Optical recognition and removal of Hg(II) using a new self-chemosensor based on a modified amino-functionalized Al-MOF

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ABSTRACT

We developed a simple self-chemical optical sensor for the monitoring and removal of ultra-trace levels of Hg(II) from aqueous media. The development of this sensor was based on the covalent attachment of amino-functionalized aluminum-based MOF particles with ninhydrin. The new sensor is densely coated with a chelating ligand to permit an ultra-fast, selective, pH-dependent visualization for removal of Hg(II) with detection limit ($LOD \sim 0.494\,\mu g\,L^{-1}$). Monitoring was accomplished via both a colorimetric signal visible to the naked eye as well as UV–vis absorption spectroscopy. Digital image-based colorimetric analysis has also used as a semi-quantitative analysis for determination the concentration of Hg(II) ions as a fast, sensitive and low-cost colorimetric detection system. Further, the new robust sensor exhibited long-term stability and high reusability. The developed sensor was also successfully applied to the determination and removal of Hg(II) from silver oxide button cells.

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1. Introduction

Highly toxic metal ions, such as mercury, must be removed from industrial waste because of their threat to the environment and all living systems [1–5]. The primary sources of these ions include industrial waste from metal finishing, pigments, electroplating, batteries, electronic devices, metallurgical alloying activities, mine drainage, and natural sources. These ions are finally bioconcentrated through the food chain. According to the US Environmental Protection Agency (EPA) and the World Health Organization (WHO), the permissible levels of inorganic Hg^{2+} ions in drinking water are around $2\,\mu g\,L^{-1}$ [6]. The toxicity of Hg^{2+} arises from its high binding affinity for the thiol (–SH) and the amino (–NH$_2$) groups of proteins [7] and may contribute to adverse effects on the central nervous system, pulmonary, kidney functions, chromosomes, and the immune system [7].

The selective recognition and simultaneous removal of metal ions from aqueous solutions, either for pollution control or raw recovery, are still industrial challenges. Thus, searching for a rapid, sensitive, and simple analytical methods for the detection and monitoring of these metal ions is important. Several methodologies are available for analyzing heavy metal ions, such as atomic absorption spectroscopy (AAS), inductively coupled plasma atomic emission spectrometry (ICP-AES), and inductively coupled plasma mass spectrometry (ICP-MS) [8–10]. However, these spectrometric methodologies are expensive and are not suitable for in situ analysis, which prevents their widespread use, especially in developing countries as in the field work. Therefore, the design of high-performance adsorbents for environmental cleanup and heavy metal ion removal has attracted considerable attention [11–17]. Since most pollutants in various matrices are found at concentrations far below the detection of limits of most common analytical methods, society faces a great challenge to develop new materials for an accurate, selective, sensitive and fast measurement of these pollutants.

Sensors that can change their color show advantages such as versatility, ease of use, high sensitivity, low cost, and fast response time. This change can be induced by receptor "molecular probe"–analyte "cation" interactions [11–17]. These binding events transduce signaling responses that pose considerable constraints based on the chemosensor design. In this sense, the functionality and manipulation of the chromophore probes in nanoscale materials as sensing receptors have received attention. Hence, the design of flexible chemosensors for the responsive recognition of several metal species [11–17], as well as for charged and neutral organic molecules [18] have been described.

Metal-Organic Frameworks (MOFs) are nowadays at the front of research in materials science. In recent years, the combination of organic and inorganic subunits in fully crystalline porous materials has led to thousands of MOF structures with a vast topological variety [19,20].Their high porosity, crystallinity, compositional and structural variability, large surface area and acceptable thermal and chemical stability make these materials ideals to be satisfy the needs of several applications such as catalysis, gas and vapor sorption, chemical separation, etc. [21–23]. Only a few amino-functionalized MOFs are known out of the more than 10,000 MOF structures reported in the literature [24]. Thus, Hatton et al. [25] prepared two MOFs based on Al^{3+} as a nontoxic alternative to Cr^{3+}, Cu^{2+} and other metal ions commonly used in MOFs preparation. These materials have been used in many fields [24–30], but no one of them has been applied in the field of sensing.

In the present work, a self-chemosensor was designed by using aluminum aminoterephthalate MOFs as starting material. Such materials with MIL-101 crystal topology have a large content of primary amino groups available, which were used to covalently attach ninhydrin. These designed functional surfaces were capable of capturing and sensing Hg(II). The impact of several experimental parameters was investigated, and the analytical performance of this novel self-chemosensor was also assessed. The developed sensor showed a high response over a wide range and a low detection limit of perceptible metal analytes (up to $0.638\,\mu g\,L^{-1}$). To evaluate the content of the analyzed metal ions, either UV–vis spectrophotometric or digital image-based colorimetric analysis strategies were used. A procedure for specifically detecting and removing Hg(II) ions from silver oxide button cells was also reported.

2. Experimental

All chemicals were used without further purification. For all the experiments, Milli-Q water was used. Mercuric chloride, aluminum chloride hexahydrate ($AlCl_3 \cdot 6H_2O$), 2-amino terephthalic acid, N, N-dimethylformamide, KCl, CH_3COONa, HCl, and CH_3COOH were purchased from Sigma-Aldrich (St. Louis, MO, USA). Ninhydrin (2,2-dihydroxyindane-1,3-dione) was purchased from TCI (Zwijndrecht, Belgium). Buffer solutions of 0.2 M KCl-HCl and 0.1 M CH_3COOH-CH_3COONa were used to adjust the pH in the 2–6 range. 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES) and 0.1 M disodium hydrogen phosphate were used to adjust the pH in the 7–12 range by using 0.1 M NaOH.

2.1. Synthesis of the Nin-NH-MIL-101(Al) self-chemosensor

The NH_2-MIL-101(Al) was synthesized by a solvothermal treatment involving N, N-dimethylformamide (DMF) as solvent [24]. Starting reactants were $AlCl_3 \cdot 6H_2O$ (0.51 g), 2-amino terephthalic acid (0.56 g) and N,N-dimethylformamide (30 mL). The reactants were placed in a Teflon-lined autoclave and heated for 72 h at 130 °C under static conditions. The resulting yellow powder was filtered under vacuum and washed with acetone. The materials were activated in boiling methanol overnight and stored for 24 h at 100 °C, to remove organic species trapped within the pores.

The Nin-NH-MIL-101(Al) sensor was prepared by dissolving ninhydrin (0.1 g) in 50 mL ethanol. After that, the NH_2-MIL-101(Al) (0.25 g) was added. The mixture was refluxed for 4 h under stirring. Then, the resulting beige powder was filtered, washed with ethanol, and dried at 80 °C.

2.2. Recognition of ultra-trace levels of metal ions

The colorimetric determination and visual detection of Hg(II) ions using the Nin-NH-MIL-101(Al) sensor was carried out over a wide range of pH solutions. About 10 mg of the sensor were added to several aqueous solutions (with a total volume of 25 mL) containing specific concentrations of Hg(II) and adjusted increasing pH values (within 2–12 range). Then, these solutions were sonicated for 5 s. After equilibration, in which a prominent color change and the signal saturation of the nanosensor absorbance spectrum was achieved, the solid chemosensor was collected by using vacuum filtration on a 25 mm diameter filter paper (Whatman filter papers No. 2). The color of the collected sample was evaluated by either the naked eye, UV–vis spectrometry and Digital image-based colorimetric analysis.

2.3. Metal ions sensing using digital image-based colorimetric analysis (DIC)

Scanning of the color balances was performed using the camera of Sony Z2 mobile (20 megapixels). Determination of the colorimetric characteristics of the obtained images and transformations of the color coordinates were achieved using Adobe Photoshop CS6 (64 Bit) on a personal laptop. An elliptical region was selected in the middle of the image of the colored sample using the "Crop" tool called "Elliptical Marquee Tool." The average color intensities of Red, Green, and Blue (RGB) of each image were gotten by using the "Histogram" tool. All data were transferred to Microsoft Excel 2016 spreadsheet for subsequent data analysis using Origin Pro 2016 (64 Bit) for data plotting.

2.4. Removal of Hg(II) from aqueous media

For the preparation of the solid-phase extraction (SPE) cartridges, fifty milligrams of Nin-NH-MIL-101(Al) sensor were packed between two frits (1/16′, 20 μm, Análisis Vínicos, Tomelloso, Spain) into a 1 mL empty propylene cartridge (Análisis Vínicos). Then, 10 mL of 10 mgL^{-1} of Hg(II) solution at pH 6 was loaded on the SPE material at a flow rate of 0.1 mL min^{-1}. The retained Hg(II) was eluted with 0.1 M thiourea (10 mL). The inductively coupled plasma atomic emission spectrometer (ICP-AES) was used to determine the Hg(II) both before and after the removal process.

2.5. Determination of Hg(II) from silver oxide button cells

The industrial samples used in this experiment were silver oxide button cells regardless of brand. These cells were grinded, and the cases were dismantled. The obtained cell powder was dried in an oven at 100 °C and leached in a mixture of 2 M H_2SO_4 and 0.2 M H_2O_2 at 90 °C for 6 h to dissolve base metals (Cu, Fe, Ni, Al, Li, Mn, Co and Zn). After filtration, the residue was leached with 50% HNO_3 at 70 °C for 5 h to obtain a solution of Hg(II), Ag(I) and some other ions. Fe (III), Sn(IV) and Al(III) ions were precipitated and filtered by increasing the pH of the filtrate up to 5.0 using 2 M NaOH. ICP-AES was used to determine the concentration of the metal ions under investigation after and before removal of Hg(II) at its specific collection conditions.

2.6. Instruments

Absorption spectra of the new self-chemosensor were collected using a PerkinElmer Lambda 950 model solid-state UV–vis spectrophotometer. The infrared absorption spectra were recorded using a Thermo-Scientific (Nicolet 6700) Fourier transform infrared (FT-IR) spectrometer. XRD patterns were obtained using a powder diffractometer D5005 model from Bruker with a 0–20 configuration, Cu anode provided with an X-ray tube, secondary monochromator of diffracted beam, scintillation detector, automatic slits and rotating sample holder (15–120 rpm), with an automatic charger of 40 specimen containers. Surface area and pore size values were calculated from nitrogen adsorption–desorption