A review on various electrochemical techniques for heavy metal ions detection with different sensing platforms

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ABSTRACT

Heavy metal ions are non-biodegradable and contaminate most of the natural resources occurring in the environment including water. Some of the heavy metals including Lead (Pb), Mercury (Hg), Arsenic (As), Chromium (Cr) and Cadmium (Cd) are considered to be highly toxic and hazardous to human health even at trace levels. This leads to the requirement of fast, accurate and reliable techniques for the detection of heavy metal ions. This review presents various electrochemical detection techniques for heavy metal ions those are user friendly, low cost, provides on-site and real time monitoring as compared to other spectroscopic and optical techniques. The categorization of different electrochemical techniques is done on the basis of different types of detection signals generated due to presence of heavy metal ions in the solution matrix like current, potential, conductivity, electrochemical impedance, and electrochemiluminescence. Also, the recent trends in electrochemical detection of heavy metal ions with various types of sensing platforms including metals, metal films, metal oxides, nanomaterials, carbon nano tubes, polymers, microspheres and biomaterials have been evoked.

1. Introduction

Heavy metal ions (HMI) are one of the micropollutants that represent a growing environmental problem and have affected various components of environment including terrestrial as well as aquatic biota. Major sources of these heavy metal ions are cosmetics and their by-products, fertilizers and other chemicals generated from industrial or household waste (Callender, 2004; Roy, 2010). These HMI do not decompose and have a tendency to accumulate in living organisms, causing various diseases and disorders to the nervous, immune, reproductive and gastrointestinal systems (Afkhami et al., 2013a; Tag et al., 2007; Turdean, 2011). Once let out in the environment, these HMI continue to exist for decades or even centuries as these are non-biodegradable (Gong et al., 2016). Among various heavy metals, lead (Pb), cadmium (Cd), mercury (Hg), chromium (Cr) and arsenic (As) are highly toxic (Cui et al., 2015; Pujol et al., 2014; Gumpu et al., 2015). Even small doses of these highly toxic metals can lead to serious problems on environment and human health (Tag et al., 2007; Gumpu et al., 2015; Array and Merkoci, 2012). Human beings are mainly exposed to these metal ions from air, water and food with fish being the major source of mercury exposure (Pujol et al., 2014; Maria, 2011; Musarrat et al., 2011; Prabhakar et al., 2012). Heavy metals are also

considered as one of the most dangerous water pollutants, extremely destructive for nature and injurious to human health (Guo et al., 2016a; Wanekaya, 2011; Kim et al., 2012; Lin et al., 2011; Aragay et al., 2011a; Bernalte et al., 2011). The detection of these heavy metal ions in natural and drinking water and determining their quantities is of paramount importance. Several international organizations like World Health Organization (WHO), Joint Food and Agricultural Organization (FAO), the US Environmental Protection Agency (EPA), Centre for Disease Control (CDC) and the European Union have included heavy metals as the priority substances to be monitored and have set certain permissible limits for their concentrations in water following the environmental quality standards (EQS) (Gumpu et al., 2015; WHO, 2011; US, 2009; Directive, 2013; Standard methods for the examination of water and wastewater, 2012). This requires development of highly sensitive and selective methods for determination of trace levels subparts per billion, ppb) of these toxic heavy metal ions in various complex matrices like biological samples (blood, serum, saliva, etc.), natural and waste water, food, air and soil.

Highly sensitive spectroscopic techniques like atomic absorption spectroscopy (AAS) (Gong et al., 2016; Array and Merkoci, 2012; Afkhami et al., 2013b; Barbosa et al., 1999; Trindade et al., 2015; Kenawy et al., 2000; a to z; Pohl, 2009), inductively coupled plasma

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mass spectroscopy (ICP-MS) (Gong et al., 2016; Silva et al., 2009; Caroli et al., 1999; Wang et al., 2015), X-ray Fluorescence Spectrometry (XRF) (Sitko et al., 2015), Neutron activation analysis (NAA) and inductively coupled plasma-optical emission spectrometry (ICP-OES) (Losev et al., 2015) are employed for detection of heavy metals in complex matrices. These techniques are versatile in terms of simultaneous determination of heavy metal ions concentration for a large range of elements. These techniques also offer very low detection limits in femtomolar range (Pujol et al., 2014). However, these spectroscopic techniques are very expensive and require trained personnel to work on the complex equipments and require multi sample preparation involving difficult analytical procedures. Also, these techniques are only suitable for quantitative analysis and needed to be coupled with other chromatographic techniques for performing metal ion speciation (Feldmann et al., 2009). This could lead to the risk of sample changes while storage and handling. Optical techniques like spectrophotometric measurements are also employed for detection of heavy metal ions (Array and Merkoci, 2012). These optical methods again involves costly and complex equipment with lasers, photo detectors, etc. that require high precision and high power operations, again not suited for in-field applications. Therefore, development of rapid, low cost, simple and reliable techniques suitable for in-situ and on-time measurements of heavy metal ions is an ongoing area of research (Cui et al., 2015; Pujol et al., 2014; Array and Merkoci, 2012). Electrochemical techniques on a contrary are more economic, user-friendly, reliable and suitable for in-field applications. These electrochemical techniques allow simple procedures and well suited to fabricate on small circuits in the form of portable devices for in-situ monitoring of contaminated samples. These techniques are also fast in terms of short analytical time as compared to other spectroscopic techniques allowing on-line monitoring of water samples (Pujol et al., 2014). However, these electrochemical techniques offer lower sensitivity and Limits of detection (LOD) as compared to other spectroscopic and optical techniques and require developments in the design to improve its performance in detection of heavy metal ions. Various electrochemical techniques are coupled with different biosensing electrodes for enhancing their sensitivity and limits of detection by modifying the electrode material. This paper reviews various electrochemical techniques employed for detection of HMI in water samples and recent advances in the development of various interface materials for modifying electrodes employed in these techniques.

2. Electrochemical sensing of heavy metal ions

Electrochemical sensing of HMI involves the use of biosensing electrodes that are employed for the purpose of passing current to the aqueous solution and generate some useful and measurable electrical signal in correspond to the electrochemical reactions within the solution due to presence of metal ions. It is due to the miniaturization of these electrodes and easy electrode modifications, the electrochemical instrumentation setup is generally compact, simple and portable making this technique effective and widely useful for HMI detection (Kudr et al., 2015; Nejdi et al., 2014, 2013; Locatelli and Melucci, 2013). These electrochemical techniques usually employ a setup having three electrodes, working electrode (WE), count electrode (CE) and reference electrode (RE) (Fig. 1) (Cui et al., 2015). The WE can be modified with different materials for specific determination of heavy metal ions (Bontidean et al., 1998; Pan et al., 2009). These interface

materials play a vital role in sensitive and selective determination of HMI. Earlier, mercury and carbon was employed most frequently as interface material for construction of these electrodes. However, due to its mechanical instability and toxicity, dropping mercury electrodes and hanging mercury drop electrodes are unsuitable for automated analysis of HMI recently. A lot of research is ongoing in the field of designing chemically modified electrodes using various interface materials including electrochemical biosensors, nanomaterials, polymers, metal oxides, carbon nanotubes, and many more.

3. General experimental setup for electrochemical detection of HMI

General experimental setup for electrochemical detection of HMI usually consists of an electrolytic cell consisting of an ionic conductor (an electrolyte) and an electronic conductor (an electrode) (Bard and Faulkner, 1944). In this case, an aqueous solution consisting of HMI acts as the electrolyte. The cell potential is measured at the interface of the electrode and electrolyte solution. Various half reactions take place in the electrolytic cell and one of the half reactions of interest is usually at the working electrode (WE). The other electrode with respect to which the cell potential is measured is termed as reference electrode (RE). A general electrochemical experiment uses an external power supply to provide an excitation signal and measure the response function in the chemical solution considering various system variables to be kept constant as represented in Fig. 1.

For a three electrode cell arrangement, the third electrode is referred to as the counter electrode (CE). The current is usually passed between the WE and CE.A general three electrode cell setup for electrochemical detection of heavy metal ions in aqueous solution is represented in Fig. 2 (Cui et al., 2015).

This setup has three electrodes as mentioned above placed in an electrolytic cell with WE modified with different interface materials as platform for heavy metal ions. In this electrochemical setup, the current is generally passed between the WE and CE. CE is placed in a separate section from the WE by some glass separators and its material is chosen such that it doesn't affects the WE. The potential is measured between the WE and RE with some high input impedance device in order to prevent any current drawn from the RE. These electrodes are connected electrically to an electrochemical workstation that are basically laboratory equipments or portable in-field devices embedded with inbuilt power source for providing excitation signals to the electrode setup and measurement units for receiving and measuring the response signals. The electrochemical workstation is connected to a computer installed with required software platforms to interpret and analyze the data received from the experiment. For the solutions with small solution resistance, a two electrode cell setup having WE and RE is employed to measure the electrode potential. The two electrode cell setup is depicted in Fig. 3(a). However, for electrochemical experiments having larger solution resistance involving non-aqueous solutions with low conductivities, a three electrode cell setup having WE, RE and CE is used as depicted in Fig. 3(b).

4. Various electrochemical techniques for HMI Detection

Electrochemical techniques for detection of heavy metal ions in an aqueous solution are classified according to the different electrical signals generated in the solution due to the presence of HMI. The presence of HMI can cause change in various electrical parameters like current, voltage, electrochemical impedance, charge and electroluminescence (Cui et al., 2015; Combellas et al., 2008; Fan et al., 2009). Based on various electrical signals, electrochemical techniques are classified into Amperometric, voltammetric, potentiometric, impedance measurement, coulometric and electrochemiluminescent techniques. In most of these techniques, either one of the current or potential is controlled to measure the change in the other parameter.
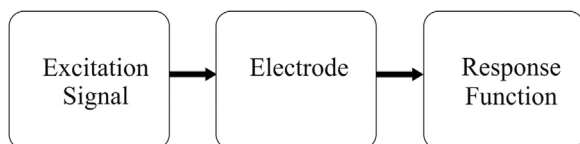

Fig. 1. General concept for performing electrochemical experiment.