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Facile mercury detection and removal from aqueous media involving ligand impregnated conjugate nanomaterials

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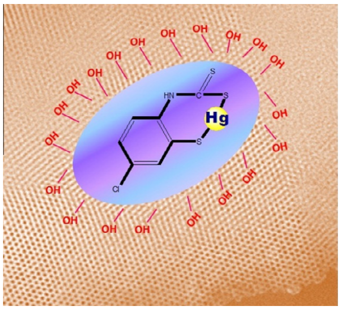
HIGHLIGHTS

- Ultra-trace Hg(II) ions was optically removed by the ligand conjugated nanomaterials.
- The diverse competing ions did not interfere in selective Hg(II) ions removal.
- The conjugate nanomaterials were able to reuses without significant deterioration.

GRAPHICAL ABSTRACT



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ABSTRACT

The conjugate nanomaterial (CNM) was prepared by sulfur donor containing organic ligand onto the silica substrate for simultaneous mercury (Hg(II)) ions detection and removal from water samples through a batch technique. The potential and feasibility of the CNM as Hg(II) ions selective materials were evaluated in terms sensitivity, selectivity both in the detection and removal operations. In detection, the absorbance spectra increment was linear with the Hg(II) ions concentration in low concentration area, and the detection limit of the CNM was 0.26 μg/L. In addition, the colorimetric changes were extremely specific for Hg(II) ions, and no significant color change was evident in case of other competing metal ions in the sample matrix. In removal, the optimization of experimental conditions, including effect of pH, equilibrium time, initial Hg(II) ion concentration was examined. Due to the strong interaction between Hg(II) ions and sulfur atoms of the active surface, the CNM exhibited high adsorption capacity and excellent selectivity during Hg(II) adsorption. The experimental results showed that the solution pH had a major impact for Hg(II) adsorption by the CNM. The experimental data were well fitted with the linear form of Langmuir model the maximum adsorption capacity of Hg(II) ions was 164.22 mg/g. The Hg(II) loaded CNM could be successfully desorbed with 0.20 M HCl solution, and the adsorption capacities were not decreased sharply even after six cycles showing the practical significance in remediation of Hg(II) contaminated wastewater. In addition, the present approach has the advantages of sensitivity, selectivity, rapidity, simplicity, and low cost for Hg(II) detection and removal, and the newly developed assay might open a new assay avenue for Hg(II) ions contaminated water treatment.

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1. Introduction

Removal of toxic pollutants from waters is one of the major challenges for scientists in the last few decades. Mercury (Hg(II)) is a highly toxic pollutant and widely distributed in air, water and soil [1–3]. Even in low concentration, the Hg(II) is toxic to the environment and human health due to the non-biodegradable property and can enter the food chain [4,5]. The Hg(II) ions can cause respiratory failure, kidney injury, chronic diseases, central nervous system disorders, brain damage [6,7] and severe environmental pollution. The maximum permissible level in drinking water recommended by WHO is 6 ppb and the USEPA imposed it to 2 ppb [8,9]. Then the Hg(II) removal up to the maximum permissible limit from contaminated water is a challenging task, and the scientific community has to develop new efficient, rapid, facile and applicable techniques for sensitive and selective detection and removal of Hg(II) ions from the environment samples.

Over past few decades, the molecular probes are importantly investigated for the efficient and selective detection of physiologically and environ-mentally important toxic metal ions and anions [10–12]. A number of analytical methods are reported for Hg(II) ions detection such as atomic absorption spectrometry, electrochemical analysis, inductively coupled plasma mass spectrometry, and selective cold vapor atomic fluorescence spectrometry [13–15]. These are sensitive, selective, and also exhibited the low detection limit, however, they are complicated sample treatment, expensive, sophisticated instrument-intensive, and require trained technicians which limit their application for rapid and on-site analysis. Therefore, simple, reliable and instrument-free method is highly desired for Hg(II) ions detection concerning in resource-poor settings. Several materials based sensors have been designed by utilizing electrochemical techniques, fluorescence methods, and colorimetric methods [16,17]. Among these methods, colorimetric method is considered as a good tool for divers ions sensing due to its simplicity, short responsive time and visualization without aids of instruments. In this connection, we have developed different functional based solid-state nanomaterials for diverse ions detection and removal under optimum conditions [18–21]. Herein, we have developed a novel optical nanomaterials for Hg(II) ions detection and based on the sufficient color optimization at suitable pH area. This can be simple, efficient, convenient, and versatile for sensitive Hg(II) ions monitoring in contaminated water samples.

Several removal processes have been assessed including reduction, coagulation, precipitation, ion exchange, membrane separation [22–26] and adsorption for Hg(II) ions removal from industry effluents. Among these, adsorption deserves the specific attention, because the adsorbent materials are highly efficient and easy to handle and in many cases, they can be regenerated from the stand point of repeated use. Recently, the functional nanomaterials have received the attention in environmental remediation and pollutant removal due to their excellent properties such as high surface area, high adsorption property, easy-to-use, and cost-effective. Such unique features of the functional mesoporous materials are quite desirable for many designated environmental cleanup applications [27–29]. The surface functionalization using novel organic ligand endows the mesoporous silica for the strong affinity to the target metal ions at optimum conditions to remove heavy metals from aqueous wastes [30–33]. From the stand point functionality, we have developed functional ligand immobilized conjugate nanomaterial (CNM) for efficient, sensitive and selective Hg(II) ions monitoring and removal from environmental contaminated water samples. However, the carrier inorganic materials have always bear the significant influence to open the functionality of the embedded organic ligand [34].

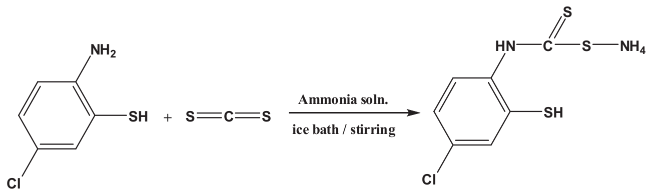
Recently, several researchers have explored the nano-sized solid based adsorbents such as nanoparticles and nanotubes for metal ions removal from water [35,36]. Compared with these micro-sized particles, the ligand based meso-structure based nanomaterials offer a significantly higher surface area-to-volume ratio that promises much greater adsorption capacity [37]. Despite the great structural advantages of nanoporous silica, the lack of active sites limits their applications in the areas of metal separation, wastewater treatment, drug delivery and catalysis. However, the porous walls and rich surface hydroxyl groups could facilitate the modification of their skeleton and surface using organic ligand molecules to make efficient functionalized mesoporous silica materials [38–40]. Over the past decade, the nanomaterials have advanced the efficiency and applicability for metal ions separation. However, the solid design CNM stability remains were unresolved [41]. Then the designing of robust technology that can remove the contaminants from wastewater with rapid environmental analysis and low-cost is highly demanded. The present work describes our investigations of the detection and removal of Hg(II) ions in colorimetric methods.

In this study, the specific functional group containing organic ligand of ammonium (4-chlro-2-mercaptophenyl)carbamodithioate (ACMPC) was synthesized (Scheme 1). Then mesoporous silica materials were then functionalized by the direct immobilization of ACMPC and tested for the ability to detect and remove of Hg(II) ions in aqueous solution. The mesoporous silica consisted of highly ordered structure to be used as an excellent substrate for successful immobilization of organic compound such as ACPMC. However, ACMPC was associated onto the silica based on non-specific interaction via hydrogen bonding, Van der Waals forces and reversible covalent bonds. Therefore, the highly ordered mesostructured silica materials enabled the easy generation and transduction of optical color signals as a response to organic ligand (ACMPC)–Hg(II) binding events during the monitoring and removal low-level of Hg(II) ions. The Hg(II) monitoring was performed in colorimetric methods without significant interference even in the presence of diverse foreign ions. Several parameters such as solution acidity, initial concentration, contact time, foreign ions, adsorption capacity and reuses were systematically investigated.

2. Materials and methods

2.1. Materials

All materials and chemicals were of analytical grade and used as purchased without further purification. Tetramethylorthosilicate (TMOS), F108 ($EO_{141}PO_{44}EO_{141}$), $Al(NO_3)_3 \cdot 9H_2O$, 2-Amino-4-chlorobenzenethiol, carbon disulfide and ammonium hydroxide solution were purchased from Sigma–Aldrich Company Ltd. USA. The $HgCl_2$ was purchase from Wako Pure Chemicals, Japan and Hg(II) stock solutions (200 mg/L) were prepared by dissolving $HgCl_2$ in Millipore water. For pH adjustments in monitoring systems, buffer solutions of 3-morpholinopropane sulfonic acid (MOPS) and sodium acetate were procured from Dojindo



Scheme 1. Preparation steps of organic ligand of ammonium (4-chloro-2-mercaptophenyl)carbamodithioate (ACMPC).