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Sensors and Actuators B: Chemical

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

Synthesis of fluorescent naphthalimide-functionalized Fe₃O₄ nanoparticles and their application for the selective detection of Zn²⁺ present in contaminated soil

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ARTICLE INFO

Article history:

Received 6 October 2016

Received in revised form

22 November 2016

Accepted 23 November 2016

Available online 16 December 2016

Keywords:

Zinc

Naphthalimide

Fe₃O₄ nanoparticles

Nanomagnet

Soil contamination

ABSTRACT

A fluorescent dopamine–naphthalimide–dipicolylamine (DPA) was synthesized as a sensing receptor for Zn²⁺. Naphthalimide–DPA (**2**) was immobilized onto the surface of iron oxide nanoparticle to prepare a hybrid nanomagnet **1-Fe₃O₄**. Naphthalimide–DPA (**2**) and **1-Fe₃O₄** were observed to bind with Zn²⁺, leading to significant increase in fluorescence intensity at 527 nm. The fluorescence increases of **2** (10 μM) and **1-Fe₃O₄** (0.33 wt%) by addition of Zn²⁺ were linear over the [Zn²⁺] range of 0–7 μM and 0–20 μM, respectively. These fluorescence changes were highly selective for Zn²⁺, which were readily monitored even in the presence of other competitive cations. In particular, **1-Fe₃O₄** exhibited an excellent limit of detection determined to be 0.0345 ppb. Furthermore, this system was found to be suitable for detecting Zn²⁺ in a wide pH range of 3–11 and could be reused with the addition of ethylenediaminetetraacetic acid (EDTA). Moreover, nanomagnet **1-Fe₃O₄** was employed for the selective detection and removal of Zn²⁺ from a soil sample. These results confirm that the use of **1-Fe₃O₄** is a novel and simple method for detecting Zn²⁺ in environmental samples.

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1. Introduction

Particular attention has been focused on heavy and transition metal (HTM) ions and their detection methods. Exposure to HTM through diverse pathways can lead to accumulation in the human body, causing severe illness [1]. In particular, zinc is an indispensable element as it plays an essential role in biological processes (e.g., protein synthesis, neurotransmission, and signal transduction) [2]. However, the accumulation of zinc in the human body causes fatal organ failure, copper deficiency, stomach cramps, skin irritations, vomiting, nausea and anaemia [3,4]. Thus, the detection and removal of Zn²⁺ in contaminated samples are of significant interest due to this cation's unique role in physiological functions and harmful effects to human body.

Currently, fluorescent sensors have been reported as powerful tools for detecting metal ions in water and biological samples,

attributed to their high sensitivity and selectivity, as well as ease of operation [5–15]. In particular, development of fluorescent sensors for Zn²⁺ have engaged great attention, due to the biological significance of Zn²⁺ ions. In general, fluorescent molecules are linked to Zn²⁺-chelators such as dipicolylamine (DPA), bipyridine, cyclic polyamines, and etc [16–22]. However, most of the sensors exhibit a poor selectivity for Zn²⁺ ions over other metal ions. Specially, there is difficulty in distinguishing Cd²⁺ and Zn²⁺ ions, owing to their similar binding properties [23,24]. Recently, Yoon et al. reported a Zn²⁺-selective fluorescent sensor based on amide tautomerization of naphthalimide linked to DPA and this was used for detecting Zn²⁺ ions in human cells and zebrafish [16].

Compared to the detection of HTM present in contaminated water, that of HTM present in contaminated soil is considerably more difficult. Soil demonstrates potential to buff the contamination level of groundwater and river [25]. HTM adsorbed on soil surfaces may leach into groundwater and stream water, which are important sources of drinking water [26]. Thus, it is necessary to investigate the contamination of zinc in soil.

Conventional analytical methods widely employed for detecting HTM in soil samples include atomic adsorption spectrometry [27],

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