, voltammetry is the only electrochemical method that has high sensitivity and can be applied for the *in situ* identification and detection of HMIs pollution.

Significant developments have occurred in electrochemical techniques over the years, including the modification of various types of solid electrodes, which are currently applied to analyze different types of

Abbreviations: HMIs, Heavy metal ions; ICP-MS, Inductively coupled plasma mass spectrometry; ICP-OES, Inductively coupled plasma optical emission spectrometry; ICP-AES, Inductively coupled plasma atomic emission spectrometry; FAAS, Flameless atomic absorption spectrophotometry; AAS, Atomic absorption spectroscopy; CV, Cyclic voltammetry; SWV, Square wave voltammetry; LSV, Linear sweep voltammetry; DPV, Differential pulse voltammetry; WE, Working electrode; RE, Reference electrode; CE, Counter electrode; ASV, Anodic stripping voltammetry; GCE, Glassy carbon electrode; SAMs, Self-assembled monolayers; SPCEs, Screen-printed carbon electrodes; BiFEs, Bismuth film electrodes; SWASV, Square wave anodic stripping voltammetry; ZnO NFs, ZnO nanofibers; ZnO NTs, ZnO nanotubes; CPE, Carbon paste electrode; CNFs, Carbon nanofibers; VACNF, Vertically aligned carbon nanofiber; CNTs, Carbon nanotubes; NEA, Nanoelectrode array; SWCNTs, Single-walled carbon nanotubes; MWCNTs, Multi-walled carbon nanotubes; SPEs, Screen-printed electrodes; CMEs, Chemically modified electrodes; RGO, Reduced graphene oxide; ERGO, Electrochemically reduced graphene oxide; AG, Activated graphene; GO, Graphene oxide; DPASV, Differential pulse anodic stripping voltammetry; NPs, Nanoparticles; NCEs, Nafion-coated electrodes; LSSV, Linear sweep voltammetry; DPSV, Differential pulse voltammetry; SWSV, Square wave voltammetry; CTS, Chitosan; EIS, Electrochemical impedance spectra; EDTA, Ethylenediaminetetraacetic acid; PBS, Phosphate-buffered saline; BRB, Britton–Robinson buffer solution

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samples [11,12]. Lately, inorganic materials have attracted considerable attention owing to their low cost, compatibility, and strong adsorption to HMIs [13,14]. In particular, nanomaterial-based metals, metal oxides, carbonaceous metals, and their composites are the most commonly used materials in the electrochemical detection of HMIs [1–15].

Heavy metal pollution in the environment is generally attributed to Pb, Cd, Hg and Cu. This paper mainly discusses the use of voltammetry for co-detecting the existence of two or more heavy metals in different mediums, and highlights the modification of inorganic materials on the surface of the working electrode.

2. Basic principles of voltammetry for heavy metal detection

The types of voltammetry are cyclic voltammetry (CV), square wave voltammetry (SWV), linear sweep voltammetry (LSV), and differential pulse voltammetry (DPV) [16]. The difference among these techniques lies in the time waveforms produced by the respective functional application [17]. Moreover, DPV and SWV have the best detection sensitivity.

A standard analytical electrochemistry system mainly consists of three parts: an electrochemical sensing device, electrochemical detecting instrument, and electrolyte. The electrochemical detection instrument is usually composed of three electrodes: a working electrode (WE), reference electrode (RE), and counter electrode (CE). After the surfaces of the WEs are modified using different materials, they can be used for the specific detection of various kinds of metal ions [18].

Stripping voltammetry includes two steps: pre-concentration and dissolution. The pre-concentration step involves accumulating the metal cations on the surface of the WE using Faraday's reaction or adsorption, and then obtaining a correlated signal by anodic stripping voltammetry (ASV). During the Faraday reaction, the heavy metal cations are reduced to zero-valent metals under the constant negative potential, and then, they are deposited on the surface of the WE. On the other hand, the adsorption is a reaction between appropriate ligands and heavy metal cations on the surface of the WE, to produce complexes and reduce the heavy metal cations to zero-valent metals.

Following the pre-concentration step, the dissolution step is carried out by sweeping the electrode potential in the anodic direction to re-oxidize the zero-valent metals to cations [19]. A high dissolution current peak is reached during the rapid oxidation process, and the stripping current peak potential changes according to the different kinds of HMIs.

Surface modifications, such as polishing the glassy carbon electrode (GCE) with 0.1 mm and 0.05 mm alumina slurry using a polishing cloth to produce a mirror-like surface, ensure that the WE has a uniform surface area and maintains sensitive response.

3. Preparation of a modified electrode

The sensitivity of some electrodes can be improved after surface modifications. These modifications can be achieved by different ways, such as applying other materials to the electrode's surface. The preparation methods needed to construct a modified electrode could be classified into four categories according to the different reactions that occur inside or on the surface of a working electrode: adsorption, covalent bond formation, electrochemical polymerization, and electrochemical deposition [20]. It should be noted that screen-printing and incorporation are considered as preparation methods and not modification methods of the WEs.

Adsorption is a method of fixing the modified suspension on the surface of the WE by non-covalent interaction, and could be classified into three types: chemical adsorption, self-assembled monolayers, and coating. Chemical adsorption is a simple method to directly modify the electrode and is irreversible. The electrodes are modified through natural mutual adsorption between the solid material and the solution interface. Pyrolytic graphite and glassy carbon are widely used as electrode materials. Graphite has high stability and electron transfer efficiency, because it contains a large number of small organic molecules with highly conjugated systems, which are irreversibly attached to the surface of the WE by the carbon atoms under the effect of the conjugated bond. Currently, this method is not frequently applied in the laboratory because only limited materials can be used for electrode modification. On the other hand, self-assembled monolayers (SAMs) are created on the surface of the electrode through physical and chemical interactions among the functional groups with film-forming molecules, or through the spontaneous adsorption between these groups and gold [21], silver [22], or platinum [23,24] electrodes. Five types of film-forming materials are commonly used: sulfur organic compounds, organic silicon, fatty acids, alkanes, and bis-phospholipids. SAMs can ensure the structure, thermal, and electronic properties of the functional groups to strengthen the binding interactions. Coating is much easier than the above methods, and thus, it the most common adsorption method. This method is carried out by mixing the modified solution and material, and then covering the bare electrode surface with this mixture. When the solvent completely evaporates, only a stable film formed with the modified compounds remains on the surface. The coating method can be conducted through one of the following operational techniques: a) Dip coating, where the surface of the bare electrode is completely submerged into the mixture and is then exposed to the air to remove the mixture and form a film [25]; b) dispensing, where a micro syringe is used to dispense a known amount of modified droplets on the electrode surface (this method can effectively control the coated amount [26] like Liu et.al [27] dripped 2.0 μL of Co_3O_4 ethanol (0.1 mM) solution onto the surface of a freshly polished GCE and demonstrated different adsorption capacities of the porous Co_3O_4 toward Pb (II); and c) spin coating, where the electrode is submerged into the solution, rotated using a spin coating machine, and then removed to let the modified solution dry and form a film on the electrode surface [28,29], Maria [30] also used the same method to coat the graphite rod electrode surfaces by a spin-coating machine assembly consisted of a power supply and a dc motor.

The modified substance is attached to the surface through chemical reactions forming covalent bonds. In this process, some oxygen-containing groups bind to the solid electrode surface by oxidation and reduction reactions, and then bond to the modified substances to form carriers [31], Chow et.al [32] found it considerable potential for using peptides to detect metals and immobilized it at electrode surface. So an electrode array for the simultaneous determination of Cu (II), Cd (II) and Pb (II) which used the peptides Gly-Gly-His, GSH and angiotensin I respectively has recently been described. The three peptides were covalently attached to thioctic acid (TA) SAMs on gold electrodes with a fourth electrode modified with TA only.

Electrochemical polymerization and deposition are two similar methods of modifying the electrodes in an electrochemical apparatus. In the former, the pretreated electrode is placed into an electrolytic cell system with a certain concentration of monomer and electrolyte. When the electrolyzation takes place, the electrically active monomer is divided into free radicals and ions that start to polymerize and form a uniform and stable polymer film [33]. Heineman et.al [34] reported the first use of a polymer film chemically modified electrode as a potentiometric sensor whose response to Co(II) was tested over a concentration range of 10^{-2} to 10^{-6} M. Rahman et.al [35] fabricated an EDTA bonded conducting polymer modified electrode to detect Pb(II), Cu(II), and Hg(II) ions. The polymerization onto a GCE was carried out by cycling the potential between 0.0 and +1.6V. On the other hand, the electrochemical deposition relies on electrochemical redox reactions in aqueous or non-aqueous solvents, which can form insoluble deposits on the electrode surface owing to the changes in the central and external ions in the oxidation state [36-38]. Liu et al [39] developed an electrodeposited Au-NP modified SPE for Cr (VI) determination in the first time and a less density of Au-NPs on the surface attributed to the