Chemical Engineering Journal 327 (2017) 725–733

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

Chemodosimeter functionalized diatomaceous earth particles for visual detection and removal of trace mercury ions from water

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HIGHLIGHTS

- Detection and removal of Hg^{2+} from water using chemodosimeter P2 were realized.
- P2 has been successfully immobilized onto naturally available diatoms (P2D).
- Organic receptor and hazardous Hg^{2+} ions were physically contained in diatoms.
- Eco-friendly cartridge containing P2D was developed for the removal of Hg^{2+} ions.
- Device efficiency (time to replace) could be realized through visual colour change.

ARTICLE INFO

Article history:
Received 23 May 2017
Received in revised form 23 June 2017
Accepted 24 June 2017
Available online 26 June 2017

Keywords:
Diatomaceous earth
Chemodosimeter
Mercury detection and removal
Through bond energy transfer
Cartridge
Colour change

ABSTRACT

The rhodamine based receptor, P2 has been developed for the detection of environmentally hazardous Hg^{2+} ions with a limit of detection, 1.5×10^{-6} M. The P2 showed a significant colour change from colourless to pink upon binding with Hg^{2+} ions. As a result, a new peak at 533 nm was observed in UV–vis spectroscopy which was attributed to spirolactum ring opening followed by through bond energy transfer (TBET). In addition, the presence of other competing cations did not interfere the detection of Hg^{2+} ions. Further, P2 has been successfully immobilized onto the naturally available and highly porous diatomaceous earth particles (P2D) for removal of Hg^{2+} ions from water. The covalently attached organic molecule in P2D forms complex with Hg^{2+} ion present in the water and thus traps the Hg^{2+} ions. Based on this, a proof-of-concept cartridge has been developed for water purification. The cartridge having 450 mg of P2D was able to purify 30 mL of water containing 1 ppm Hg^{2+} ions. The efficiency of cartridge could be visualized with a colour change from colourless to pink.

1. Introduction

Heavy metals have biological relevance to the animals and plant species, the essential heavy metals induce biochemical and physiological functions by providing several key enzymes, proteins to animals and plants, which play an important role in oxidation-reduction reactions of metabolism [1]. Apart from their biochemical and physiological relevance, the heavy metals are also being used extensively for domestic and industrial applications, and their excess amount in the environment has led to serious health issues [2]. Among such heavy metals, mercury is one of the most toxic metal and is widespread pollutant due to natural and human activities. The major sources of mercury contamination are industrial effluents, mining, tannery industries and combustion of fossil fuels [3]. Therefore, detection of mercury has attracted a significant attention of scientific community [4]. Thus, US Environmental Protection Agency (EPA) has set a standard for the permissible level of inorganic Hg^{2+} ions in drinking water as 2 ppb [5,6]. The instrumental methods such as atomic absorption spectrometry (AAS), atomic fluorescence spectrometry (AFS) and inductively coupled plasma-mass spectrometry (ICP-MS) etc. are extensively being used for the analysis of Hg^{2+} ions [7–9]. Nevertheless, the wide utilization of these methods are largely limited due to the expensive instrumentation and time consuming protocols. Therefore, an

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http://dx.doi.org/10.1016/j.cej.2017.06.138
1385-8947/

alternative approach for the detection of Hg^{2+} ions present in potable water which is fast and inexpensive is highly sought.

Owing to many advantages such as rapid detection, ease of handling and requirement of simple equipment, much efforts were made to develop fluorogenic and chromogenic chemodosimeter, which can selectively detect Hg^{2+} ions [10–12]. Among these chemodosimeter, rhodamine derivatives have been widely employed due to their long absorption and emission wavelengths, high extinction coefficient and high fluorescence quantum yield [13]. Rhodamine based chemodosimeters are not only show change in absorbance/fluorescence intensities upon binding with Hg^{2+} ions, but also induce a strong colour change, facilitating a "naked eye" detection which makes them highly attractive as Hg^{2+} ion sensors [14–16]. However, earlier reports show some disadvantages such as strict reaction conditions, complicated synthetic routes and cross-sensitivity towards other metal ions. In addition, majority of the chemodosimeters are being used in solution form with mixed organic solvents to detect Hg^{2+} ions which hinder the practical applications [17,18].

Organo–inorganic hybrid materials, such as silica-chemodosimeter offer a promisingly simple and rapid approach to monitor and remove Hg^{2+} ions from water. Recently, fluorescent probes immobilized on solid substrates have been investigated for metal ion recognition. However, most of the organic receptor functionalized solid substrates have been used just to detect the metal ions in water [19–23]. Majority of these chemodosimeters are of synthetic origin and could leach into the environment if used in solution state, hence it is very important to physically contain such receptors to realize the greener approach of toxic ion detection and removal. Instead of using synthetic materials, it would be added advantage if we can utilize widespread natural nanoscale material such as diatom which exhibit similar properties as synthetic materials for the above said applications. These diatoms have inherent properties such as; high porosity, surface area, biocompatibility, chemical inertness, surface tunability and hollow structure [24]. Furthermore, they have been used in broad applications such as nanofabriaction, sensing, chromatographic separation, water purification, environmental remediation, drug delivery, catalysis, pest control, solar cell and supercapacitor [25–29]. However, these particles have not been explored as solid support for the immobilization of chemodosimeter till date. Diatom particles can easily replace synthetic and conventional silica particles which are usually produced through harsh chemical processes [30]. Earlier mercaptosiliane treated diatoms have been used for the selective adsorption of Hg^{2+} ions in water [31]. Recently, Kabiri et al. prepared 3D graphene aerogel composite based on graphene-diatom and iron oxide nanoparticle to remove mercury ions using adsorption method which showed outstanding performance and adsorption capacity of 800 mg/g [32]. However, high cost of graphene and usage of expensive instruments hinder the translation of this technique for the practical applications. These drawbacks could be solved by developing cheaper methods such as grafting of organic receptor on diatoms as adsorbent: which offers both sensing and remediation of mercury contaminated water.

With this background, herein we report the synthesis and characterization of rhodamine-6G derivative (P2) as a chemodosimeter for the detection of Hg^{2+} ions in aqueous media. Further, we propose a new concept where porous diatom material can be used as solid support for chemodosimeter (P2D) with an aim to develop new low-cost water purification device for the detection and removal of Hg^{2+} ions from potable water. The concept is based on immobilization of P2 onto the surface of diatom particles and use them to develop water purifying cartridge that could remove Hg^{2+} ions from water. The colour change of the packed material can be translated into saturation point of the cartridge (time to replace).

2. Experimental section

2.1. Chemical reagents and methods

Diatom silica particles (DE) were obtained from Mount Sylvia (Australia) Pvt. Ltd. Rhodamine-6G, Terephthalaldehyde and 3-aminopropyl-triethoxy silane (APTES) were purchased from Sigma-Aldrich (India) Pvt. Ltd. Glacial acetic acid was obtained from Fischer Scientific (India) Pvt. Ltd. All metal salts in the form of nitrates were purchased from NICE chemicals (India) Pvt. Ltd. Ethanol was procured from Changshu Hongsheng Fine Chemicals (China) Co. Ltd. Analytical grade reagents and solvents have been used as received without any further distillation/purification throughout the experiments. All metal ion solutions were prepared using deionized water.

The organic molecules P1 and P2 were characterized by ^{1}H-NMR and ^{13}C-NMR using Bruker (500 MHz) instrument with TMS as an internal reference and DMSO-d_6 as solvent. ATR-IR spectra of the compounds were recorded using Bruker ECO-ATR spectrophotometer in the range of 500–4000 cm^{-1}. Electronspray ionization mass spectrometry (ESI-MS) analysis were carried out using Shimadzu ESI-MS instrument. UV–vis spectroscopic studies have been carried out using Shimadzu 1700 PC UV–visible spectrophotometer in standard 10 mm cuvette. Fluorescence studies were done using Shimadzu RF 5301 PC spectrofluorometric instrument.

2.2. Synthesis

2.2.1. Synthesis of 2-amino-3′,6′-bis(ethylamino)-2′,7′-dimethylspiro[isoindoline-1,9′-xanthen]-3-one (P1)

Rhodamine-6G (2.09 mM) was dissolved in 5 mL of ethanol, 6.26 mM of hydrazine hydrate was then added dropwise. The mixture was ultra-sonicated for 5 min to get solid product (Scheme 1). Thus obtained solid product was filtered and thoroughly washed with ethanol and dried at room temperature to obtain P1.

IR data for P1: IR spectrum was taken in order to evaluate the conformation of compound P1. As shown in Fig. SI 1, the peaks from 600 to 1600 cm^{-1} is due to xanthene moiety of the rhodamine 6G [33]. In P1, emergence of peak at 3740 cm^{-1} is due to N–H stretching which confirms that hydrazine hydrate has been reacted with rhodamine-6G.

^{1}H NMR (500 MHz, DMSO-d_6, δ/ppm): 7.75 (1H, J = 5 Hz, d), 7.46 (2H, J = 5 Hz, d), 6.93 (1H, J = 5 Hz, d), 6.26 (2H, s), 6.10 (2H, s), 5.00 (3H, J = 5 Hz, t), 4.22 (1H, s), 3.13 (2H, J = 5 Hz, m), 1.86 (3H, s), 1.21 (3H, J = 10 Hz, t) (Fig. SI 2)

^{13}C NMR (100 MHz, DMSO-$d6$, δ/ppm): 165.69, 151.86, 147.86, 132.75, 129.99, 128.49, 127.48, 123.89, 122.59, 118.28, 105.53, 96.39, 65.488, 37.958, 17.47, 14.69 (Fig. SI 3)

ESI-MS, m/z + 1 calculated 429.5; found 429.0 (Fig. SI 4).

2.2.2. Synthesis of (Z)-4-{[(3′,6′-bis(ethylamino)-2′,7′-dimethyl-3-oxospiro[isoindoline-1,9′-xanthen]-2-yl)imino]methyl}benzaldehyde (P2)

P1 (0.5 g, 1.17 mM) was dissolved in 20 mL of ethanol and terephthalaldehyde (0.2 g, 1.17 mM) was added to with constant stirring. Further, the reaction was catalysed with a drop of glacial acetic acid (Scheme 2) and refluxed at 80 °C for 12 h to yield yellow precipitate (P2) which was filtered, washed with ethanol for 5 times to remove the unreacted reactants followed by drying at room temperature overnight.

IR data for P2: as shown in Fig. SI 5, the peaks from 600 to 1600 cm^{-1} are attributed to xanthene moiety of the rhodamine-6G [33]. The emergence of peaks at 2967 and 2872 cm^{-1} are due to C–H stretching corresponds to aldehyde group. The peak at