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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.

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 $\mu g\,mL^{-1}$ 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 $\mu g\,mL^{-1}$ 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

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

where q_e is the adsorption capacity ($\mu mol\,g^{-1}$) of the adsorbent at equilibrium; C_0 and C_e are the initial and equilibrium concentrations of solute ($\mu g\,mL^{-1}$), 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 $\mu g\,mL^{-1}$ 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 $\mu g\,mL^{-1}$).

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 $\mu g\,mL^{-1}$ 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 $\mu g\,mL^{-1}$ 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 $\mu g\,mL^{-1}$ 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

Table 1
Operation conditions used in Hg (II) recovery experiments.

	Low energy MWD	High energy MWD
Working frequency	2450 MHz	2450 MHz
Power applied to the sample	800 W	1600 W
Heating rate	Ramped to 80 °C for 5 min held 85 °C for 10 min	Ramped to 180 °C for 15 min held 180 °C for 5 min
Solvent	1% HNO_3	10% HNO_3
Volume of solvent (mL)	20 mL	20 mL
Weight of sample (g)	0.125 g	0.3 g

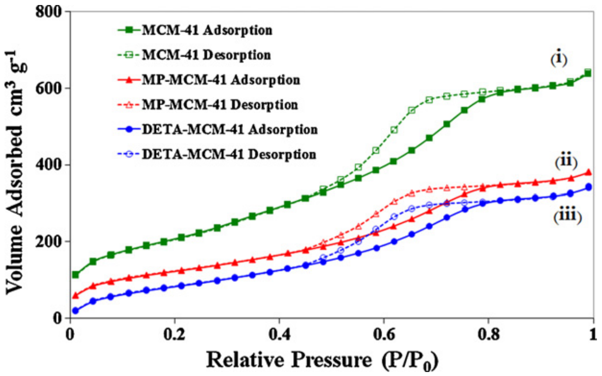

Fig. 1. BET isotherm patterns of (i) MCM-41, (ii) MP-MCM-41 and (iii) DETA-MCM-41.

energy of the microwave so that the S–Hg bonds would be disrupted whilst leaving the chelating agent on the surface of the silica. Table 1 summarises the parameters used in high or low energy microwave digestion experiments. The efficacy of the regeneration process was evaluated by calculating the percentage of mercury desorbed as the ratio of the amount of mercury in solution after low energy microwave digestion (LE-MWD) to the mass of mercury removed by high energy conditions (HE-MWD):

$$\%\,\text{Regeneration} = \frac{\text{Mass of Hg}_{\text{LE-MWD}}}{\text{Mass of Hg}_{\text{HE-MWD}}} \times 100 \qquad (2)$$

3. Results and discussion

3.1. Parent material characterisation

The functionalised samples of MCM-41 were characterised using BET to compare the N_2-adsorption isotherms, see Fig. 1. In each case typical Type IV N_2-adsorption isotherms were obtained with distinct hysteresis loops and steep adsorption/desorption steps indicating a well-ordered array of pores. All samples display parallel and nearly vertical isotherm branches typical of hexagonal mesoporous silica. The type IV isotherm shape is preserved for all samples suggesting the pore structure has been maintained post-functionalisation. The physicochemical data for the 3 samples are summarised in Table 2. As expected significant reductions in surface area and pore volume (calculated from the BJH model) were observed for the modified materials; DETA-MCM-41 had the lowest surface area consistent with the longer length of the chelate compared to MP. However the average pore diameter remained similar post-modification. The degrees of functionalisation (L_0) were high indicating that materials were successfully functionalised with both chelates.

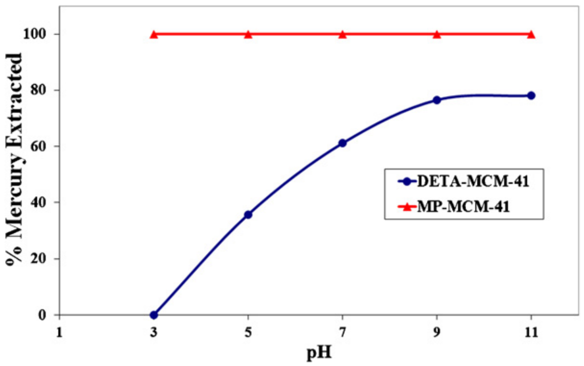

Fig. 2. Effect of pH on the extraction of mercury ions from water using functionalised MCM-41.

3.2. Mercury (II) extraction and adsorption capacities using spiked solutions of distilled water

Samples of MCM-41 and functionalised MCM-41 (MP-MCM-41 and DETA-MCM-41) were each added to aqueous solutions containing known amounts of Hg (II) at solution pHs of 3, 5, 7, 9 or 11. Interestingly, unlike the other chelating agents tested, the results indicated that there was no effect of changing pH on the efficiency of MP-MCM-41 for Hg (II) extraction from water over the pH range used in this study (Fig. 2), making it applicable as a sorbent material for a wide range of potential applications. Moreover, the adsorption capacity for Hg (II) was measured resulting in an adsorption capacity value (1245 μmol g^{-1}) that is higher than previous, similar studies (see Table 3). The high values obtained appear to be a direct result of the optimised preparation method used for the parent material as other research groups using MP-MCM-41 achieved lower adsorption capacities of 1050 [26] or 590 μmol g^{-1} [27]. Using FAAS with a LOD of 1.4 μg mL^{-1}, it was possible that best recoveries achieved were 93% after just one exposure of the sorbent to 100 μg of Hg (II). Therefore to provide evidence that the sorbent was capable of extracting a high mass of Hg (II) with good efficiency the sorbent was introduced to 5 mL solutions containing Hg (II) at a concentration of 800 μg mL^{-1}. Hg (II) was measured in the extracted aliquot only after the sorbent was introduced to the 3rd solution containing a high mass of Hg (II). Overall the sorbent was exposed to 10,000 μg of Hg (II) and 90 μg of Hg (II) was measured in the solution indicating an extraction efficiency of approximately 99.1%.

The DETA-MCM-41 sorbent showed a much lower adsorption capacity, of approximately 50 μmol g^{-1}, and also a strong depen-

Table 2
Physiochemical data recorded for the MCM-41, MP-MCM-41 and DETA-MCM-41 samples.

Sample name	BET surface area ($m^2\,g^{-1}$)[a]	Pore size (nm)[b]	Pore volume ($cm^3\,g^{-1}$)[c]	L_0 (mmol g^{-1})[d]
MCM-41	760.21	6.74	0.9868	–
MP-MCM-41	448.83	6.67	0.5924	2.96
DETA-MCM-41	237.56	5.48	0.409	7.19

[a] Calculated by the BJH model from sorption data in a relative pressure range from 0.05 to 0.25.
[b] Calculated by the BJH model from the adsorption branches of isotherms.
[c] Calculated from N_2 amount adsorbed at a relative pressure P/P_0 of 0.99.
[d] Functionalisation degree (L_0 = millimoles of ligand per gram of functionalised silica).

Table 3
A list of maximum adsorption capacities for Hg (II) using modified adsorbents.

Material	Ligand	Adsorption capacity (μmol g^{-1})	Ref.
MCM-41	2-(3-(2-Aminoethylthio) propylthio) ethanamine	700	[14]
MCM-41	2-Mercaptothiazoline	700	[15]
HMS	3-Mercaptopropyl	550	[21]
Sol–gel silica	1,5-Diphenylcarbazide	29	[22]
Silica gel	Dithizone	320	[23]
MCM-41	2-Mercaptopyridine	120	[24]
MCM-41	3-Aminopropyl	400	[25]
MCM-41	3-Mercaptopropyl	1050	[26]
MCM-41	3-Mercaptopropyl	590	[27]
MCM-41	3-Mercaptopropyl	1245	This work

dence on pH with the highest extraction efficiency when the solution pH was adjusted to values of 9 and above (Fig. 2). The difference in performance between MP- and DETA-MCM-41 over the pH range can be used as an advantage. For example, MP-MCM-41 can be used to extract Hg from contaminated solutions over a wide range of pH values which will expand its use in environmental remediation. The DETA-MCM-41 material was easily regenerated by lowering the solution pH value to 3; with successful removal of all the encapsulated Hg (II). The regenerated DETA-MCM-41 was then re-used to extract further Hg (II) from aqueous solution and the results highlighted the ease at which this material could be regenerated whilst still performing at approximately 99% of the original extraction efficiency.

The dramatic difference in performance over the pH range studied can be related to the stability of the chelate attached to the silica material. For MP-MCM-41 the –S–Hg– bond has a high stability constant [17] whereas for DETA-MCM-41 the –N–Hg– has much lower stability constant [26]. The high stability of the –S–Hg bond over the observed pH range of 3–11 allowed the chelate to extract Hg (II) at high efficiencies. Indeed the stability of the –S–Hg– bond is higher than those for other divalent metal ions with SH groups [28]. Further explanation of this phenomenon was given by Walcarius and Delacote [29] who reported that the complexation of Hg (II) to thiol groups led to the formation of a positive charge (see Eq. (3)).

$$\equiv \mathrm{Si{-}C_3H_6{-}SH} + \mathrm{Hg^{2+}} + 2\mathrm{NO_3}^- \rightarrow \equiv \mathrm{Si{-}C_3H_6{-}S{-}Hg^+}, \quad \mathrm{NO_3}^- + \mathrm{HNO_3} \tag{3}$$

The formation of positively charged complexes inside the mesoporous adsorbents could prevent Hg^{2+} being replaced by H^+ at low pH. Note however that there are limits to the use of mesoporous silica at much lower pH values (<1) where damage to the silica meso-structure has been reported [17–19,26,29].

3.3. The selectivity of MP-MCM-41 towards Hg (II) in the presence of other heavy metal ions

A multi-element solution was used to evaluate the selectivity of MP-MCM-41 and DETA-MCM-41 towards Hg (II). Approximately 25 mg of each sorbent was added to an individual solution containing 20 μg mL^{-1} of Cd (II), Cr (III), Hg (II), Mn (II), Pb (II), and Zn (II). The solutions were stirred for 2 h, filtered and the filtrates were analysed by FAAS. Approximately 80% of Hg (II) was extracted by DETA-MCM-41, with greater than 97% extraction efficiencies for Cd (II), Cr (III), Mn (II), Pb (II), and Zn (II). This is in contrast with the results obtained for MP-MCM-41 which was almost exclusively selective towards Hg (II) despite the presence of other heavy metals in solution (Table 4). These results reflect the expected performance of amino- and mercapto-ligands based on metal ion-ligand stability constants which are 19.2 [26] and >23 [27] for amino-ligands with mercury and other metal ions, respectively and 37.3 [17] for sulfur and mercury.

Table 4
The efficiency of DETA-MCM-41 and MP-MCM-41 for Hg (II) in selected multi element water samples.

Metal	Spiked (μg mL^{-1})	Found after 2 h stirring (μg mL^{-1})	
		DETA-MCM-41	MP-MCM-41
Cd (II)	20	0.7	18.1
Cr (III)	20	0.3	20.5
Hg (II)	20	4.3	0
Mn (II)	20	0.1	19.8
Pb (II)	20	0.3	20.3
Zn (II)	20	0.5	19.4

The ability of MP-MCM-41 to extract Hg (II) in the presence of other potentially toxic metals (PTMs) was also assessed by adding the sorbent to a sample of river water and tap water. The water samples were first analysed by ICP-MS to determine the concentration of other heavy metals in each solution before being spiked with mercury ions to produce solution concentrations of 25 μg mL^{-1} of Hg (II), the results are give in Table 5. In spite of the high concentrations of Ca and Mg in the solutions, Hg (II) removal was 100% from river water and tap water, which implied that the Hg–S co-ordinating bond was not appreciably hindered by the presence of other co-ordinating ions at high concentration, thus proving further evidence of the high performance, and selectivity, of MP-MCM-41 for Hg (II).

3.4. Removal of Hg (II) from loaded samples of MP-MCM-41 or DETA-MCM-41 and regeneration of the sorbent

During the filtration procedure step discussed in Section 3.3, sorbents were recovered and washed with 20 mL of 1 M HCl in an attempt to remove the encapsulated Hg (II). FAAS analysis of the washings indicated that all metal ions, including Hg (II) were almost fully recovered from the DETA-MCM-41 sample (Table 6). The selectivity of MP-MCM-41 towards Hg (II) was further evidenced during the 1 M HCl washing procedure where no Hg (II) was

Table 5
ICP/MS concentration data recorded for heavy metals in river and tap water samples.

Heavy metal	River water (ppb)[b]	Tap water (ppb)[b]
As	0.7 ± 0.1	2.5 ± 0.1
Ca[a]	43,600 ± 1000	11,500 ± 1000
Cd	5.5 ± 0.1	12.7 ± 0.1
Cr	4.3 ± 0.4	14.3 ± 0.4
Cu	12.0 ± 0.3	60.3 ± 0.3
Fe	60.1 ± 0.2	249.9 ± 0.2
Mg[a]	6000 ± 1000	8500 ± 1000
Mn	3.4 ± 0.1	9.9 ± 0.1
Ni	12.0 ± 0.2	50.4 ± 0.2
Pb	3.1 ± 0.1	54.8 ± 0.1
Zn	2.7 ± 1	353.9 ± 1

[a] Measured by FAAS.
[b] Reported values are based on an average result of three experiments.

Table 6
The masses of heavy metal ions retained by sorbents after being washed in 1 M HCl samples.

Metal	Masses (μg) of ions in pre-washed (loaded) sorbent		Masses retained (μg) by chelate after washing in 1 M HCl	
	DETA-MCM-41	MP-MCM-41	DETA-MCM-41	MP-MCM-41
Hg (II)	314	400	20	400
Cd (II)	386	38	0	0
Zn (II)	390	12	14	0
Mn (II)	398	4	0	0
Cr (III)	394	0	6	0
Pb (II)	394	0	20	0

Table 7
Elemental analysis data recorded for sorbent samples.

Sorbent	%C	%H	%S
MCM-41	Trace/nil	0.52	Trace/nil
MP-MCM-41	12.33	2.58	9.07
Hg-MP-MCM-41	10.09	2.19	8.56
LE-MWD-MCM-41	7.30	1.84	6.37
HE-MWD-MCM-41	4.18	1.90	1.29

removed. As an increase in the concentration of acid used is undesirable, (previous reports suggested high concentrations of protons could damage the silica mesostructure [19,26]), a new method was developed to remove Hg (II) from MP-MCM-41 using aqueous 0.2 M nitric acid and low energy microwave assisted digestion (LE-MWD). Microwave conditions used are outlined in Table 1. A second set of conditions, using high energy microwave digestion (HE-MWD), was used to break the chelating group from the surface of the silica so that the exact mass of Hg (II) encapsulated by the sorbent could be measured.

Samples (40 mg) of MCM-41 and MP-MCM-41 and a functionalised sample loaded with 400 μg of Hg (II); (Hg-MP-MCM-41) were examined by microanalysis and FTIR before and after microwave treatment. The elemental analysis results shown in Table 7 indicate a 70% retention of mercaptopropyl groups on the surface of the silica after LE-MWD treatment. The use of HE-MWD conditions resulted in a loss of almost all mercaptopropyl functional groups from the silica surface. Additionally, analysis of the filtered nitric acid solutions collected after microwave treatment indicated that both LE- and HE-MWD methods led to a recovery of approximately 97% of Hg (II) from loaded sorbents. Extraction by MP-MCM-41 followed by LE-MWD treatment would therefore lead to a useful method for the selective recovery of Hg (II) from contaminated waters.

The FTIR spectra of all samples (Fig. 3) contain similar features expected of a silica containing material associated with the inorganic backbone such as (i) a large broad band between 3500 and 3200 cm^{-1} which is assigned to the O–H stretching mode of silanol groups and adsorbed water, (ii) a broad adsorption band at around 1030–1240 cm^{-1} which can be assigned to the Si–O–Si stretching and (iii) the water bending mode band around 1650 cm^{-1} [20]. In addition to those peaks, the spectrum of the MP-MCM-41 sample contained extra bands at 2850 and 2930 cm^{-1} which were assigned to the C–H stretching of sp^3 carbon, and a weak band at 2557 cm^{-1} was assigned to a SH stretching mode, supporting the theory that MP is present on the surface of the silica. The Hg-MP-MCM-41 spectrum lost the SH stretching mode at 2557 cm^{-1} presumably because the hydrogen had been replaced with Hg (II). The sample spectrum for LE-MWD-MCM-41 was similar to that of MP-MCM-41 but a reduced intensity of the 2557 cm^{-1} band was observed, supporting the theory that some mercapto-functionality was lost during treatment. The sample spectrum for HE-MWD-MCM-41 had no band at 2557 cm^{-1} but very small bands at 2850 and 2930 cm^{-1} were observed, indicating that the functional groups were destroyed by the high energy microwave conditions.

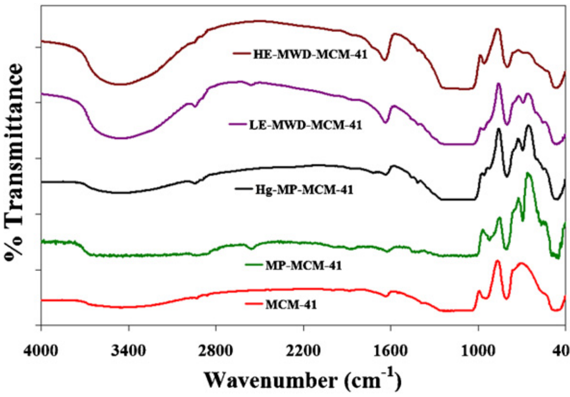

Fig. 3. FT-IR spectra of MCM-41, MP-MCM-41, Hg-MP-MCM-41, LE-MWD-MCM-41 and HE-MWD-MCM-41.

The results indicated that the new treatment method using nitric acid (0.2 M) and low energy microwave assisted digestion could successfully remove Hg (II) from loaded sorbents without removal of all functionality from MP-MCM-41. To evaluate the efficiency of regenerated MP-MCM-41 its adsorption capacity was re-determined. Using the regenerated sorbent an adsorption capacity of 950 μmol g^{-1} was measured indicating that the material can be successfully re-used after LE-MWD treatment. This method improves on results reported previously where harsher conditions (12 M HCl) were used to remove 90% of Hg (II) from thiol-functionalised mesoporous silica and on re-use only 40–60% of the original value of Hg (II) was extracted from solution [29].

4. Conclusions

A new room temperature preparation method, which involves surfactant extraction by MWD, produced a better-prepared MCM-41 base material for chelate functionalisation. This in turn led to a material which has higher adsorption capacities for Hg (II) than those reported previously. The sorbent is almost exclusively selective to Hg (II), even in the presence of a wide range of other heavy metal ions, such as those present in contaminated water samples. Removal of Hg (II) from loaded sorbents can also be achieved using a new method involving LE-MWD conditions. All of these features combined provide a highly selective removal and preconcentration method for Hg (II) from aqueous solutions. Selective recovery (97%) of Hg (II) from contaminated waters can be economically favourable and provides an alternative application method in addition to environmental mitigation strategies. Regeneration of MP-MCM-41 is presented, for the first time, with mild acid conditions. Examination of the material after treatment suggests that the recovery method proposed will not disrupt the chelate on the surface of the silica and so the material can be reused (with approximately 76% of the original adsorption capacity). It is anticipated that the sorbent can be re-used for at least 3–4 times using LE-MWD conditions with high extraction efficiencies for Hg (II) removal.

After that time removal of the thiol-group from the silica surface is recommend using HE-MWD condition and the material refunctionalised as described in Section 2.4.

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