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Selective extraction of mercury(II) from water samples using mercapto functionalised-MCM-41 and regeneration of the sorbent using microwave digestion

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ABSTRACT

Silica sorbents, based on mesoporous crystalline material-41 (MCM-41), were functionalised using mercaptopropyl (MP) or diethylenetriamine (DETA) to extract mercury (II) ions from water. MP-MCM-41 is an extremely efficient and selective sorbent for the removal of mercury (II) from samples of distilled water doped with heavy metal ions and additionally from more complex matrices including tap and river water. In contrast DETA-MCM-41 preferentially removes hard metal ions (chromium, manganese, lead and zinc) over soft metal ions such as mercury. During extraction, the influence of pH on adsorption capacity was examined; a maximum adsorption capacity of 1245 μmol g^{-1} was achieved for MP-MCM-41 even at pH values as low as 3. Significantly, a method has been developed for the first time to remove Hg (II) from loaded MP-MCM-41 allowing this analyte to be selectively recovered from water contaminated with a wide range of heavy metal ions. The regeneration method does not disrupt the chelating agent which remains on the surface of the silica permitting reuse of the sorbent in further extractions.

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1. Introduction

In recent years the presence of heavy metals in polluted waters has become an area of great environmental concern presenting significant hazards to human health. Mercury ions (Hg^{2+}) are thought to be one of the most hazardous substances and are included on the US Environmental Protection Agency's (EPA) list of priority pollutants. Numerous separation processes have been assessed to reduce the concentration of mercury in aqueous solutions including; ion exchange [1–3], solvent extraction [4–6], adsorption [7,8], precipitation [9,10] and membrane separation [11,12]. These conventional methods are generally useful, but less so when applied to dilute solutions, they are costly and, more importantly, they show little-no selectivity. To improve the selectivity of sorbents for Hg (II) removal, chelating resins have been applied but results indicate they have limited applicability due to factors including; poor hydrophilicity, small surface areas, slow rates of adsorption and expense (due to lack of regeneration methods) [13]. The direct interaction of Hg (II) with mercaptopropyl (MP) groups has been proposed previously for the adsorption of mercury on MP-functionalised mesoporous silicas [14]. Several research groups have studied the selectivity of mercapto functionalised MCM-41 to extract the Hg (II) from aqueous media and their results show high adsorption capacities and selectivities towards mercury [14–16]. However, the limitations of previous studies include the length of time required to prepare MCM-41, the difficulties in increased batch size during preparation and the inability to remove Hg (II) from the loaded sorbent to allow reuse (thus drastically increasing cost). MCM-41 based materials will only be useful as metal ion scavengers if they can be economically regenerated whilst maintaining high adsorption capacities for the analyte of interest after multiple use. It has been previously demonstrated that the regeneration of MP-MCM-41 materials after mercury adsorption cannot be carried out under thermal treatment and acidic conditions [17]. Some research groups have worked with similar mercapto-modified MCM-41 reporting effective regeneration of loaded materials by treatment with hydrochloric acid or hydrobromic acids. However, high concentrations (12 M) are used and that could lead to damage of the silica mesostructure [18,19].

This paper presents an assessment of MP-MCM-41 for the selective extraction of Hg (II) in contaminated aqueous solutions. Further, a new method is reported which allows 100% recovery of Hg (II) from loaded MP-MCM-41 without disruption of the chelating agent. MP-MCM-41 can be reused after removal of Hg (II) without the need for surface reactivation and the Hg (II) selectively recovered from contaminated water. Extraction results for MP-MCM-41 are compared to those obtained by DETA-MCM-41.

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2. Experimental

2.1. Materials and reagents

Cetyltrimethylammonium bromide (CTAB), 98%, was supplied by BDH. Aqueous ammonia (30% NH_3), tetraethoxysilane (TEOS) 98%, hydrogen peroxide solution (30 wt.%), 3-mercaptopropyltrimethoxy-silane (MP-TMS), 99%, N-(3-trimethoxysilylpropyl)diethylenetriamine (DETA-TMS), ethanol absolute, 1000 μg mL^{-1} of Hg (II) standard solution and toluene (+99%) were purchased from Sigma Aldrich. Nitric acid (HNO_3, 65 wt.%) and ammonium hydroxide (35%) were purchased from Fisher Scientific. Glassware was soaked in 5% HNO_3 overnight and cleaned with deionised water before use. All products were used as supplied and deionised water was used throughout this work.

2.2. Synthesis of MCM-41

To obtain MCM-41 prior to functionalisation a room temperature preparation method [20] was used with no specialised equipment on the bench, obtaining 100 g of material in one batch. To increase the number of silanol groups on the surface of the silica and provide large mesopores for functionalisation the surfactant was removed by microwave digestion (MARS 5 microwave, CEM Corporation, Buckingham, UK) using a solution of nitric acid and hydrogen peroxide [20]. Briefly, operating conditions included a power output of approximately 1600 W, a pressure and temperature lower than 1.3 MPa and 200 °C, respectively and a working frequency of 2450 MHz and 220 V for 15 min. The product was filtered, washed with copious amounts of distilled water and dried at 100 °C for 2 h.

2.3. Characterisation of MCM-41

The surface area of the MCM-41samples obtained for this study were measured using nitrogen physisorption isotherms on a Micromeritics Gemini 2375 volumetric analyser. Each sample was degassed prior to analysis for 12 h at 200 °C. The Brumauer–Emmett–Teller (BET) surface areas were calculated using experimental points at a relative pressure (P/P_0) of 0.05–0.25. The total pore volume was calculated from the amount of N_2 adsorbed at the P/P_0 of 0.99 for the sample and the average pore size distribution of the material was calculated using the Barrett–Joyner–Halanda (BJH) model from a 30-point BET surface area plot. The MCM-41 obtained exhibited a Type IV adsorption isotherm typical of mesoporous solids. Desorption isotherms were used to calculate pore diameters. Infrared spectra of all samples were obtained using pressed KBr pellets in the 4000–400 cm^{-1} region with a resolution of 4 cm^{-1}, by accumulating 64 scans using an ATI Mattson FTIR spectrometer. Elemental analysis (EA) was carried out using an Exeter Analytical CE440 elemental function.

2.4. Functionalisation of MCM-41 by mercaptopropyl or diethylenetriamine

In a typical experiment, approximately 5 g of microwave digested MCM-41 was pre-treated at 140 °C for 2 h and then immersed into 50 mL toluene and 10 mL MPTMS or DETA-TMS in a 250 mL flask. The mixture was refluxed for 4 h and the solid produced was filtered, washed with 100 mL ethanol, and oven-dried at 80 °C for 1 h to produce a mercapto-functionalised (MP-MCM-41) or diethylenetriamine-functionalised (DETA-MCM-41) MCM-41 sorbent, respectively.

2.5. Determination of adsorption capacity

Approximately 10 mg samples of MP-MCM-41 or DETA-MCM-41 were suspended in 20 mL solutions containing 20 μg mL^{-1} Hg (II) and the solution was stirred (250 rpm) for approximately 2 h. After this time a 5 mL aliquot of the solution was removed and analysed for Hg (II) by FAAS. This process was repeated until saturation of the sorbent, as indicated by a measured presence of Hg (II) in the aliquot. The extraction was repeated at various pH values (between 3 and 11) with solution modification achieved via the addition of small amounts of 1 M ammonium hydroxide. The amounts of Hg (II) removed by each sorbent were calculated and adsorption capacities determined as outlined below

$$q_e = \frac{(C_0 - C_e)V}{W \times \text{metal atomic weight}} \tag{1}$$

where q_e is the adsorption capacity (μmol g^{-1}) of the adsorbent at equilibrium; C_0 and C_e are the initial and equilibrium concentrations of solute (μg mL^{-1}), respectively; V is the volume of the aqueous solution (mL) and W is the mass (g) of adsorbent used.

The concentration of Hg (II) in water samples was determined using a PerkinElmer AAnalyst200 flame atomic absorption spectrometry (FAAS) instrument. The optimum sensitivity for each analyte and calibrant solutions were reagent matched. Calibrants were prepared in the range 0–25 μg mL^{-1} and a regression line obtained ($y = 0.0014x - 0.00005$, $r^2 = 0.9987$, $n = 6$) to determine the concentration of Hg (II) in analysed solutions. The limit of detection (LOD) was calculated as 1.4 μg mL^{-1}).

2.6. The selectivity of functionalised-MCM-41 in distilled water containing a range of heavy metals and in doped tap and river water samples

To demonstrate the potential selectivity of MP-MCM-41 for Hg (II) when present in solutions containing other mixed metal ions, a 20 μg mL^{-1} non-buffered water solution containing selected metals (Cd, Cr, Hg, Mn, Pb, and Zn) was prepared. In each experiment 25 mg of MP-MCM-41 was added to the solution and stirring commenced immediately after addition of sorbent. Additionally, the performance of MP-MCM-41 in real samples was evaluated by adding 25 mg of sorbent to a river water sample (collected from the Bothlin River in Glasgow) and a tap water sample (taken from a building in the Drygate campus in Glasgow). The tap and river water samples were known to contain high concentrations of metal ions, but not Hg (II) and so they were spiked to produce solutions containing 25 μg mL^{-1} of Hg (II). To assess extraction performance, aliquots were removed from stirring solutions at known time points, filtered (Fisherbrand QL100) and the presence of metal ions in solution was determined by FAAS.

2.7. Recovery of Hg (II) from loaded sorbents using microwave digestion

A 1 g sample of MP-MCM-41 was added to a 40 mL aqueous solution containing 1000 μg mL^{-1} Hg (II) to pre-load the sorbent with analyte. A reduction in Hg (II) concentration measured after sorbent addition was used to provide evidence that the target analyte was extracted by the sorbent. The loaded sorbent was removed from the solution by filtration and dried in air. Approximately 0.125 g of loaded sorbent was immersed in 20 mL of 1% HNO_3, and the resulting suspension was placed in a 50 mL capacity Teflon microwave vessel. To assess the ability to recover Hg (II) from the MP-MCM-41 two different conditions were used with the microwave. The first set of conditions examined the use of high energy to break the Si–O–S–Hg bonds ensuring that all the Hg (II) could be taken back into solution. The second set of experiments was to decrease the

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