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Review

Fluorescent sensor based models for the detection of environmentally-related toxic heavy metals

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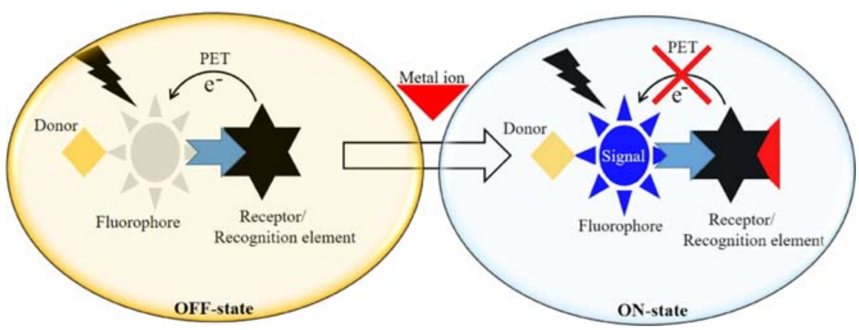
HIGHLIGHTS

- Fluorescent-based sensors for lead, cadmium, and mercury detection are reviewed.
- A simplified working scheme of fluorescent sensor for heavy metal ion detection is presented.
- Various heavy metal sources, major consequences and adverse health effects of lead, cadmium, and mercury are presented.
- Small molecule and rhodamine-based fluorescent sensors, radiometric and colorimetric probes are discussed.

GRAPHICAL ABSTRACT



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ABSTRACT

The quest for industrial and biotechnological revolution has been contributed in increasing environmental contamination issues, worldwide. The controlled or uncontrolled release of hazardous pollutants from various industrial sectors is one of the key problems facing humanity. Among them, adverse influences of lead, cadmium, and mercury on human health are well known to cause many disorders like reproductive, neurological, endocrine system, and cardiovascular, etc. Besides their presence at lower concentrations, most of these toxic heavy metals are posing noteworthy toxicological concerns. In this context, notable efforts from various regulatory authorities, the increase in the concentration of these toxic heavy metals in the environment is of serious concern, so real-time monitoring is urgently required. This necessitates the exploration for novel and efficient probes for recognition of these toxic agents. Among various methodologies adopted for tailoring such probes, generally the methodologies, in which changes associated with spectral properties, are preferred for the deceptive ease in the recognition process. Accordingly, a promising modality has emerged in the form of radiometric and colorimetric monitoring of these toxic agents. Herein, we review fluorescent sensor based models and their potentialities to address the detection fate of hazardous pollutants for a cleaner environment. Second, recent advances regarding small molecule and rhodamine-based fluorescent sensors, radiometric and colorimetric probes are discussed. The information is also given on the photoinduced electron transfer (PET) mechanism, chelation enhancement fluorescence (CHEF) effect and spirocyclic ring opening mechanism.

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Contents

1. Introduction

In recent years, poisonous heavy metal ions have gained much attention because of severe hostile environmental and health related issues to human and biotic life (Campbell et al., 2003; Kim et al., 2012; Neupane et al., 2013). Detection and monitoring of heavy metals in the environment and living cells are of great importance to avoid the harmful effects. It is established that lead, cadmium, and mercury are highly toxic metals and play no useful role in the living bodies; aggregation of these metal may cause disorders to the normal functionalities. Due to carcinogenic effects, these metals have been forbidden for use in electronics by the European Union's Restriction of Hazardous Substances (RoHS). Also, United States Environmental Protection Agency (EPA) and World Health Organization (WHO, 2004) have established allowable limits on the basis of their toxicity in potable water.

Herein, we review fluorescent sensor based models and their potentialities to address the sensing strategies of hazardous heavy metals. The present work was summarized based on the following points, i.e. (1) major health-related and environmental consequences of various lethal pollutants, (2) efficient detection of environmental pollutants, (3) recent advances regarding small molecule and rhodamine-based fluorescent sensors, (4) cost-effective and highly efficient remediation strategies, (5) the photoinduced electron transfer (PET) mechanism, chelation enhancement fluorescence (CHEF) effect and spirocyclic ring opening mechanism insights are also discussed.

2. Heavy metals occurrence – lead, cadmium, and mercury

Currently, 300 million tons of lead is found in the terrestrial and underground water as a result of mining which is a continuous threat to human life (Claudio et al., 2003). It is second largest element in the list of toxic metals and very low quantities of this metal can cause large number of diseases to human life including nervous system syndrome, memory disruption, anemia, hypertension, reduced IQs, as well as reproductive and cardiovascular issues (Fig. 1) (Kim et al., 2001; Chen et al., 2005). Cadmium is mainly used in the areas of metallurgy, pigments for plastic industry, electroplating of steel, agriculture, etc. It is extremely toxic and known as carcinogenic (Satarug et al., 2003; Zalups and Ahmad, 2003). Cadmium can accumulate through the food chain as is not biodegradable and can cause severe health problems for humans (McLaughlin et al., 2007). Another source of cadmium introduction to the body is smoking and breathing in the cadmium-dust polluted environment. The high introduction of cadmium can damage liver, bones, kidneys, and can lead to diabetes, cancer and cardiac diseases. Mercury contacts with environment both by natural (Volcano, ocean, soil, wind and water destructions) and human activities (forest fires, burning of fuels, electric equipment, industrial applications) (Fig. 2) (Harris et al., 2003; Kim et al., 2012). Mercury is a toxic and carcinogenic metal ion that infects the endocrine systems along with central nervous system (CNS) upon conception by the body (Von Burg, 1995; Clarkson et al., 2003). Biomethylation of mercury produces methylated mercury which is a neurotoxin and increases chances of chronic diseases (Geier and Geier, 2003). Fig. 2 illustrates various sources of lead, cadmium, and mercury.

3. Methodologies for heavy metal detection

Common methods employed for the detection of heavy metals include electrochemical sensors (Daud et al., 2011), inductively coupled plasma mass spectrometry (Bidari et al., 2012), cold vapor atomic absorption spectrometry (Konieczka et al., 2010) and inductively coupled plasma atomic emission spectrometry (Fong et al., 2007). These traditional methods have high selectivity and sensitivity and can calculate contents of the analyte species (Vengaian et al., 2016). But these methods are expensive, complex and time intensive (Huy et al., 2011), have limits of hiring skilled personnel, complex apparatus, high operating expenditures and difficult sample preparation processes become hard for real-time evaluations (Pujol, 2014). To overcome these issues, efficient and low-cost sensors are preferred that can detect and calculate the metal ions in-line real-time with little time consumption for environment, aquatic and biotic life surveillance. Continuous efforts have been made to develop sensors for the detection of heavy metals in real-time without time-taking sample preparation procedures (Yang et al., 2005a, 2005b; Nolan and Lippard, 2007; Avirah et al., 2007; Lee et al., 2007a, 2007b; Chen et al., 2008a, 2008b; Wang et al., 2011; Sivaraman et al., 2012; Sivaraman et al., 2014). Fluorescent or colorimetric sensors with high selectivity and sensitivity are considered to be the most suitable sensors for low-limit detection of heavy metal ions (Fig. 3) (Quang and Kim, 2010; Chen et al., 2010; Zhang et al., 2011; Zhou et al., 2011; Shanmugapriya et al., 2016). Intercellular detection is another important advantage of fluorescent sensors. Up to now, papers on the literature review on optical sensors for lead is reported in 1998 (Fitch, 1998) and for mercury metal ions in 2008 (Nolans and Lippard, 2008).

4. Fluorescent-based sensors for lead detection

Lead is highly toxic metal that can affect every organ as it can be easily assimilated into the bloodstream. Acute exposure to lead can cause anemia, high blood pressure, abdominal pain and weakness in wrist, ankles, fingers and reduces fertility in males. In children, it can affect the brain development, neurochemical development, and formation of the cerebral cortex, etc. So, enormous attention has been given in developing the techniques for the recognition of lead (Sunnapu et al., 2016). Many conventional methods for the detection of lead have been developed in a recent era such as atomic absorption spectroscopy, high-performance liquid chromatography, and electrochemical sensing (Leermakers et al., 2005; Butler et al., 2006; Li et al., 2006). The conventional methods are time-consuming, so the considerable attention has been given to synthesize new fluorescent sensors, which can detect these toxic metal ions with high efficiency and accuracy. Fig. 4 illustrates a simplified schematic of the Pb-based fluorescent sensor for the