Analytica Chimica Acta 651 (2009) 227–233

Contents lists available at ScienceDirect

Analytica Chimica Acta

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

Trace mercury (II) detection and separation in serum and water samples using a reusable bifunctional fluorescent sensor

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ARTICLE INFO

Article history:
Received 8 June 2009
Received in revised form 28 August 2009
Accepted 2 September 2009
Available online 6 September 2009

Keywords:
Trace mercury
Fluorescent sensor
Detection
Separation
Serum

ABSTRACT

In this work, a reusable bifunctional fluorescent sensor for simultaneous detection and separation of trace Hg^{2+} in water and serum, which contains a naphthalimide derivative of 2,6-bis(aminomethyl)pyridine covalently grafted to the surface of silica particles, was developed. Meanwhile, the fluorescence characteristics and the adsorbent properties of the sensor were investigated in detail. This sensor showed a very good linearity (correlation coefficient of $R^2 = 0.9991$) in the range 0.1–1 μM of Hg^{2+} with detection limits lower than 6.8×10^{-9} M. It can also be used as an adsorbent for the removal of mercuric ions from the contaminated aqueous solution. The regeneration of this sensor is very simple, only by modulating the pH value of the aqueous solution. It can be reused at least four cycles. In addition, the present approach has the advantages of rapidity, simplicity, and low cost. We believe that this approach may serve as a foundation for the preparation of practical fluorescent sensor for the rapid detection of Hg^{2+} in aqueous biological and environmental samples.

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1. Introduction

Mercury, one of the most prevalent toxic metals, is widely distributed in the air, water, and soil with recognized accumulative and persistent characteristics [1]. When accumulated in the human body, mercury will lead to DNA damage, mitosis impairment, and nervous system defects [2]. As a consequence, mercury-indicating methodologies, which are developed to provide critical information for mercury hazard assessment and mercury pollution management, have received much attention. Among these techniques, atomic absorption spectroscopy, cold vapor atomic fluorescence spectrometry, and inductively coupled plasma atomic emission spectrometry are the widely used quantitative approaches. But those analytical methods require expensive and sophisticated instrumentation and/or complicated sample preparation processes. The interests in fluorescent chemosensors have led to a great development in the past few years, as they can provide a sensitive and selective method to recognize and evaluate the concentration of different substrates [3,4]. Recently, fluorescence detection with mercury-responsive sensors offers a promising approach for simple and rapid tracking of mercury ions in biological, toxicological, and environmental samples [5–9]. Although small-molecule fluorometric and colorimetric mercury sensors have been extensively investigated owing to the immediate optical feedback between the mercury-responsive ligands and Hg^{2+} ions, these sensors usually cannot be reused and the analyte also cannot be used further for other purposes.

Meanwhile, there are various techniques to remove heavy metal from environment, such as chemical precipitation, oxidation/reduction sedimentation, ion exchange, membrane filtration and solid phase extraction [10–17]. However, most of these processes require high capital investment and operation costs and purification procedures for wastewater. It is worth noted that solid phase extraction (SPE) exhibit numerous advantages such as flexibility, high preconcentration factors, high retention capacity, speed and simplicity, possibilities for field sampling, ease of automation [18].

Recently, new methods are emerging to develop highly sensitive solid-state sensors [19–22], and the detection of heavy and transition metal ions carried out by fluorescence spectrum were reported [23–34]. These sensors offer considerable advantages over other methods in the area of optical chemical sensors. But the detection limit of these solid sensors is still challenging in the practical applications. So, there is a growing demand in highly sensitive and selective detection and separation of the trace concentration of heavy metal with a rapid-assessment process in environment, biological and medicinal application.

Considering the importance of detecting and separating the trace concentration of Hg^{2+} in the environment and physiological media, we focused on the modification of our previous reported

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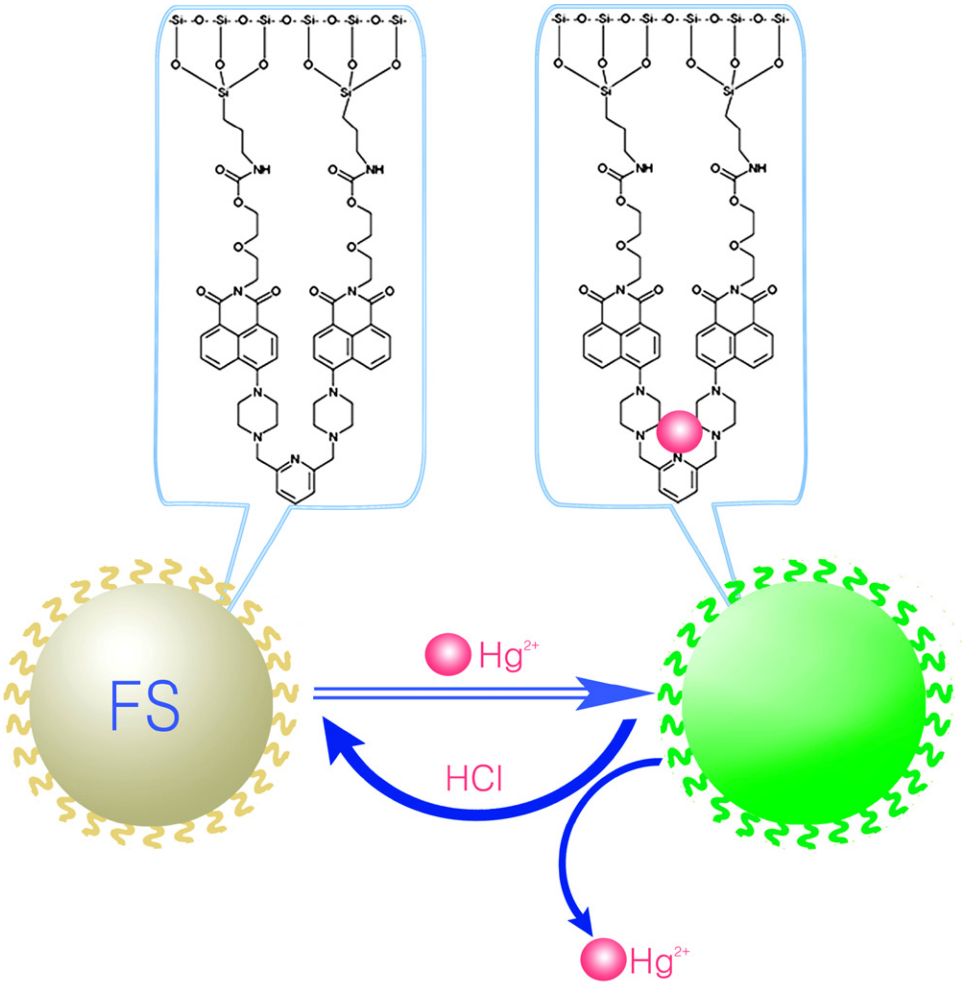
doi:10.1016/j.aca.2009.09.006



Scheme 1. Plausible mechanism of fluorescent sensor (FS) for detecting and separating Hg^{2+} ion.

fluorescent sensor **2** [35], which has a high selectivity and sensitivity for Hg^{2+}, and covalently grafted the modified small-molecule **1** onto the surface of silica particles to obtain the inorganic-organic hybrid sensor with dual functionality for Hg^{2+} detecting and separation (compounds **1** and **2**, see Scheme 2). The results showed that the hybrid sensor could be reused to detect and adsorb toxic mercuric ions with high selectivity and sensitivity (Scheme 1).

2. Materials and methods

2.1. Materials and apparatus

All the solvents were of analytical grades without further purification unless otherwise noted. ^1H NMR spectra were measured on a Bruker AV-500/400 spectrometer with chemical shifts reported in ppm (in $CDCl_3$, TMS as internal standard). Mass spectra were measured on a HP 1100 LC–MS spectrometer. Melting points were determined by an X-6 micro-melting point apparatus and were uncorrected. All pH measurements were made with a Sartorius basic pH-Meter PB-20. Fluorescence spectra were determined by using a Varian Cary Eclipse Fluorescence Spectrometer. Absorption spectra were determined on a Varian Cary 100 UV–vis Spectrophotometer. Elemental analysis was preformed by a Germany Elementar Vario EL III. Concentration of mercury was analyzed by a Varian 710ES Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES).

2.2. Synthesis of fluoroionophore 1

Organic fluorescent sensor **2** was prepared according to the reported procedure [35]. The modified fluoroionophore **1** was prepared as follows: compound **2** (40 mg, 0.0475 mmol) and triethoxy(3-isocyanatopropyl)silane (46.997 mg, 0.19 mmol) were dissolved in anhydrous THF (10 mL) with 2–5 drops of Et_3N under nitrogen atmosphere. The yellow solution was stirred for 48 h under reflux; then the solvent was removed by rotary evaporation and the residue was directly purified by flash column chromatography (silica gel, $CHCl_3/CH_3OH = 20/1$, v/v) to provide **1** (53 mg, 83.3%) as the yellow powder. m.p. > 300 °C ^1H (400 MHz, $CDCl_3$, 25 °C): $\delta = 8.58$ (d, $J = 8$ Hz, 2H), 8.52 (d, $J = 8$ Hz, 2H), 8.41 (d, $J = 8$ Hz, 2H), 7.70 (t, $J = 8$ Hz, 1H), 7.67 (t, $J = 8$ Hz, 2H), 7.45 (d, $J = 8$ Hz, 2H), 7.20 (d, $J = 8$ Hz, 2H), 4.95 (br, 2H, $-NH-$), 4.45 (t, $J = 6$ Hz, 4H, $-COOCH_2-$), 4.18 (t, $J = 5$ Hz, 4H), 3.86 (q, 12H, $-CH_3CH_2-$), 3.84 (q, 4H), 3.67 (q, 4H), 3.66 (q, 4H), 3.35 (s, 8H), 3.14 (q, 4H, $-NHCH_2-$), 2.84 (s, 8H), 1.54–1.64 (m, 4H, $-NHCH_2CH_2-$), 1.22 (t, $J = 5$ Hz 18H, $-CH_3CH_2-$), 0.58 (t, $J = 8$ Hz 4H, $-SiCH_2-$). IR (KBr): 3378, 2926, 1379, 1249, 1651, 1049, 908 cm^{-1}. HRMS (EI): $[M+Na^+]$ calcd. for $C_{67}H_{93}N_9O_{16}Si_2$, 1358.6177; found, 1358.6163 (100%).

2.3. Preparation of the fluorescent sensor (FS)

To a solution of anhydrous toluene (25 mL) was added compound **1** (40 mg, 0.03 mmol) and the dry silica particles (500 mg, surface density = 200 $m^2 g^{-1}$, activated in vacuum drier at 150 °C

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