



Preconcentration and selective extraction of chromium species in water samples using amino modified mesoporous silica

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ABSTRACT

Speciation and separation of chromium (VI) and chromium (III) from aqueous solutions were investigated using amino-propyl functionalised mesoporous silica (AP-MCM-41) as an adsorbent. The as-synthesised adsorbent was produced following a simple synthesis method at room temperature prior to template removal using microwave digestion. The maximum adsorption capacity at 111.1 mg/g was calculated according to the Langmuir isotherm model, suggesting a 1:1 monolayer adsorption mechanism. Moreover, AP is a simple chelate, yet it can extract Cr (VI) exclusively from solutions containing other mixed metal ions simply by tuning the solution pH. Recovery of Cr (VI) from loaded sorbents is equally easy to perform with 100% extraction efficiencies allowing reuse of the sorbent and recovery of Cr (VI) from aqueous solutions containing a complex mixture of ions. The material would find use in environmental remediation applications, as a selective adsorbent of Cr (VI) or even as a solid-phase extraction stationary phase to remove and pre-concentrate Cr (VI) from aqueous solutions; this study demonstrates enrichment factors of 100 although higher levels are also possible.

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1. Introduction

The presence of chromium in water has received much attention in recent years. Chromium contamination is generated from different industries such as metal finishing, pigment manufacture, electroplating and leather tanning [1–3]. Chromium exists in oxidation states from +2 to +6, but only two states, the trivalent and hexavalent, are of environmental significance [4]. Trivalent chromium, Cr (III), is considered to be a trace element that is essential for the functioning of living organisms; but at high concentration, it can be dangerous to health as it can co-ordinate with organic compounds which in turn leads to inhibition of some metallo-enzyme systems [5]. Hexavalent chromium, Cr (VI), is about 100 times more toxic than Cr (III) [6]. Occupational exposure to Cr (VI) compounds causes a wide range of clinical/health problems [5,7]. Methods of analyses are required to determine the concentration of Cr (VI) in a variety of matrices; however, the accurate and reliable removal of Cr (VI) presents a number of challenges such as the need to differentiate chromium species on the basis of both oxidation state and solubility [8,9]. Selective extraction methods for Cr (VI) in contaminated solution are therefore desirable.

Different materials (activated carbon [10,11], ion exchangers [12,13], zeolites [14,15], or clays [16,17]) have been used to extract Cr (VI) from environmental samples. However, the success of the

conventional porous materials is limited due to low loading capacities and low selectivity [18]. For example, the maximum adsorption capacity of Cr (VI) on activated carbon was reported as 22.29 mg/g [11], and in the case of modified natural clinoptilolite and ZSM-5 zeolites, the Cr (VI) loading capacities were 29.7 or 10.6 mg/g [19]. To improve on these capacity values, functionalised mesoporous materials have been used to enhance the interaction with Cr (VI) [1,4,6,20,21]; improvements in maximum adsorption capacity values of approximately four times have been reported [19]. Further, methods have recently been adapted to produce mesoporous silica materials with larger pores, increased functionalisation and higher adsorption capacity values for removal of VOCs from indoor air [22,23], Pb (II) and Hg (II) from aqueous solution [24,25] compared with conventional sorbents like activated carbon, zeolites and clays.

This study examines the potential advantages of MCM-41 material using a modified method of mesoporous silica production to provide a functionalised material for the selective removal of Cr (VI) from contaminated solution.

2. Experimental

2.1. Materials and reagent

Potassium dichromate (+99%), 1000 $\mu\text{g cm}^{-3}$ of Cr (III) standard solution, 1,5-diphenylcarbazine, aqueous ammonia (30% NH_3),

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tetraethoxysilane (TEOS) 98%, hydrogen peroxide solution (30 wt.%), 3-aminopropyltrimethoxy-silane (AP-TMS), 99%, *N*-(3-trimethoxysilylpropyl) diethylenetriamine (DETA-TMS), ethanol absolute and toluene (+99%) were purchased from Sigma Aldrich. Nitric acid (HNO₃, 65 wt.%), hydrochloric acid (36%) and ammonium hydroxide (35%) were purchased from Fisher Scientific. Cetyltrimethylammonium bromide (CTAB), 98%, was supplied by BDH. Glassware was soaked in 5% HNO₃ 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

MCM-41 was prepared according to the method reported in ref [24]. Briefly, 8.8 g of CTAB was dissolved in a mixture of 208 cm³ of distilled H₂O and 96 cm³ of aqueous NH₃ under slight warming (35 °C). Then, 40 cm³ of TEOS was slowly added under stirring. After further stirring for 3 h, the gel was aged at room temperature for 24 h in a closed container. The product was obtained by filtration, washed with distilled H₂O and dried in air at room temperature. The organic template was removed using microwave digestion [24]. Approx. 0.3 g of as-synthesised material was added to multiple Teflon vessels to which 5 cm³ of HNO₃ and 2 cm³ of H₂O₂ were added to each vessel. A MARS 5 microwave system (CEM Corporation, Buckingham, UK) was used with a power output of approximately 1600 W, a pressure and temperature lower than 1.3 MPa and 200 °C 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 in oven at 100 °C for 2 h.

2.3. Functionalisation of MCM-41 by aminopropyl or diethylenetriamine

Surface modification of MCM-41 was carried out by condensation using the organosilane of choice with MCM-41 (scheme 1). Briefly, approximately 5 g of MCM-41 was pre-treated at 140 °C for 2 h before being immersed in 50 cm³ of toluene and 10 cm³ of AP-TMS, or DETA-TMS, in a 250 cm³ flask. The mixture was refluxed for 4 h and the solid produced was filtered, washed with 100 cm³ ethanol, and oven-dried at 80 °C for 2 h to produce an amino-functionalised (AP-MCM-41) or diethylenetriamine-functionalised (DETA-MCM-41) MCM-41 sorbent, respectively.

2.4. Colorimetric determination of chromium (VI) in solution

To measure the concentration of Cr (VI) in water, a method reported in ref [26,27] was used with slight modification. A 1000 ppm stock solution of Cr (VI) (0.2828 g of potassium dichromate, dissolved in 100 cm³ distilled water) was used to prepare

six calibration standards in the range 0.1–1.0 µg cm⁻³ with a reagent blank as first level. Calibration was performed colorimetrically after derivatisation. A 1 cm³ aliquot of diphenylcarbazide solution (250 mg of 1,5-diphenylcarbazide was dissolved in 50 cm³ acetone and stored in brown bottle) was added to 1 cm³ of each calibrant, and the pH of the solution was adjusted to 1–2 by adding 0.2 cm³ of 1 M hydrochloric acid. Prior to measurement, the solution was allowed to stand for 15 min to ensure full colour development. Derivatised solutions were measured using a SI Photonics (M-420) CCD array uv-vis spectrophotometer using a 1 cm absorption cell and an absorbance wavelength of 540 nm. Linear regression analysis of concentration versus absorption gave typical regression lines of $y = 0.3555x + 0.0057$ with a correlation coefficient of 0.9986. Solutions of unknown Cr (VI) concentration were determined after derivatisation using the regression coefficients.

2.5. Determination of total chromium (Cr_{Total}) in aqueous samples by ICP-OES

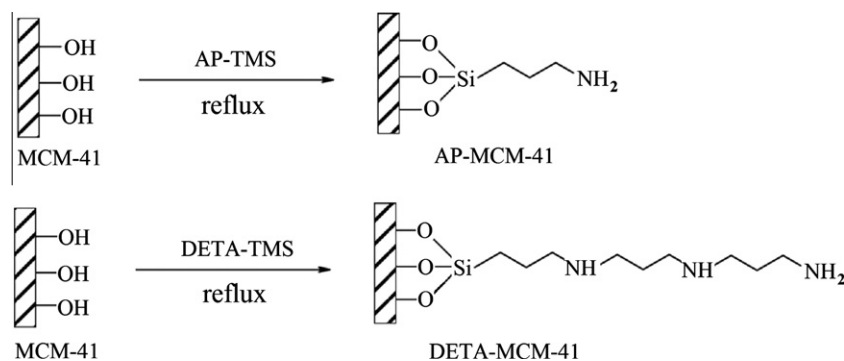
A Thermo Scientific iCAP 6200 ICP-OES was used for the determination of total Cr in aqueous solutions. Calibration standards (0.1–10 µg cm⁻³) were prepared in 5% HNO₃. A quality control check solution was prepared at 1 µg cm⁻³ to ensure the accuracy of the method used and was repeatedly analysed after 20 samples. Method parameters used are shown in Table 1. The method detection limit (MDL) for Cr (VI) was 0.004 µg cm⁻³ or 0.003 µg cm⁻³ using wavelengths of 267.7 or 283.6 nm, respectively. Cr (III) concentrations were calculated according to the mass balance between the ICP method Cr_{Total} and the colorimetric method, which was used to determine the concentration of Cr (VI).

2.6. Extraction, recovery and regeneration procedures

The general procedure for the extraction of Cr (III) or Cr (VI) from solution can be summarised as follows. Approximately 25 mg samples of AP-MCM-41 or DETA-MCM-41 was suspended in 25 cm³ solutions containing known concentrations of Cr (III) or Cr (VI) at various pH values (between 1 and 11). Solutions were stirred (250 rpm) for approximately 2 h then filtered (Fisherbrand QL100) under vacuum, and the filtrate was analysed using ICP/OES. To recover Cr ions from loaded sorbents, the silica material was washed with 25 cm³ water adjusted to pH 3 for Cr (III) or pH 9 for Cr (VI).

2.7. Adsorption isotherms for the maximum adsorption capacity evaluation

To study the maximum adsorption capacity of Cr (VI) on AP-MCM-41, the Langmuir and Freundlich isotherm models were ap-



Scheme 1. Modification of activated silica using 3-aminopropyltrimethoxy-silane and *N*-(3-trimethoxysilylpropyl) diethylenetriamine.

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