Biotechnology Advances 34 (2016) 47–60

Contents lists available at ScienceDirect

Biotechnology Advances

journal homepage: www.elsevier.com/locate/biotechadv

Progress in the biosensing techniques for trace-level heavy metals

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ARTICLE INFO

Article history:
Received 31 July 2015
Received in revised form 21 November 2015
Accepted 2 December 2015
Available online 2 December 2015

Keywords:
Sensors
Biosensors
Biomolecules
Heavy metals
Practical utilization

ABSTRACT

Diverse classes of sensors have been developed over the past few decades for on-site detections of heavy metals. Most of these sensor systems have exploited optical, electrochemical, piezoelectric, ion-selective (electrode), and electrochemical measurement techniques. As such, numerous efforts have been made to explore the role of biosensors in the detection of heavy metals based on well-known interactions between heavy metals and biomolecules (e.g. proteins, peptides, enzymes, antibodies, whole cells, and nucleic acids). In this review, we cover the recent progress made on different types of biosensors for the detection of heavy metals. Our major focus was examining the use of biomolecules for constructing these biosensors. The discussion is extended further to cover the biosensors' performance along with challenges and opportunities for practical utilization.

Contents

1. Introduction

Environmental pollution in manufacturing sectors is often accompanied by the release of diverse forms of pollutants, including heavy metals and hazardous organic pollutants (Kim et al., 2005; Deep et al., 2014, 2015; Kumar et al., 2015a,b). Heavy metals such as cadmium, mercury, lead, arsenic, chromium, nickel, and copper represent a class of environmental pollutants that are highly stable but have low levels of biodegradability. These elements are involved in various environmental and ecological processes from mass to trace level concentrations (Merian and Clarkson, 1991; Schlatter, 1994; Trautwein and Deutsche, 1997; Lim et al., 2008). As heavy metals accumulate in living organisms and the environment, they contribute to a wide spectrum of adverse effects, including ecological consequences and human diseases (Merian and Clarkson, 1991; Schlatter, 1994; Trautwein and Deutsche, 1997). The carcinogenic, mutagenic, and toxicological effects of these elements have been examined to assess their effects on different organs (Merian and Clarkson, 1991; Schlatter, 1994; Trautwein and Deutsche, 1997;

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http://dx.doi.org/10.1016/j.biotechadv.2015.12.001
0734-9750/

Lim et al., 2008). In the case of Hg^{2+}, Pb^{2+}, and As^{3+}, the possible role of impairing the central nervous system has been recognized. Likewise, the kidney and liver can be damaged by Cu^{2+}, Cd^{2+}, Hg^{2+}, and Pb^{2+}, while skin, bones, and teeth can be damaged by Ni^{2+}, Cu^{2+}, Cd^{2+}, and $Cr^{3+/6+}$. The permissible levels of different heavy metal ions have been recommended by several environmental agencies including World Health Organization (WHO), US Environmental Protection Agency (EPA), and European Medical Agency (EMA). Most of these permissible limits are generally set to range from ppt to ppm levels, as well described in the literature (IOSHIC, 1999; WHO, 2011). Therefore, there exists an immense need of techniques for carrying out routine analysis of heavy metals in a variety of samples to meet the demands of environmental protection, quality control, general public health, industrial operations, etc (Farré et al., 2009).

Many techniques have been proposed for the detection of heavy metals, including optical, electrochemical, piezoelectric, and ion selective electrode (ISE) sensors (Anderson et al., 1996; Aragay et al., 2011; Burlingame et al., 1996; Cabrera et al., 1998; Dzantiev et al., 2004; Hamilton et al., 1998; Jackson and Mahmood, 1994; Merian and Clarkson, 1991; Moore and Ramamoorthy, 2012; Partanen et al., 1991; Perez-Bendito, 1999a, 1999b; Tekaya et al., 2013; Vallee and Ulmer, 1972). However, most of these sensors suffered from poor selectivity, accuracy, and irreversibility. In addition, ion sensing methods with optical fibers were also established based on the intrinsic optical properties of various ionic species such as Cu^{2+} (Eggins, 2008) and the uranyl ion (Turner, 1989). In such applications, light is guided by a fiber (or a fiber bundle) directly into the sample in order to observe the spectral properties of the analyte. However, these sensors were limited by specificity issues (particularly in turbid samples) and/or the interference of other metals absorbed at the same wavelength.

Advancements in the biosensing of heavy metals have been made continuously over the past several years, offering advantages including specificity, selectivity, sensitivity, and continuity (Sherma and Zweig, 1983; Turner, 1989; Anderson et al., 1996; Perez-Bendito, 1999a, 1999b; Satofuka et al., 1999; Blake et al., 2001; Bontidean et al., 1998, 2003; Castillo et al., 2004; Eggins, 2008). Heavy metal ions act as either catalysts (cofactors) or inhibitors in biosensing systems during their interaction with biomolecules (proteins, enzymes, antibodies, nucleic acids, etc.). The consumption or production of low-molecular weight species (oxygen, ammonia, carbon dioxide, etc.) in enzymatic reactions can also aid in the determination of enzyme activity. The most prominent example is the inhibition of urease by mercury, silver, and copper ions that can be detected via pH or ammonia levels (Blake et al., 2001). Although purified enzymes have very high specificity for their substrates or inhibitors, their application in biosensor construction may be limited by: (1) tedious, time-consuming, costly enzyme purification steps, (2) requirement of multiple enzymes to generate measurable product, or (3) need for cofactors/coenzymes. Different enzymes and cofactors that exist in cells are able to catalyze the degradation of targeted analytes, thus forming the basis for detection of a large number of chemicals. However, the simultaneous degradation of a host of chemicals compromises selectivity. Certain types of metalloenzymes/metalloproteins have also been proposed for the fabrication of heavy metal sensors because of their capacity for specific metal-binding (Ramos et al., 1993).

This review paper aims to describe the current knowledge of heavy metal biosensing approaches, and to determine basic solutions for their practical utilization. This review is organized to highlight the major aspects of biosensors with respect to their source biological recognition materials, properties, sensing mechanisms, and future prospects for real world applications.

2. Necessity of biosensors over conventional analytical methods and sensors

For the sensitive detection of heavy metals, a number of techniques have been developed and employed, including atomic absorption spectroscopy, mass spectroscopy, neutron activation analysis, optical emission spectroscopy, chromatography, ion selective electrode (ISE), and polarography (Anderson et al., 1996; Burlingame et al., 1996; Cabrera et al., 1998; Jackson and Mahmood, 1994; Perez-Bendito, 1999a, 1999b). These techniques can be used to detect single and/or multiple species at low concentrations (Bontidean et al., 1998). The above techniques, although highly precise, suffered in practice due to several limitations, including complexity, high cost, and the need for trained personnel for proper operation (Sherma and Zweig, 1983). In most cases, the number of samples for testing was limited to one. To meet the detection range of the instruments, large sample volumes were required, and pre-treatment steps often had to be introduced (Satofuka et al., 1999). These analytical methods were able to detect the total elemental concentration, rather than the bioavailable amount of specific heavy metals (Bontidean et al., 2003). Moreover, in-situ analysis with such techniques is not feasible. Thus, there is an urgent need to develop alternative methods for heavy metal detection that are easy to use, cost effective, specific (or selective), rapid, sensitive, and provide an opportunity for on-site analysis of heavy metals with little or no pre-treatment (Castillo et al., 2004). In this respect, biosensors are gaining attention as an alternative to conventional detection methods (Eggins, 2008).

Biosensors are analytical devices that incorporate a biological sensing probe and a physicochemical transducer (Bontidean et al., 1998; Blake et al., 2001; Turner, 1989). The bioprobe is responsible for the specificity, while the level of sensor sensitivity depends on the choice of transducer (Aragay et al., 2011). There are many biorecognition probes that can be coupled to different transducer elements for developing biosensors (Fig. 1). These include whole cells (Ramos et al., 1993; Mattiasson, 1997; Lehmann et al., 2000), enzymes (Dzyadevych et al., 2003; Malitesta and Guascito, 2005), antibodies (Khosraviani et al., 1998; Zhu et al., 2007), proteins (Berggren and Johansson, 1997; Cherian et al., 2003), peptides (Forzani et al., 2005), phytochelatins (Bontidean et al., 2003), nucleic acids (Lee et al., 2007; Oliveira et al., 2008), and DNAzymes (Li et al., 2009b, 2009c). Likewise, there are various types of transducers: capacitive (Berggren and Johansson, 1997; Bontidean et al., 2003), potentiometric (Liu et al., 2007), impedimetric (Ehret et al., 1997), amperometric (Guascito et al., 2008), optic (Preininger and Wolfbeis, 1996), conductometric (Berezhetskyy et al., 2008; Soldatkin et al., 2012), spectrophotometric (Bontidean et al., 1998; Bradley and Rechnitz, 1985), surface plasmon resonance (SPR) (Forzani et al., 2005), square wave voltammetry (Trnkova et al., 2011), cyclic voltammetry (Malitesta and Guascito, 2005), and MEMS-based mechanical transducers (Gimzewski et al., 1994; Raiteri and Butt, 1995; Tekaya et al., 2013). Selection of a proper bioprobe or transduction technique may depend upon several factors, including manufacturing cost constraints, response time, and consideration of the environmental complexity. When optimal characteristics of a desired biosensor are met, it presents remarkable advantages over conventional techniques. The selection of a suitable biological base and transduction module makes the biosensor target specific, sensitive, portable, and efficient for toxicological studies, while also facilitating real-time monitoring (Verma and Singh, 2005). Biosensors also make in-situ analysis possible with minimal sample preparation steps (Castillo et al., 2004).

3. Classes and progress of biosensors for heavy metal detection

In the present literature, various biorecognition elements from different sources have been proposed for the development of biosensors for heavy metal detection. Different working mechanisms of these biorecognition elements are compared in Table 1. Furthermore, performance of the biosensing methods reported in many recent studies is compared with respect to probes and biomolecules in use (Table 2).