



Facile synthesis and characterization of thiol-functionalized graphene oxide as effective adsorbent for Hg(II)



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ABSTRACT

In this work, we report the synthesized and characterization of mercaptobenzothiazole (MBT) functionalized graphene oxide (GO) as a novel adsorbent material for the adsorption of Hg(II). This adsorption process could be realized with GO and MBT acting as host-guest in the first instance followed by the subsequent complexation of Hg(II) with MBT, the soft-soft interaction between Hg(II) & sulphur enhances the effective complexation. The prepared graphene-based adsorbent was characterised by X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, Powder-X-ray diffraction (Powder-XRD), Transmission electron microscopes (TEM), Fourier transform infrared spectroscopy (FT-IR), UV-vis spectroscopy, scanning electron microscopes (SEM) and energy-dispersive X-ray analysis (EDX). The capability of ICP-MS for Hg(II) adsorption was extensively studied under different optimal parameters, the developed method was successfully applied to mercury adsorption from water samples.

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1. Introduction

Mercury is a highly toxic metal that can accumulate in ecological systems and adversely impact the environment. The main chemical species of mercury are elemental mercury (Hg^0), ionic mercury (Hg^+ , Hg^{2+}), methylmercury (MeHg^+), and ethylmercury ($\text{CH}_3\text{CH}_2\text{Hg}^+$). Methylmercury is a neurotoxin and is commonly found in aquatic environments due to its affinity with fatty tissue in animals; methylmercury tends to bioaccumulate and biomagnify more readily than other species of mercury. In particular, divalent mercury (Hg^{2+}) is a widespread environment pollutant, found mainly in surface water [1]. Hg(II) causes permanent harmful effects of living organisms, even at minimal doses [2]. Mercury could be found in significant amounts in wastewater such as chloralkali manufacturing plants, electrical and electronics manufacturing, sulphide ore roasting operations; manufacture of batteries, lamps, paints, paper industries are common and, therefore, requires to effective treatment for mercury remediation. Exposure to mercury can have toxic effects on reproduction, central nervous system, liver and kidneys cause sensory and psychological impairments. Mercury is one of the

most hazardous heavy metals due to the reinforcement of its intrinsic toxicity by bioaccumulation through metabolic processes of the food chain [3]. The elemental mercury vapour released into the atmosphere is subsequently converted to Hg(II) and transferred to water and sediments. Mercury is well-known for toxicity, even at very low concentrations; the drinking water criterion for mercury [4], established by the US EPA, is 2.0 mg L^{-1} , permitted discharge limit of total mercury in waste water is 10.0 mg L^{-1} .

Removal of various toxic heavy metals, including mercury compounds, from the environment, is a big challenge. Among the various available technologies, adsorption is widely used, simple, and easy operation and it could effectively remove various heavy metals from the environment [5,6]. However, a very similar work which has been recently published by Hami Dindar et al. [6].

Adsorption techniques are simple and work very effectively for any adsorption process; an adsorbent with large surface areas, pore volume and proper functionalities is the key to success. The adsorption capacities of materials depend on their porous structure and surface properties; nevertheless, given its large specific surface area and strong hydrophilic nature, graphene oxide (GO) shows great potential in the removal of toxic heavy metals in aqueous solutions. Currently, many different porous materials have been developed, such as thiols based on GO adsorbent [3], a glycidyl methacrylate grafted cellulose adsorbent [4], a thiol modified $\text{Fe}_3\text{O}_4/\text{SiO}_2$ as a robust [7], a cerium functionalized PVA-chitosan composite nanofibers [8], 1-octadecanethiol monolayers

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modified on graphene [9], mercaptobenzothiazole-modified cellulose [10], thermally reduced GO decorated with functionalized gold nanoparticles [11], and trioctylamine-modified sodium montmorillonite clay [12], polyaniline/reduced GO nanocomposite [13], showing varying effectiveness in removing toxic mercury from the environment. GO and graphene are new carbonaceous adsorbent materials and, in the past few years, GO has attracted tremendous interest. Graphene is two-dimensional, with a single layer of sp^2 -hybridized carbon atoms arranged in six-membered rings [14]. Graphene has strong mechanical, thermal, and electrical properties and a large theoretical specific surface area, GO has many functional groups, indicating their potential for adsorption processes. GO to contain a range of surface oxygen-functionalities, such as carboxyl, carbonyl, hydroxyl and phenol groups these functional groups markedly increase the hydrophilicity of GO, making it easily dispersible in aqueous solutions and stable under common environmental conditions [14]. Carbonaceous-based adsorbents, including activated carbon, carbon nanotubes and GO, usually show high adsorption capacity [15–18]. In the past few years, many investigations focused on the applications of GO in the removal of toxic mercury from aqueous solutions [19–23]. The ability of a material to adsorb toxic heavy metals is controlled, in part, by the number of available functional groups used for binding metals; functional groups with a known affinity for specific metals can be attached to other substances to create an effective adsorbent.

The functionalization of thiol groups (–SHs) on suitable solid supports offers favourable performances by taking advantage of the coordination of sulphur (S) groups with heavy metal species. The –SH forms stable complexes with soft heavy metals of high polarizability, such as Hg, Ag, Au, and, to a lesser extent, Cd and Zn, failing to coordinate well with the more abundant smaller, lighter metals, such as Ca, Na, and Mg [2,23,24]. Based on the preference of a cation for complexation with ligands, mercury is classified as a B-type metal cation, characterized by a “soft sphere” of highly polarizable electrons in its outer shell. Soft metals like mercury show a pronounced preference for S ligands. The presence of thiol groups improves adsorption capacities for removal of Hg(II) [2,23,25] since the reaction against the Hg(II) ions and the –SHs are highly thermodynamically favourable [26] and metal adsorption is directly related to the amount of –SHs available in the adsorbent [25]. The adsorption properties of these adsorbents depend on the functional groups of their surfaces, adsorbents containing S-based ligands (such as thiol, thiourea, and thioether groups) effectively form complexes with mercury ions [27–29]; thiol-functionalized adsorbents exhibited a specific binding capability toward highly toxic heavy metal ions, including Hg(II), due to the –SHs [30]. The functionalized MBT onto GO for Hg(II) adsorption was not previously explored, despite how MBT is a well-known complexing agent able to bind soft metal ions in aqueous solution. The MBT bears a –SH that could interact with GO hydroxyl, carboxyl groups through covalent bond interaction, non-covalent π – π stacking, hydrophobic interaction, hydrogen bonding, van der Waals forces. Here, we report that thiol-functionalized GO adsorbent shows a strong affinity for Hg(II) adsorption.

2. Materials and methods

2.1. Materials

The starting material, graphite used in the preparation of GO was procured from Sigma Aldrich. A stock solution of $1000 \text{ mg L}^{-1} \text{ Hg}^{2+}$ solution was prepared using A. R. grade mercuric chloride, CH_3Hg^+ solutions was prepared to use CH_3HgCl , and $\text{CH}_3\text{CH}_2\text{Hg}^+$ solution was prepared to use $\text{CH}_3\text{CH}_2\text{HgCl}$, a working solution of 80 mg L^{-1} of Hg^{2+} ,

30 mg L^{-1} of CH_3Hg^+ and 30 mg L^{-1} of $\text{CH}_3\text{CH}_2\text{Hg}^+$ for batch adsorption was prepared by appropriate dilution with Milli-Q water, 2-Mercaptobenzothiazole (MBT) was purchased from Merck chemicals. The other required reagents were procured from Merck chemicals respectively.

2.2. Instruments and characterizations

Raman spectra were recorded on a WITec Confocal Raman Microscope Alpha 300R using a 532 nm He-Ne laser with 5 mW. The TEM analysis was carried out using a PHILIPS CM-200 TWIN instrument an operating voltage at 200 kV, samples were prepared by drop-wise addition of an appropriate solution to the carbon-coated 400 mesh Cu grid followed by solvent evaporation in hot air oven. A Perkin Elmer FT-IR spectrum100 spectrometer was used to characterize the material functional groups identifications with the range of $400\text{--}4000 \text{ cm}^{-1}$ by mixing 0.01 g of the material with 0.1 g KBr (spectroscopy grade). The XPS (Kratos Axis Ultra) instruments were used to record samples, X-ray Sources: 500 mm Rowland Circle Monochromator Al-Mg/Al achromatic Source 450W max power. The spectra were recorded using a monochromatic Al $K\alpha$ X-ray source (15 mA, 14 KV). All obtained spectra were calibrated to a C 1s peak at 284.6 eV, and fitted with a mixed Gaussian-Lorentzian function by XPSPEAK (a freeware). The pressure in the analyzer chamber was 1×10^{-8} Torr. High-resolution spectra were collected using 40 eV pass energy, the spot size of $300 \times 700 \mu\text{m}$ slots and 0.05 eV step size. UV–vis spectra were taken by Jasco V-630 (Jasco, Japan), the X-ray diffraction (Powder-XRD) was carried out on a D8 Discover X-ray diffractometer with Cu $K\alpha$ radiation ($k=0.1541 \text{ nm}$, Bruker, Germany) was utilized to record the characteristic changes in the diffraction pattern of the adsorbent material. A JEOL JSM-6330TF analyzer was used to observe the morphological changes and the energy dispersive X-ray analysis spectra (EDX) were recorded adsorbent and after adsorption of Hg(II). The concentration of mercury in the aqueous solution was measured using ICP-MS PerkinElmer, Sciex-Elan DRC Plus, Software which we used Elan-6100 DRC PLUS respectively. The pH adjustments were done using METTLER TOLEDO pH meter S20.

2.3. Preparation of exfoliated graphene oxide from graphite

An improved method was used for the synthesis of GO [14–16,31], which was reported in our earlier study [23]. About 1.5 g of graphite powder was taken and gradually added to a 9:1 mixture of concentrated $\text{H}_2\text{SO}_4/\text{H}_3\text{PO}_4$ (180:20 mL). Subsequently, KMnO_4 (9.0 g) was gradually added to the mixture with stirring, a maintaining the reaction temperature below 40°C . The reaction was slightly exothermic to $35\text{--}40^\circ\text{C}$, after which it was heated up to 60°C with continuous stirring for 12 h. The above reaction mixture was cooled to room temperature and slowly poured onto ice (200 mL) with 2 mL of H_2O_2 (30%) where the brown color was entirely turned to yellow. Afterwards, centrifugation of the filtrate was done at 4500 rpms for 30 min, the supernatant was decanted. The solid material obtained, centrifugation was thoroughly washed with 200 mL of water followed by 200 mL of 30% HCl and 200 mL of ethanol. After each wash, the filtrate was centrifuged at 4500 rpms for 30 min and the supernatant was decanted off. The leftover solid material was dried at room temperature for 12 h. A 1.0 g of GO was dispersed into mixture of 1:1 ratio, an SOCl_2/DMF (25:25 mL, v/v) were slowly added, the resulting mixture was refluxed at 70°C for 24 h, the final product were washed with tetrahydrofuran (THF) and dried under the vacuum [23].

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