



Improved uptake of mercury by sulphur-containing carbon nanotubes

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ABSTRACT

Sulphur containing multi-walled carbon nanotubes (S-MWCNTs) and sulphur-containing activated carbon (S-AC) were employed as adsorbents for the solution uptake of both inorganic and organic forms of mercury. The results revealed that both materials could adsorb mercury at the parts per billion (ppb) level. The adsorption performance of S-AC was substantially reduced in the presence of excess SO₂ while that of the S-MWCNTs was not affected, indicating the superiority of the S-MWCNTs over S-AC. The amount of mercury adsorbed by S-MWCNTs was enhanced by higher sulphur content, increasing contact time and increasing pH. Adsorption by the S-MWCNTs and S-AC were affected by changes in pH but not by the presence of competing ions (Pb²⁺, Cd²⁺ and Cu²⁺ and Cl⁻). This also applied to the uptake of mercury from a real industrial effluent. The Freundlich Isotherm provided the best description of the equilibrium adsorption giving a maximum uptake capacity for Hg (II) as 72.8 μg g⁻¹ for S-MWCNTs and 44.7 μg g⁻¹ for S-AC. Preliminary results also reveal that S-MWCNTs can be used for the treatment of industrial wastes that are rich in mercury and contain multiple competing anions and cations. Both S-MWCNTs and S-AC may be regenerated with thiourea.

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1. Introduction

Mercury has been classified as one of the most toxic heavy metals due to its ability to bioaccumulate in living tissue and to biomagnify in food chains [1–3]. This has caused organisations like the European Union, the US Environmental Protection Agency (EPA) and the World Health Organisation (WHO) to restrict the concentration of mercury in drinking water to 1 μg L⁻¹ and the concentration in waste discharge to 5 μg L⁻¹ [4], nil and 0.0001 ppm respectively [5,6].

Various industries such as the chlor-alkali industry utilise mercury extensively [1,5,7]. As a result large amounts of mercury are generated in the wastes produced by these industries. Owing to its toxicity, there is thus a need to eliminate mercury from these industrial wastes.

It has been suggested that all mercury present in industrial wastes should be eliminated prior to disposal [8]. A number of technologies including adsorption onto solid surfaces like activated carbon have been explored for the removal of mercury [1,7–11]. However, each of these processes have their inherent disadvantages [7,8,10,11]. Furthermore, adsorption capacities of adsorbents like activated carbon are hindered by competing molecules and ions including high concentrations of SO₂ and SO₃ [12,13]. This has led to a demand for new technologies and adsorbents for the removal of mercury.

Numerous low cost organic and inorganic adsorbents have been explored for mercury removal [3–11,14,15]. However, all suffer from disadvantages like low adsorption capacities, poor physical stability, poor selectivity for mercury, poor regeneration of the adsorbent, leaching of organics and the release of Hg (0) vapour into the atmosphere [13–15].

Most of these studies have also focussed on the uptake of parts per million concentrations of the inorganic forms of Hg. Very little emphasis has been placed on the removal of parts per billion (ppb) levels of mercury as this is more difficult to achieve. Limited studies on the uptake of ppb levels of Hg from flue gas have been fairly successful [7,16,17]. However, this is yet to be demonstrated for the organic forms of mercury.

Most adsorbents used for the uptake of Hg and metal ions in general are said to be non-selective and adsorb most metal ions [6]. Thus, the need for selective adsorbents has arisen [9]. An increasing need for nanostructured adsorbents with high mercury adsorption capacities has been expressed [6]. Such materials should be chemically specific and must have a high binding capacity for the toxic metal ion [6].

The environmental applications of carbon nanotubes have increased over the years [18–21]. MWCNTs in particular have been effective in adsorption due to their large surface area, high chemical purity, adequate intraparticle pores and chemical stability [19]. Recently, the synthesis of phosphine-derivatized MWCNTs for Ni ion uptake has also been reported [22].

Mercury is known to have a high affinity for sulphur especially in cationic forms [2,10]. Studies where specific adsorbents have been modified with sulphur containing functional groups and used for

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the uptake of mercury have been reported in the literature [1,6]. To date, there have only been three reports on the remediation of mercury by carbon nanotubes but in these studies the possibility of using sulphur-doped carbon nanotubes to improve the selectivity for Hg was not considered [23–25]. Herein, we report on the possibility of using sulphur functionalised MWCNTs (S-MWCNTs) as adsorbents for Hg removal. As control experiments the uptake of Hg by unmodified MWCNTs and commercial activated carbon (both unmodified and sulphur-containing forms) was studied. All studies were conducted on both organic and inorganic forms of mercury.

2. Materials and methods

Powdered activated carbon was obtained from Merck. The MWCNTs were synthesised by a method developed in our laboratories (surface area: 25 m²/g). [26]. Unless otherwise stated all chemicals used were purchased from Sigma Aldrich and are of analytical grade. The sources of Hg (II), monomethyl and dimethyl mercury were mercuric nitrate, monomethyl mercury chloride and a synthetic chloride derivative of dimethyl mercury (3,6-didodecyloxy-4,5-dimethyl-*o*-phenylene-bis (mercury chloride)) (See Fig. S1 for structure) respectively. Basically a stock solution of 1000 ppm of each solution was prepared and then diluted to give a 100 ppb solution of each form of mercury.

The synthesised MWCNTs were heated in a tube furnace under argon at 900 °C prior to use. An IR spectrum (not shown) verified the removal of functional groups such as carboxyl and hydroxyl groups from these MWCNTs. A modified procedure for loading sulphur onto the MWCNTs is described in the appendix.

2.1. Uptake studies

These studies were performed by use of 0.1 g of adsorbent placed into a sample vial to which 20 mL of a mercury solution was added. The MWCNT–mercury solution mixture was then agitated on a shaker for different contact to facilitate contact between the MWCNT and the mercury solutions. The resulting suspensions were then filtered through a 0.45 µm filter (Microsep). Typically contact times of ranging between 10 and 120 min were used [5–7]. Similar control studies using S-AC, unmodified MWCNTs and unmodified activated carbon as adsorbents were also conducted. The filtrates were analysed by Inductively Coupled Plasma–Mass Spectrometry (ICP–MS).

To investigate the influence of the pH of each MWCNT–mercury solution, the mixture was adjusted either with 0.1 M NaOH or 0.1 M HCl until a desired pH value was obtained. The pH of each solution was carefully monitored during the reaction using a Metrohm pH meter and the pH of the solutions was varied across the pH scale (1, 2, 4, 6, 8, 10, 12 and 14).

2.2. The effect of competing cations

(Pb(NO₃)₂, Cd(NO₃)₂ and Cu(NO₃)₂; 10–2000 ppb), SO₂ (by bubbling SO₂ at a flow rate of 100 mg SO₂ per m³ through the mercury adsorbent suspensions for contact times ranging from 10 to 240 min) as a function of pH (by bubbling the SO₂ through Hg (II) solutions (100 ppb) with the pH 1–14 using either 0.1 M NaOH or 0.1 M HCl); chloride ions [27] (NaCl solution, 10–2000 ppb); of an industrial water solution from Durban, SA, (Table S2 for content) were studied.

The desorption capacity of each type of adsorbent was studied by maintaining the mercury solutions in contact with each type of adsorbent for a contact time of 120 min. The Hg-adsorbent suspensions were then filtered and washed with 0.1 M HCl. The washings were collected and then analysed for mercury by ICP–MS. In an additional desorption experiment, the S-MWCNTs and S-AC were also washed with 0.5% thiourea in 0.05 M HCl [28].

All filtrates and washings collected from the adsorption and desorption experiments were analysed for their mercury content using

ICP–MS (Spectromass 2000). The software package used for the data analysis was Smart Analyzer supplied by Spectro. The optimized instrumental parameters are given in the supplementary material.

2.3. Characterisation of studies

The S-MWCNTs and S-AC were characterised using a Jobin Yvon T6400 Raman spectrometer to verify the presence of carbon–sulphur bonds. The Raman spectra of S-MWCNTs and S-AC are shown in Figs. S2 and S3 respectively. The point of zero charge of each type of adsorbent used in this study was determined by measuring the Zeta-potential of each adsorbent as a function of pH on a Malvern Zetasizer (type: Zetasizer Nano). These results are shown in Table S3. Details of validation of the analytical data and quality assurance procedures are provided in the appendix.

The sulphur content of both adsorbents was measured on a Perkin-Elmer C, H, S analyser (CHS – 500). The mercury uptake capacity of each adsorbent was studied as a function of sulphur content using a 100 ppb Hg (II) solution and a pH of 12.15. The data are reported in Fig. 1 and Table S1.

3. Results and discussion

3.1. Effect of sulphur content

The sulphur content of a series of activated carbons and MWCNTs was varied by reaction of the carbons and MWCNTs with phosphorus pentasulfide (Table S1). A linear increase in mercury uptake (100 ppb solution) with increasing sulphur content for both the S-MWCNTs and S-AC samples was observed (Fig. 1).

The original synthesis conducted by Cech et al. [29] only gave a 0.73% sulphur content of the MWCNTs. Even when 500 g phosphorus pentasulfide was used this method only resulted in a sulphur content of 1.12% for S-MWCNTs and 0.95% for S-AC. Microwave radiation [30] of 50 g phosphorus pentasulfide and 5.00 g MWCNTs and activated carbon respectively (2 h) also gave similar results (Table S1). As the quantity of phosphorus pentasulfide was increased more sulphur was incorporated into the MWCNTs and activated carbon respectively (Fig. 1, Table S1). The maximum amount of sulphur that could be incorporated onto the MWCNTs and activated carbon was 3.97% and 2.98% respectively.

3.2. Synthesis and characterisation of the S-MWCNTs and S-AC

Fig. S2c) shows the Raman spectra of the S-MWCNTs obtained after treatment with the suspension of phosphorus pentasulfide in

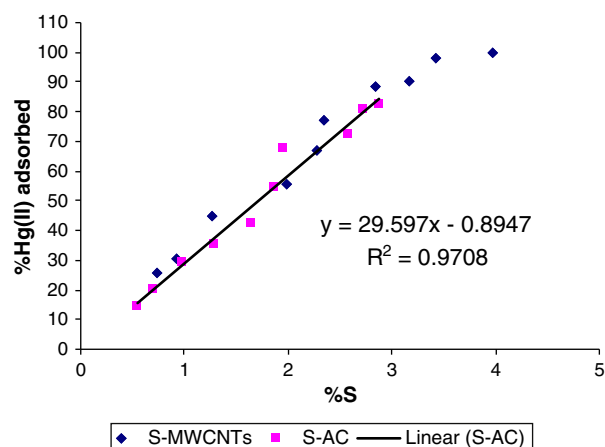


Fig. 1. The effect of sulphur content on the uptake of Hg(II) by S-MWCNTs and S-AC.

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