



Large pore diameter MCM-41 and its application for lead removal from aqueous media

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ABSTRACT

A room temperature method to create large pore size and pore volume ordered mesoporous silica (MCM-41) is demonstrated. Template removal was achieved with a microwave digestion procedure using a solution of nitric acid and hydrogen peroxide. The silica product exhibited an ordered hexagonal mesostructure, large pore volume (up to 0.99 cm³/g), and large pore size (up to 6.74 nm) indicating its potential as a high capacity adsorbent. Surface modification, to enhance the ability of the material to extract potentially toxic metals (PTMs) from water was performed using different amino- and mercapto-functional groups. This paper reports on the extraction of lead ions from aqueous solution to demonstrate the material's significant improvement in adsorption capacity (up to 1000 μmol g⁻¹ for lead). Moreover, methods have been developed to regenerate the sorbent allowing 100% recovery of Pb and reuse of the sorbent material in subsequent extractions. The performance of the material was also demonstrated for environmental samples containing relatively high concentrations (ppmv) of mixed metal ions reducing them to lower values (<100 ppbv) indicating that the sorbent may have applicability for environmental remediation of polluted water.

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1. Introduction

MCM-41 can be synthesised following the original preparation method reported by Beck et al. [1] or by modification of this method to enhance the material's physicochemical properties [2–8]. In most published methods of MCM-41 production, the surfactant template is removed by calcination or solvent extraction to produce materials with a high surface area, large pore size and pore volume. Research on the adsorptive applications of mesoporous silica has been explored in various environmental applications using both unmodified and functionalised silica. In the last decade alone attention has been focused on the use of MCM-41 as a sorbent trap for volatile organic compounds (VOCs) from indoor air [9–11] by physical adsorption or chemisorption (after surface functionalisation). Modified mesoporous silicas have also shown promise as adsorbents for the removal of heavy metals from aqueous solutions [12–15]. The adsorption mechanism for the removal of potentially

toxic metals (PTMs) in an aqueous solution is either by electrostatic interaction or by chelation [16]. Although the cost for mesoporous adsorbents per unit is relatively high compared to other materials commonly used for this application, they prove to be useful high-capacity adsorbents when they can be economically regenerated whilst maintaining high adsorption capacities for the analyte of interest after multiple use [17–19]. Moreover if the production method for MCM-41 is improved (faster, more economical and larger batch production) it is anticipated that its use would expand in industrial and environmental applications.

Ritter et al. [20] recently reported a scale-up, room temperature procedure for the production of unmodified MCM-41, with template removal by calcination. Wan et al. [7] discussed a method that permits the production of mesoporous silica with higher amounts of surface silanol groups by introduction of a microwave digestion method for template removal. Gu et al. [8] also used microwave digestion to increase the pore size of SBA-15 (from 6 nm using a conventional method of template removal to approximately 23 nm); here it was hypothesised that the increased pore size was due to the joining of two or three pores together after pore wall teardown.

In this work these method modifications have been combined, for the first time, providing a new preparation method for MCM-41 that is faster, providing larger quantities of material per batch and is

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more economical than conventional approaches. It is also proposed that the material has a high surface area with a larger number of surface silanol groups, higher average pore size, and pore size distribution than commonly prepared lending it to be an ideal material for functionalisation and use as a scavenger of PTMs from water. In a proof of concept study the material was modified using different amino- and mercapto-functional groups and each modified material was used to extract Pb from water. The capacity of the material, effect of extraction pH, extraction temperature, regeneration of the sorbent and applicability for cleanup of environmental samples were assessed.

2. Experimental

2.1. Materials and reagent

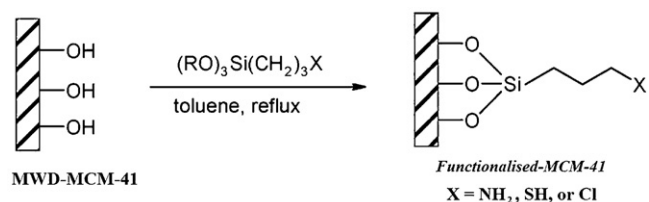
Cetyltrimethylammonium bromide (CTAB) 98%, was supplied by BDH. Aqueous ammonia (30% NH_3), tetraethoxysilane (TEOS) 98%, hydrogen peroxide solution (30 wt.%), 3-aminopropyltrimethoxysilane (APTMS) 99%, 3-mercaptopropyltrimethoxy-silane (MPTMS) 99%, 3-chloropropyltrimethoxysilane (CPTMS) +97%, ethanol absolute, diethylenetriamine (DETA) 99%, $1000 \mu\text{g mL}^{-1}$ of lead standard solution, mercaptobutanone (99%), and toluene (+99%) were purchased from Sigma–Aldrich. Nitric acid (65 wt.%) was provided by 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

The synthesis method used was adapted from Ritter et al. [20]. Approximately 8.8 g of CTAB was dissolved under slight warming (35°C) in a mixture of 208 mL of distilled H_2O and 96 mL of aqueous NH_3 . To this clear solution, 40 mL 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 600 mL of distilled H_2O , and dried in air at room temperature. To remove the surfactant microwave digestion (MWD) was performed by modifying the method reported by Gu et al. [8]. A MARS 5 microwave digestion system (CEM Corporation, Buckingham, UK) was used at an operating power of approximately 1600 W. The pressure and temperature inside the microwave were controlled to be lower than 1.3 MPa and 200°C , respectively. Samples (approx. 0.3 g) were added to multiple Teflon vessels to which 5 mL of HNO_3 and 2 mL of H_2O_2 were added. Microwave digestion was operated at a working frequency of 2450 MHz and 220 V for 15 min. The product (to be referred to as 'MWD-MCM-41') was filtered, washed with copious amounts of distilled H_2O and dried at 100°C for 2 h. For comparison a second batch of MCM-41 was produced where template removal was performed using a conventional calcination rig by heating in air at 550°C for 8 h. This material will be referred to as 'C-MCM-41'.

2.3. Characterisation and analysis

Powder X-ray diffraction (PXRD) profiles were recorded on a Philips X'Pert diffractometer, equipped with a Cu $\text{K}\alpha$ radiation source and accelerator detector. Incident and reflected Stöller slits of 0.2° were used with a programmable divergent slit (a constant 10 mm sample footprint). The surface area of the microwave digestion and calcined mesoporous silicas was measured using nitrogen physisorption isotherms on a Micromeritics Gemini 2375 volumetric analyzer. Each sample was degassed prior to analysis for 6 h at 200°C . The Brumauer–Emmett–Teller (BET) surface



Scheme 1. Modification of activated silica using trialkoxysilanes.

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 N_2 amount adsorbed at the P/P_0 of 0.99 for each sample and the average pore size distribution of the materials was calculated using the Barrett–Joyner–Halanda (BJH) model from a 30-point BET surface area plot. All the mesoporous silicas exhibited a type IV adsorption isotherm typical of mesoporous solids. Desorption isotherms were used to calculate the pore diameters. Infrared spectra of all samples were obtained in KBr pellets in the $4000\text{--}400 \text{ cm}^{-1}$ region with a resolution of 4 cm^{-1} , by accumulating 64 scans using an ATI Mattson FTIR spectrophotometer. Elemental analysis (EA) was carried out using an Exeter Analytical CE440 elemental function. Lead solutions were analysed using a PerkinElmer AAnalyst200 flame atomic absorption spectrometer at 283.3 nm. Calibrant solutions were reagent matched. Total concentrations of metals in water samples were determined by inductivity coupled plasma atomic emission spectrometry (ICP–AES) using a Perkin Elmer Optima 5300DV instrument (Perkin Elmer, UK) at an RF power of 1300 W and with plasma, auxiliary and nebuliser argon gas flows of 15, 0.2 and 0.75 L min^{-1} respectively, and a pump flow rate of 1.5 mL min^{-1} . Multi-element calibration standards in the concentration range $0.02\text{--}1 \text{ mg L}^{-1}$ were used and the emission intensity measured at appropriate wavelengths. For all elements, analytical precision (RSD) was typically 1–5% for individual aliquots ($n = 3$).

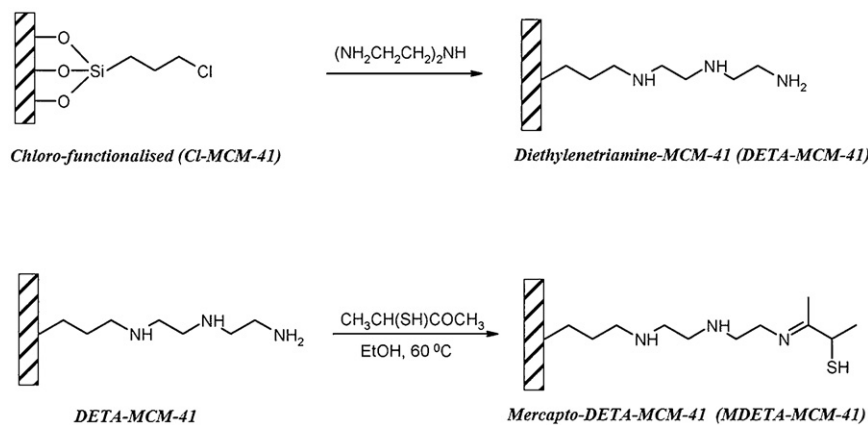
2.4. Functionalisation procedures

Chemical modification of activated MWD-MCM-41 started with a condensation reaction containing the organosilane of choice with MCM-41 (Scheme 1). Approximately 5 g of MWD-MCM-41 was pre-treated at 140°C for 2 h and then immersed into 50 mL of toluene and 10 mL of APTMS or MPTMS in a 250 mL flask. The mixture was refluxed for 4 h and the solid produced was filtered, washed with 100 mL of ethanol, and oven-dried at 80°C for 1 h to produce an amino-functionalised (N-MCM-41) or mercapto-functionalised (S-MCM-41) sorbent, respectively.

A similar procedure was followed to chloro-functionalised (Cl-MCM-41) using CPTMS. The chloro-product was then treated to produce DETA-MCM-41 or MDETA-MCM-41. For DETA functionality 10 mL was added to Cl-MCM-41 under reflux for 18 h. The solid produced was filtered, washed with 100 mL of ethanol and oven-dried at 80°C for 1 h. Finally, 3-mercaptoputanone (1.5 g) was dissolved in ethanol (50 mL) and added to a 3 g subsample of DETA-MCM-41. The reaction mixture was refluxed for 16 h at 60°C , cooled, filtered and washed with ethanol and dried at 80°C , producing 'MDETA-MCM-41'. Scheme 2 illustrates the functionalising processes thought to occur via reaction at surface hydroxyl sites.

2.5. Determination of adsorption capacity

The adsorption process used to test the material as a scavenger of PTMs from solution was adapted from Burke et al. [21].



Scheme 2. Schematic representation of DETA- and MDETA-MCM-41.

As a case study the metal ion of interest was chosen to be Pb. Approximately 10 mg of functionalised MCM-41 was suspended in 20 mL of solution containing $20 \mu\text{g mL}^{-1}$ lead ions 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 Pb by flame atomic absorption spectrometry (FAAS). This process was repeated until saturation of the sorbent as indicated by a measurement of Pb in the solution aliquot. The extraction was examined at various pH values (between 3 and 10) with solution modification achieved via the addition of small amounts of 1 M ammonium hydroxide.

The amount of lead ions adsorbed by each material was calculated and the adsorption capacity determined using Eq. (1) (according to Anbia et al. [22]).

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

where q_e is the adsorption capacity ($\mu\text{mol g}^{-1}$) of the adsorbent at equilibrium; C_0 and C_e are the initial and equilibrium concentrations of solute ($\mu\text{g mL}^{-1}$), respectively; V is the volume of the aqueous solution (mL) and W is the mass (g) of adsorbent used in the experiments. To check the results of the adsorption capacity, the procedure was repeated with a larger concentration of Pb, $200 \mu\text{g mL}^{-1}$, added to the sorbent to ensure the capacity of the sorbent was reached more quickly.

2.6. The efficiencies of sorbents in multi element and real water samples

To demonstrate the potential environmental performance of the sorbents when exposed to solutions containing mixed metal ions, 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) were analysed. Prior to addition of sorbents, both samples were analysed to determine the concentration of Pb^{2+} in solution. As the case study focuses on the extraction of lead ions from water, both solutions were spiked with lead ions to produce solution concentrations of $25 \mu\text{g mL}^{-1}$. Multi element experiments were carried out using standard solutions containing selected metals (Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, and Zn) diluted to a $1 \mu\text{g mL}^{-1}$ concentration using non-buffered H_2O as a solvent. In each experiment 0.025 g of functionalised MCM-41 was added to solutions which were stirred for 2 h. 5 mL aliquots were removed and filtered (Fisherbrand QL100) prior to analysis by ICP-AES, then the material was washed with 1 M HCl to examine the possibility to recover metals ions from the sorbent after extraction.

2.7. Regeneration of adsorbent

Regeneration of the functionalised MCM-41 material after adsorption of lead ions from water was examined. A 20 mL solution containing $20 \mu\text{g mL}^{-1}$ Pb was added to a conical flask containing 100 mg of functionalised MCM-41. After stirring for 2 h at room temperature, the suspension was separated by filtration. The filtrate was measured with FAAS to determine whether the Pb had been removed from water and trapped by the sorbent. The filter paper containing the recovered sorbent was then immersed into 20 mL of a 1 mol L^{-1} solution of HCl for 2 h at room temperature. The solution was filtered and the Pb concentration of the acid filtrate was measured by FAAS. The sorbent was then dried at 80°C for 2 h and the extraction repeated to examine the capacity of the regenerated sorbent.

3. Results and discussion

The room temperature method of preparation was used to produce as-made MCM-41 material that was subsequently treated to high temperature (C-MCM-41) or microwave digestion (MWD-MCM-41) to remove the organic template. As the silica hydrolysis does not require the use of Teflon bombs at high temperature the material could be produced on the bench, in large quantity, providing approximately 100 g of material each batch.

3.1. MCM-41 characterisation by XRD and N_2 adsorption isotherm

XRD patterns of MWD-MCM-41 and C-MCM-41 samples, shown in Fig. 1, indicated that the adsorbent materials possessed a hexagonal mesophase structure with a clear (100) peak and weaker reflections assignable to (110) and (200) reflections. The physico-chemical properties of the materials are summarized in Table 1 and indicate that the surface area of MCM-41 reduced slightly when the template was removed by MWD compared to calcination. Perhaps the increased surface area of C-MCM-41 demonstrates that smaller, well-defined, pores are obtained by this method of surfactant removal. However the average pore size of the material increased significantly from 2.53 to 6.74 nm. This larger pore size is not common for mesoporous silica materials as MCM-41 typically demonstrates a pore size of approximately 2.5–4.5 nm. The N_2 sorption isotherms (Fig. 2) were type IV confirming their mesoporous nature, however different capillary condensation steps were noted at relative pressures of 0.31–0.38 and 0.55–0.69 for the calcined and microwave-treated products, respectively, suggesting that the microwave induced larger pores in the material. The hysteresis loop

Table 1
Physicochemical properties of microwave digested and calcined MCM-41.

Sample name	BET surface area ($\text{m}^2 \text{g}^{-1}$) ^a	Pore size (nm) ^b	Pore volume ($\text{cm}^3 \text{g}^{-1}$) ^c	d-Space (\AA) ^d
MWD-MCM-41	760	6.74	0.99	42.20
C-MCM-41	813	2.53	0.69	38.48

^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 Calculated from PXRD data.

was also broader for MWD-MCM-41 suggesting that this material contained pores of different shapes to that of C-MCM-41. This was confirmed by examination of the pore distribution plots (Fig. 3). These results for MCM-41 support a hypothesis, first discussed by Gu et al. [8], who proposed that pores of SBA-15 could join together during an applied microwave digestion procedure (Scheme 3). It was thought that the inclusion of larger mesopores (or even mesotunnels) in an adsorbent material would be highly desirable if it were to be surface functionalised and used to provide a higher number of chelating groups that could extract PTMs from a contaminated matrix.

3.2. FTIR and elemental analysis of MCM-41 samples.

The FTIR spectra of all samples (Fig. 4) 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 also to some adsorbed water, (ii) several absorption bands 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} [23,24]. In addition to those peaks the spectrum of the as-made 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 band at 1490 cm^{-1} was assigned to a C–N stretching mode. These bands (due to the surfactant template in the as-made sample) were absent in both spectra for C-MCM-41 or MWD-MCM-41 confirming that both methods successfully removed the organic template. This spectroscopic result was confirmed by microanalysis (see Table 2). Moreover, if the Si–OH bands at around 970 cm^{-1} were examined in detail it was noted that the intensity of the MWD-MCM-41 band was comparable to that of the as-made MCM-41 band; whereas the peak was considerably smaller in the C-MCM-41 spectrum. This data indicated that the sample treated with nitric acid, peroxide and microwave digestion produced a material that had a larger number silanol groups. Should this be the case then it is suggested that a higher degree of functionalisation would be possible for samples of MWD-MCM-41 compared to C-MCM-41. Elemental analysis was used to estimate the amount of molecules (L_0) attached to functionalised samples (amino-, mercapto-, DETA or MDETA-MWD-MCM41) from the percentage of nitrogen, or sul-

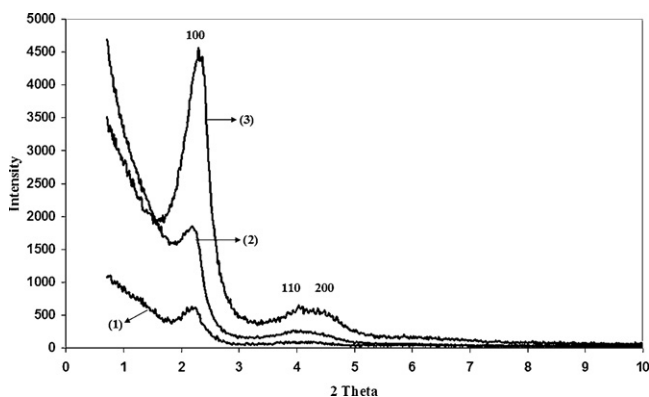


Fig. 1. XRD patterns of the (1) as-made MCM-41, (2) MWD-MCM-41 and (3) C-MCM-41.

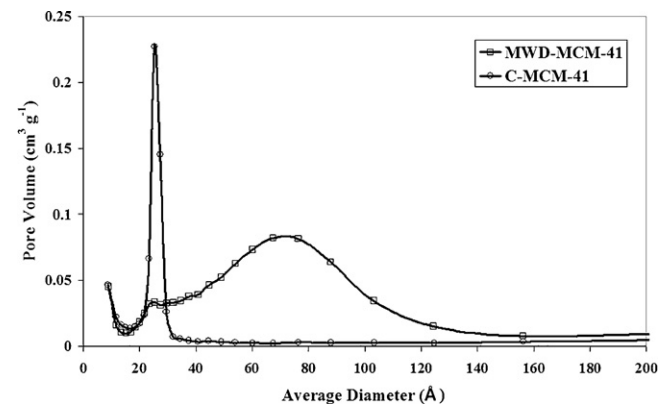


Fig. 3. BET pore size distribution patterns of the MWD-MCM-41 and C-MCM-41.

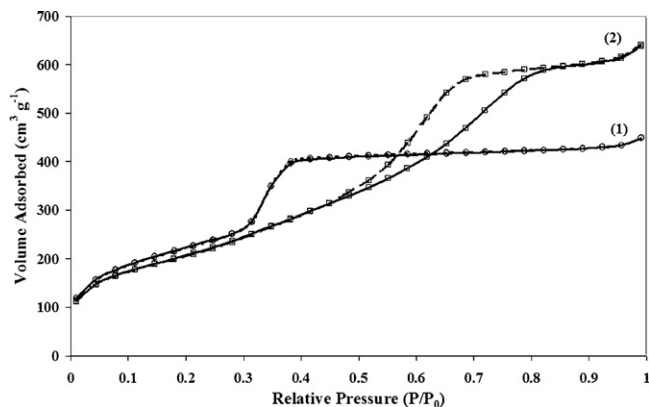
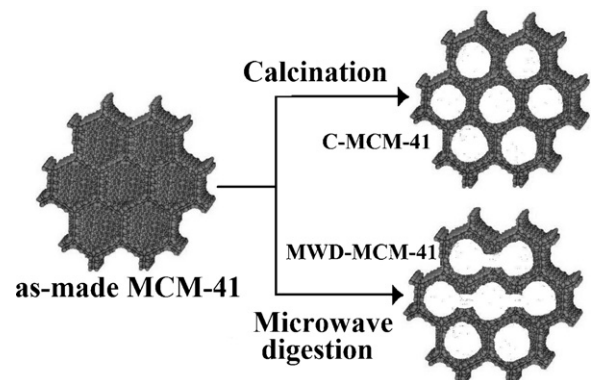


Fig. 2. Nitrogen adsorption isotherms and mesoporous silica after the template removal by calcination (1) and by MWD (2).



Scheme 3. Schematic representation of the procedure for template removal by calcination and microwave digestion.

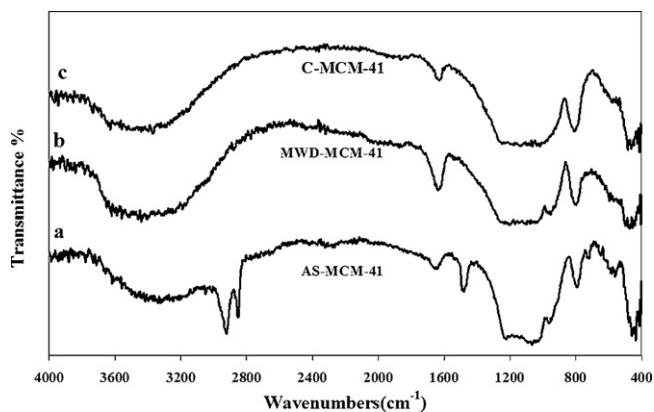


Fig. 4. FT-IR spectra of (a) MCM-41 (as-made), (b) MWD-MCM-41, and (c) C-MCM-41.

fur, in the functionalised mesoporous silica [14], using equation as an example for nitrogen (2):

$$L_0 = \frac{\%N}{\text{nitrogen atomic weight}} \times 10 \quad (2)$$

The calculated L_0 values (Table 2) were above those typically reported in the literature [13,17,22] with the DETA sample giving the highest L_0 value published to date. This set of results, supported by the FTIR data, confirmed that the new combined method of analysis for MCM-41, not reported before, can potentially produce large quantities of an optimised material for adsorptive or catalytic applications (mesoporous channels, larger pores, more silanol groups available for functionalisation) using a simple procedure in the laboratory.

3.3. Case study: lead adsorption extraction capacities of functionalised MCM-41

Samples of MCM-41 and functionalised MCM-41 (N-MCM-41, S-MCM-41, DETA-MCM-41 or MDETA-MCM-41) were each added to aqueous solutions containing known amounts of Pb^{2+} ions. Solution pH was altered (to 3, 5, 7, 9 or 11), to test the materials' extraction efficiencies over a wide pH range; conditions used are outlined in Section 2.5. The results, summarised in Fig. 5, illustrate that all functional groups were successful in removing Pb from solution. To ensure that the functionality of the material was responsible for extraction, control experiments were run using 0.02 g of non-functionalised MCM-41. The material was added to aqueous solutions containing 20 ppm of lead ions at different pH values. The solutions were stirred for 2 h and the resulting solutions were analysed for lead. In every case the measured concentration of the extracted aliquot was 20 ppm indicating that no lead had been physically adsorbed by MCM-41 without functionalisation. Lower capacities were observed for the mono-functional groups (N-MCM-41 and S-MCM-41) compared to DETA- and MDETA-MCM-41 where multi co-ordination sites led to a significant improvement in

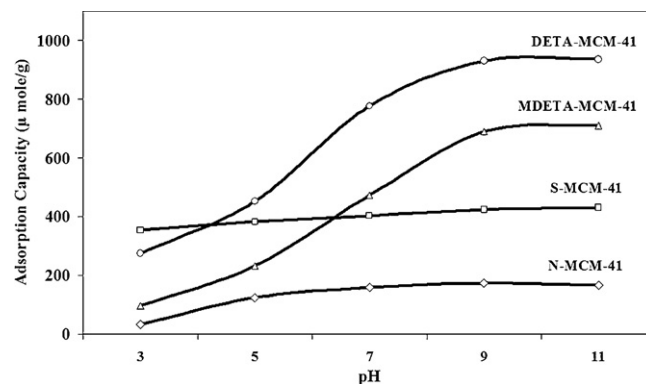


Fig. 5. Adsorption capacities of functionalised MCM-41 for lead extraction over different pH values.

extraction performance; presumably because lead prefers a trigonal chelation geometry. A strong dependence on pH was observed for co-ordination with DETA and MDETA ligands with highest capacities achieved when the solution pH was adjusted to values of 9 and above. Although adsorption capacity values for three of the materials were only comparable to what had been previously cited in the literature (Table 3), the DETA ligand in particular illustrated a tremendous improvement in adsorption capacity ($960 \mu\text{mol g}^{-1}$), at double the previously reported maximum value. This improvement in performance is in-line with expectations due to the unique character of the products produced by the microwave digestion method (larger pores to incorporate longer non-linear ligand conformation and higher degree of functionality).

3.4. Reutilisation of DETA-MCM-41 for repeated sorbent use and further removal of Pb ions.

Three samples of DETA-MCM-41 containing 200 μg of Pb were regenerated by washing the solid in 10 mL of 1M HCl. The acid washings were analysed by FAAS using matrix matched calibration solutions and it was shown that the Pb was successfully removed from the ligand (average measured concentrations were $19.7 \pm 0.5 \mu\text{g mL}^{-1}$, indicating 99% recovery of Pb). The solid sorbents were filtered and washed with distilled water before exposure to a second 10 mL solution containing 20 $\mu\text{g mL}^{-1}$ Pb. All Pb ions were removed from solution. The sorbents were acid washed for a second time and Pb was again successfully recovered from the sorbents with a 97% recovery value. The sorbents were then exposed to a third solution of Pb ions at the same concentration of Pb and again extraction was 100%. These experiments demonstrate that there will be no significant loss in performance of the sorbent when washed with HCl to recover extracted Pb. Indeed regeneration of the material is achieved at the same time allowing the materials to be easily reused. The acid treatment does not appear to remove the ligand from the silica which can go on to be used in subsequent mitigation treatments, making the material competitive with other adsorbents that are cheaper to produce but

Table 2
Elemental analysis data recorded for the MCM-41.

Silica	% C	% H	% N	% S	L_0 (mmol/g) ^a
As-made MCM-41	22.48	5.14	1.26	0.00	–
C-MCM-41	Trace/nil	0.50	Trace/nil	0.00	–
MWD-MCM-41	Trace/nil	0.52	Trace/nil	0.00	–
N-MCM-41	8.20	2.32	2.79	0.00	1.99
S-MCM-41	11.43	2.17	0.00	9.46	2.96
DETA-MCM-41	17.13	4.15	10.08	0.00	7.2
MDETA-MCM-41	12.10	2.39	3.61	2.62	2.57

^a Functionalisation degree (L_0 = millimoles of ligand per gram of functionalized silica).

Table 3
Comparison of alternative sorbents used to extract lead ions from solution.




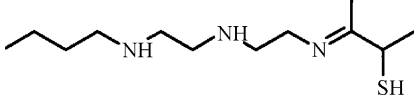
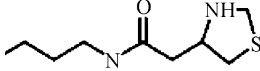
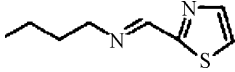
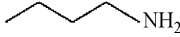


Sorbent	Immobilized ligand	Adsorption capacity ($\mu\text{mol/g}$)	Reference
N-MCM-41		174	This work
S-MCM-41		425	This work
DETA-MCM-41		931	This work
MDETA-MCM-41		690	This work
Silica (Kieselgel 100)		80	[24]
Silica (Kieselgel 100)		49	[24]
MCM-41	$-\text{H}_2\text{C}-(\text{CH}_2)_{11}-\text{N}(\text{CH}_3)_2$	410	[25]
MCM-41	$-\text{H}_2\text{C}-(\text{CH}_2)_{11}-\text{NH}_2$	250	[25]
SBA-15		342	[26]
MCM-41		408	[26]
MCM-41		493	[27]

Table 4
The performance of DETA-MCM-41 in real samples.

Sample	Spiked ($\mu\text{g mL}^{-1}$)	Extraction (%) ^a	Recovered ($\mu\text{g mL}^{-1}$)	Recovery (%) ^a
Distilled water	25	100 \pm 2	24.83	99.3 \pm 2
Tap water	25	100 \pm 1	25.31	101.2 \pm 1
River water	25	98 \pm 3	22.57	90.3 \pm 3

^a Reported values are based on an average result of three experiments.

Table 5
The efficiency of DETA-MCM-41 to extract Pb in multi elements sample.

Heavy metals	Initial concentration ($\mu\text{g mL}^{-1}$)	Conc. of metal found ($\mu\text{g mL}^{-1}$) after sorbent addition	Conc. of metal recovered ($\mu\text{g mL}^{-1}$) after acid treatment	% of metal extracted	% of metal recovered
Cd	1.000	0.003	0.791	99.7	79.3
Co	1.000	0.159	0.498	84.1	59.2
Cr	1.000	0.009	0.833	99.1	84.1
Cu	1.000	0.119	0.875	88.1	99.3
Fe	1.000	0.021	1.085	97.9	110.8
Hg	1.000	0.200	0.052	80.0	6.5
Mn	1.000	0.005	0.865	99.5	86.9
Ni	1.000	0.072	0.899	92.8	96.9
Pb	1.000	0.005	0.752	99.5	75.6

that cannot be regenerated. Further work is required to determine the number of times the sorbents can be reused before extraction efficiency is altered.

3.5. Assessment of DETA-MCM-41 extraction efficiencies in real water samples

To examine the performance of DETA-MCM-41 to extract Pb in the presence of other cations the sorbent was added to 20 mL samples of tap water and river water each spiked with Pb to a solution concentration of $25 \mu\text{g mL}^{-1}$. The results given in Table 4 indicate that the Pb was removed equally well from real samples as both extractions were within 100% for tap water and 98% for river water. The sorbents were acid washed and Pb recovery values of

101 and 90% were obtained for the sorbents applied to distilled, tap and river water, respectively. In spite of the high concentrations of Ca and Mg ions measured in the river water sample, at $43.6 \mu\text{g mL}^{-1}$ and $6 \mu\text{g mL}^{-1}$, respectively, the Pb adsorption and recovery values were only slightly less than those obtained for the spiked tap water sample, which implies that the Pb-DETA co-ordination was not appreciably hindered by presence of other co-ordinating ions at reasonably high concentration.

The ability of DETA-MCM-41 to extract Pb in the presence of other PTMs and metal ions was also assessed by adding the sorbent to a multi-element solution containing $1 \mu\text{g mL}^{-1}$ each of Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, and Zn. The extraction and recovery values for all ions in the standard solution were calculated (see Table 5). As expected each metal ion has a different response to the

DETA ligand however in general the metal ion concentrations were reduced to $<200 \text{ ng mL}^{-1}$. This ligand appears to be more suited to the extraction of Pb, Mn, Fe, Cr and Cd; less so for Hg, Co, Cu and Ni. However it should be pointed out that the main aim was to produce and optimised ligand for Pb extraction and the ability to completely remove other ions from solution at 100% is a distinct unexpected advantage. Although these tests are by no means exhaustive they do highlight the merits of DETA-MCM-41 as a scavenger of Pb from aqueous solution, giving higher extraction efficiencies than previously found.

4. Conclusions

A new method of MCM-41 production using room temperature hydrolysis and condensation conditions together with microwave and nitric acid/hydrogen peroxide digestion of the organic template has resulted in the production of a mesoporous silica with higher silanol group availability and a larger pore distribution. These suspected characteristics, (supported by BET, microanalysis and FTIR spectroscopic results), favour functionalisation; particularly allowing larger multi-site chelate groups to co-ordinate around the metal ion of interest. Although further work is required to test the DETA-MCM-41 sorbent in the field this preliminary study on the characterisation and extraction efficiency of functionalised MCM-41 suggests that the material has tremendous potential to extract Pb from aqueous solutions in industrial and environmental clean-up applications. The ion–ligand co-ordination is strong enough that the sorbent can work in static solutions where the ion is driven to the ligand by a concentration gradient alone and can work in contaminated river water samples. This will be of particular significance if the material is to be used in a remote location where stirring or agitation of the contaminated solution is not possible.

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