Journal of Industrial and Engineering Chemistry xxx (2017) xxx–xxx

Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

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

Review

Progress in the sensing techniques for heavy metal ions using nanomaterials

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ARTICLE INFO

Article history:
Received 19 April 2017
Received in revised form 31 May 2017
Accepted 5 June 2017
Available online xxx

Keywords:
Heavy metal ions pollutants
Nanomaterials
Sensing
Capture
Separation
Probing
Environmental remediation

ABSTRACT

The widespread pollution of toxic metals has globally drawn much attention due to its potential to harm both human health and the environment. .Recently, a large volume of scientific literature has identified a potent role for nanomaterials in capturing, separating, and probing for such hazardous pollutants. This review discusses the opportunities and challenges in applying nanomaterials to sense hazardous metals in relation to their general working principles. This review evaluates their performance and advantages about conventional analytical methods Our review also describes the basic features of this developing field to help establish a plan to counteract heavy metal ions contamination.

Contents

Introduction

The rapid increase in toxic heavy metal ions (e.g., As, Cr, Cu, Cd, Pb, Hg, Ni, and Zn) released into the environment and the impact on human health are now considered major environmental problems throughout the world [1–4]. Exposure to high levels of toxic heavy metal ions can cause schizophrenia, neurological disorders, cancer, kidney failure, skin disorders, and lung disease,

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http://dx.doi.org/10.1016/j.jiec.2017.06.010

while damaging the function of arteries, DNA, and liver. Considering this danger, many strategies have been established to control levels of toxic heavy metal ions in various systems about scientific toxicity standards and exposure guidelines such as those from the World Health Organization (WHO) and Environmental Protection Agency (EPA) (Table 1) [5–9].

To date, methods to detect heavy metal ions at trace levels (even in the ppt and ppq range) have been established using sophisticated analytical instruments such as atomic absorption spectroscopy (AAS), inductively coupled plasma-mass spectrometry (ICPMS), mass spectroscopy (MS), and X-ray fluorescence spectroscopy (XPS) [10–15]. Nevertheless, these techniques have drawbacks including high expense, lack of portability, low throughput, time consuming pre-treatment steps, and the need for highly skilled operators [5–15].

Many efforts have been made to develop improved sensing systems that use nanomaterials (NMs) and a wide range of detection principles (optical, electrical, ion-exchange, semiconducting metal oxides, conductive polymers, quartz crystal microbalance sensors, and electronic nose devices). These sensing systems have the potential to be highly sensitive, selective, reproducible, less susceptible to interference (from humidity), and stable. To develop such systems, two important aspects need to be considered: the receptor (e.g., a heavy metal ionophore or biological receptor) and the immobilizing/transducing platform, which can be based on optical, electrochemical, magnetic, or miscellaneous principles [5–15].

Chemically recognizing heavy-metal ions by detecting specific substances/species, called receptors, are key to developing diverse sensing techniques. These receptors generally specifically interact with heavy-metal ions through non-covalent bonds, hydrogen bonds, metal coordination, hydrophobic forces, van der Waals forces, π–π interactions, or electrostatic or electromagnetic effects. In addition, the nanomaterial properties, when bound to biological receptors (such as enzyme, DNA, RNA, and antibodies), allow for highly specific, sensitive, and cost-efficient detection of heavy metal ions [5–15].

Many advances have been achieved in the development of nanomaterial-based techniques to monitor heavy metal ions in various samples (standards and real world samples) including (a) biological, (b) optical, (c) electrochemical, and (d) miscellaneous sensing strategies (Fig. 1). These strategies have been established with diverse classes of nanomaterials, such as metal nanoparticles (MNPs), quantum dots (QDs), nanometal organic frameworks (NMOFs), magnetic nanoparticles, carbon nanotubes, and nanocomposites [5–15].

The development of various nanomaterials has not only helped enhance the selectivity, sensibility, and reproducibility of platforms for sensing heavy metals ions, but has also provided opportunities to miniaturize sensing/sensing devices. Hence, the purpose of this review is to provide a critical overview of the latest trends in this field. In this review, we describe the benefits, future directions, and opportunities for modified/unmodified nanomaterials for sensing of heavy metals and to overcome the drawbacks of conventional methods. We also help resolve many challenges associated with heavy metal ions contamination and toxicity from various sources. In conclusion, we address the main advantages of nanomaterials in heavy metal ions sensing, including device fabrication technology.

Q9 **Table 1**
Standard fundamental toxicity data for heavy metals in drinking water, as recommended by the WHO and EPA [5].

Sr. no.	Toxic heavy metals	Scientific toxicity standards (mg/L)	
		WHO	EPA
1.	Ni	0.07	0.04
2.	Cu	2	1.3
3.	Zn	3	5
4.	Cd	0.003	0.005
5.	Hg	0.001	0.002
6.	Pb	0.010	0.015
7.	As	0.010	0.010

Heavy metal ions contamination and their toxicity

Generally, heavy metal ions are defined on the basis of such variables as density, atomic number (or atmomic weight), and chemical behavoir. In light of relative density of metals, the use of term like 'heavy metals' can be applied collectively to metals/metalloids with a high atomic density [16–22]. Mostly heavy metals (expect Au and Pt) can have extensive detrimental effects on humans and the environment due to their enhanced reactivity and high density. A certain fraction of heavy metals is emitted into the environment through natural sources. However, most metals released into the environment stem from anthropogenic sources, especially industrial activities including chemical industry, mining, fossil fuel combustions, and so on [16–20]. In addition, the heavy metals released by bacterial action and methylation are also found to have high toxicities when converted into an organic form (e.g., monomethylmercury and dimethylcadmium) [16–20]. Such conversions, whether occurring through biological or non-biological routes, have a large influence on water and food sources [16–20].

The levels of heavy metal ions in organic forms have been studied extensively with different factors such as pH, colloid load, and distance downstream from the mining or industry waste sites. It is thus expected that the production of metal-bound organics should be toxic enough to degrade common natural resources like water and soil, e.g., though seepage into underground water sources [16,23–25]. Fig. 2 depicts the effect of heavy metal ions in the environment and their toxicological effect on humans [26]. For example, high concentrations of Zn ions are suspected to increase the activity of the reproductive system, while protecting against Cd-associated hepatotoxicity. Likewise, Cu ions induce metallothioneins (MTs) through conjugation to "metallothionein-like protein" (MTLP). In contrast, Cd ions cause placental abnormalities and apoptosis in testis to induce MTs [26]. Hg metal ions can damage the nervous system, reducing the ability to learn (e.g., behavioral abnormalities). Organic Hg is an estrogen mimetic that can interfere with calcium homeostasis. Pb is also known to decrease sperm count and motility [26].

Because heavy metals ions are persistent environmental contaminants, they can enter the body through food, air, soil, and water. Metal ions in seawater are readily absorbed by marine animals, and they directly enter the food chain, posing health and environmental risks. In general, heavy metal ions are bioaccumulated in living or human beings while maintaining toxic and non-degradable properties [16–23]. Thus, various techniques using advanced nanomaterials have been developed to remove or treat heavy metal ions. In subsequent sections, we discuss diverse classes of nanomaterials used to monitor heavy metal ions in recent investigations.

Advancement in nanomaterials for heavy metal ions sensor

The advent of heavy metal ions sensing has been achieved with the development of nanotechnology and nanomaterials. It is however generally found that most reported work has only demonstrated a proof-of-concept for heavy metal ion sensors that were good in buffer solutions or artificial matrices only at lab level. Thus, current or ongoing research efforts should be directed toward the development of sensors for their real-time on-site detection. The future R & D on heavy metal ions sensing based on