Large pore bi-functionalised mesoporous silica for metal ion pollution treatment

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ABSTRACT

Here we demonstrate aminopropyl and mercatopropyl functionalised and bi-functionalised large pore mesoporous silica spheres to extract various metal ions from aqueous solutions towards providing active sorbents for mitigation of metal ion pollution. Elemental analysis (EA) and FTIR techniques were used to quantify the attachment of the aminopropyl and mercatopropyl functional groups to the mesoporous silica pore wall. Functionalisation was achieved by post-synthesis reflux procedures. For all functionalised silicas the functionalisation refluxing does not alter particle morphology/agglomeration of the particles. It was found that sorptive capacities of the mesoporous silica towards the functional groups were unaffected by co-functionalisation. Powder X-ray diffraction (PXRD) and nitrogen adsorption techniques were used to establish the pore diameters, packing of the pores and specific surface areas of the modified mesoporous silica spheres. Atomic absorption (AA) spectroscopy and inductively coupled plasma-atomic emission spectrometry (ICP-AES) techniques were used to measure the extraction efficiencies of each metal ion species from solution at varying pHs. Maximum sorptive capacities (as metal ions) were determined to be $384 \,\mu mol\,g^{-1}$ for Cr, $340 \,\mu mol\,g^{-1}$ for Ni, $358 \,\mu mol\,g^{-1}$ for Fe, $364 \,\mu mol\,g^{-1}$ for Mn and $188 \,\mu mol\,g^{-1}$ for Pd.

1. Introduction

Metal ions are the most significant environmental pollutants found in wastewater and long-term exposure to solvated metals ions and their effects on human health and natural ecosystems is a concern [1,2]. The metals of primary interest include chromium, nickel, manganese, iron and various heavy metals because of a combination of toxicity and exposure levels [1,3]. E.g. in 2004 the Irish Environmental Protection Agency released the following drinking water maximum contamination guidelines: chromium: $50 \,\mu g\,l^{-1}$, nickel: $20 \,\mu g\,l^{-1}$, manganese: $50 \,\mu g\,l^{-1}$ and iron: $200 \,\mu g\,l^{-1}$. Industrial wastewaters, especially mining and metallurgical wastewaters [4], are the major sources of heavy metal ion contamination and commensurate guidelines for metal concentration in industrial wastewaters are chromium: $0.5 \,mg\,l^{-1}$ and nickel: $0.5 \,mg\,l^{-1}$ [5]. Environmental pressures have resulted in a major focus on waste treatment and cleanup research to produce economic and effective methods for the removal of these metal ions.

Methods for metal ion removal include precipitation, coagulation/flocculation, ion exchange, reverse osmosis, complexation/sequestration, electrochemical operation and biological treatment. Some limitations of these are, e.g., high operating and energy costs. Sorbents such as activated charcoal, zeolites and clays have also been used as wastewater treatment systems [6,7]. However, disadvantages of these materials include relatively low and variable loading capacities and small metal ion-binding constants.

Ordered mesoporous materials (OMMs) are becoming established sorptives that may be exploited owing to their large surface areas (typically $200–1000 \,cm^2\,g^{-1}$) and large pore volumes. Functionalising OMMs with different chelating agents (or metal ion-specific ligands) allows specific metal ion pollutants to be selectively removed from aqueous or organic systems with correspondingly large uptakes. We refer to this uptake process as sorption in this text. Although the uptake is strictly an adsorp-

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tion process it sometimes described as absorption because the metal ions are taken into the bulk of the solid particle at interior surfaces. The choice of functionalisation agent can derive from the Irving-Williams stability series that associates particular ligands with particular metal ions to form the most stable complexes [8,9]. Accordingly, aminopropyl ligands (−NH) are identified as being attracted to 'hard' metal ions such as Ni, Cr, Mn and Fe while mercatopropyl ligands (−SH) are attracted to 'soft' metal ions such as Pd and Hg [10]. Most environmental samples will contain a mixture of metal ions, therefore, bi-functionalised (both aminopropyl and mercatopropyl) mesoporous silica would allow effective removal of a diverse range of both hard and soft metallic ions.

Many procedures for mono-functionalising mesoporous silica for metal ion extraction have been reported using a diverse assortment of ligands. For example, Fryxell et al. [11] and Mercier and Pinnavaia [12] have reported the functionalisation of mesoporous silica with mercatopropyl ligands for the extraction of mercury from aqueous solution. Functionalised mesoporous silicas for removal of various metal ions have been reported [13,14]. Here, we report a facile two-step synthesis method for bi-functionalising mesoporous silica spheres with both hard and soft ligand types. Although synthesis of mesoporous spheres offers a considerable challenge compared to routes to less well-defined particle shapes, they have considerable practical advantages in terms of sorbent packing and fluid flow through a packed bed that allow more rapid uptakes. Synthetic routes are now established [17–20].

2. Experimental

2.1. Materials and reagent

Copolymers F127 ($EO_{106}PO_{70}EO_{106}$) and P123 ($EO_{20}PO_{70}EO_{20}$) were purchased from BASF. Tetraethyl orthosilicate (TEOS, 98%) was purchased from Fluka, N-3-trimethoxy-silylpropyldiethylenetriamine (TMSPA, $C_{10}H_{27}N_3O_3Si$), 3-mercaptopropyl-trimethoxysilane (MPTMS, $C_6H_{16}O_3SSi$), nickel, chromium, palladium, iron, and manganese salts, atomic absorption (AA) standard solution (1000 ppm) and atomic absorption pH buffers at pH of 4, 7 and 10 were all purchased from Sigma–Aldrich. ICP certified quality assurance metal standard containing a mix of the selected metals analysed was purchased from SPEX Certiprep Group, UK.

2.2. Synthesis of mesoporous silica spheres

Mesoporous silica spheres were synthesised using poly-(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) tri-block copolymers as supramolecular templates based on the method of Kim et al. [15]. A mixture of copolymers F127 ($EO_{106}PO_{70}EO_{106}$) and P123 ($EO_{20}PO_{70}EO_{20}$) were dissolved in an aqueous solution of HCl (1.6 M). TEOS was then added to 280 ml, 1.6 M HCl solution and stirred at 35 °C. The mixture was stirred for 15 min and maintained under static conditions at 35 °C for 24 h and finally heated to 110 °C for 5 days. The starting molar composition of the mixture was 0.0037 F127:0.0032 P123:1 TEOS:4.2 HCl:144. The white precipitate was filtered without washing and dried at 60 °C. Subsequently, the product was calcined at 550 °C for 5 h to ensure complete template removal. It is important to note that the calcination temperature is somewhat higher than that used by Kim et al. [15] and we believe this has an important effect on mesopore structure because of instability of the cubic structure reported by these authors.
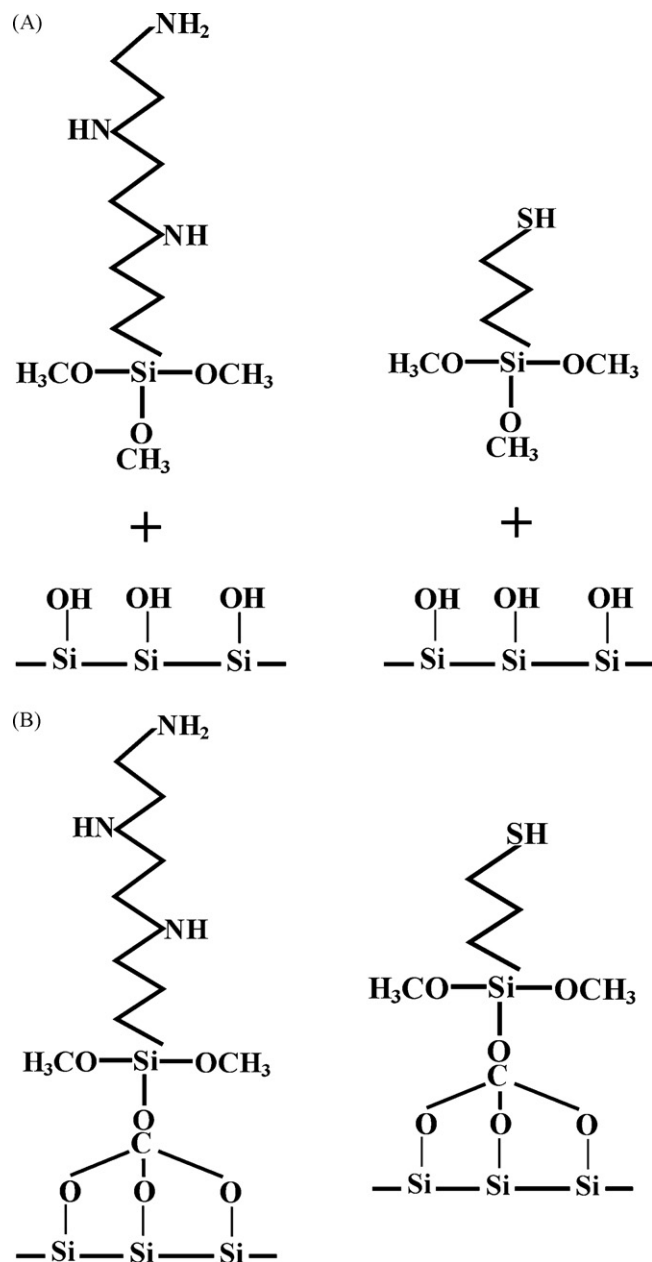

Fig. 1. Schematic representation of molecular species (A) and the functionalisation of a mesoporous silica surface (B) with aminopropyl groups (left) and mercatopropyl groups (right). Diagrams are indicative only and exact determination of bonding modes and sites is not implied.

2.3. Functionalisation procedure

Calcined mesoporous silica solid was modified with either amine or thiol groups. A sample of 5 g of the mesoporous silica material was dehydrated at 120 °C in a vacuum, and then stirred in 100 ml of dried toluene containing 5 ml of either TMSPA or MPTMS (illustrated in Fig. 1) under refluxing conditions for 6 h. Samples were then vacuum washed with dry toluene. Fig. 1 shows a schematic representation of the functionalising process which is thought to occur via reaction at surface hydroxyl sites. Bi-functionalisation followed the same procedure with the recovered sample following TMSAP treatment being refluxed in the MPTMS solution and recovery/thermal processing following the normal methodology.

2.4. Single metal ion extraction procedure

Standard metal ion (Ni, Cr, Pd, Fe and Mn) solutions of 10 ppm were buffered at pHs of 4, 7 and 10 and non-buffered to identify optimum extraction conditions. Approximately 0.05 g of TMSPA functionalised mesoporous silica or MPTMS functionalised mesoporous silica was added to 100 ml of each 10 ppm metal ion solution and stirred (250 rpm) for approximately 2 h and repeated until saturation. The solution was then filtered and the filtrates were collected and tested for the particular metal using atomic absorption. The silica samples after extraction were analysed using Brunauer–Emmett–Teller (BET) and scanning electron microscope (SEM) to identify any changes in the surface area, pore size and morphology of the parent silica.

2.5. Mixed metal ion extraction procedure

For demonstration of environmental performance samples of mixed metal content were investigated by methodology more akin to industrial extraction procedures. Here, a column filtration device (glass column, 20 mm diameter and 25 mm length) was used to mimic an industrial flow through set-up. Certified solutions containing selected metals (Zn, Pb, Cd, Ni, Fe, Cr, Mg, V, Mn, Ca and Cu) were diluted to a 1-ppm solution using non-buffered H_2O as a solvent. A glass column containing a known amount of either the mono-functionalised or bi-functionalised mesoporous silica was used to filter approximately 100 ml of the 1 ppm mixed metal solution. The samples post-filtration were then tested by inductively coupled plasma-atomic emission spectrometry (ICP-AES) to identify a reduction in the metal content.

2.6. Characterization

Powder X-ray diffraction (PXRD) profiles were recorded on a Philips X'Pert diffractometer, equipped with a Cu Kα 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 calcined mesoporous silicas were measured using nitrogen physisorption isotherms on a Micromeritics Gemini 2375 volumetric analyzer. Each sample was degassed prior to analysis for 12 h at 200 °C. 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. In all cases, very little hysteresis was observed in adsorption and desorption isotherms suggesting uniform pore shapes. Desorption isotherms were used to calculate the pore diameters. The elemental composition, surface morphology and sphere size of the mesoporous silica samples were determined with a SEM (JEOL, JSM 5510, field emission SEM equipped with Oxford EDX detector). Elemental analysis (EA) was carried out using an Exeter Analytical CE440 elemental function. Atomic absorption spectroscopy PerkinElmer 240 was used to record the reduction of metal ions in the solutions post-extraction. Each metal ion was recorded at appropriate wavelengths for optimum sensitivity. Mixed metal ion solutions were analysed by ICP-AES using a PerkinElmer Optima 2000DV optical emission spectrometer.

3. Results and discussion

XRD patterns of the calcined, aminopropyl (Si—NH) and mercatopropyl (Si—SH) modified and bi-functionalised (Si—NH—SH) SiO_2 samples are shown in Fig. 2 and summarized in Table 1. The use of differing conditions and higher calcination temperatures to
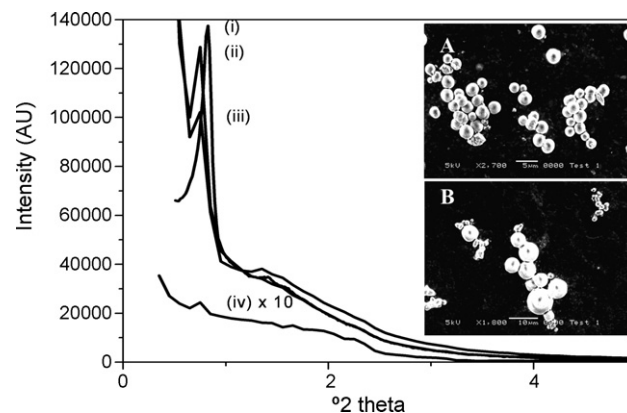

Fig. 2. XRD patterns of the (i) parent mesoporous SiO_2, (ii) Si—NH, (iii) Si—SH and (iv) Si —NH—SH (10×). Insets illustrate spherical morphology of the mesoporous silica identified before (upper) and after functionalisation (lower).

those reported in Kim et al. [15] result in generally less well ordered mesopore structures than seen by these authors. We used higher temperatures to provide more robust materials for use in harsh environments and to allow complete surfactant removal to obtain a maximum coverage of amine and thiol functionalisation agents. The XRD patterns we obtain more closely correspond to hexagonal mesophase structure with a clear (1 0 0) feature and weaker peaks assignable to (1 1 0) and (2 0 0) reflection peaks. The (1 0 0) peak occurs at 0.83 2θ, 0.75 2θ, 0.77 2θ and 0.74 2θ for the SiO_2, Si—NH, Si—SH and Si—NH—SH, respectively. After functionalisation, the intensity of the (1 0 0) reflection decreases dramatically for all the samples consistent with reduced scattering contrast between the silica wall and the pore network as well as a reduction of pore volume by the relatively large functionalisation species. The (1 0 0) reflection is very weak for the bi-functionalised silica suggesting greatest filling for this material.

Quantification of changes in XRD patterns from sample-to-sample is difficult because of sensitivity to sample position and thickness, etc. More quantifiable data is obtained from BET and Fig. 3 illustrates typical Type IV N_2-adsorption isotherms obtained from these samples. All samples have distinct hysteresis loops and steep adsorption/desorption steps indicating a well-ordered array of pores consistent with the XRD profiles. All samples display parallel and nearly vertical isotherm branches typical of hexagonal mesoporous silica (see Ref. [18], e.g.). Again, these profiles are not typical of SBA-16 type cubic structures shown, e.g. by Kim et al. [15]. The type IV isotherm shape is preserved for all samples suggesting the pore structure has been maintained post-functionalisation. All functionalised samples show a reduction in effective pore diameter indicating regular coating of the pore wall. Previous reports for bi-functionalised silica also identified a Type IV isotherm but in contrast to this work these authors observed reduced distinction of the adsorption step suggesting some loss of regularity of the structure [18].

The mean pore size, pore volume and surface area calculated from the BJH model are described in Table 1 and data are plotted in Fig. 3(b). It can be quantitatively seen that the functionalisation has a dramatic effect of the pore diameter and volume. In the case of the amine treated silica the pore diameter shifts from 76.0 Å to 52.5 Å and the pore volume changes from 0.629 $cm^3\,g^{-1}$ to 0.130 $cm^3\,g^{-1}$. Amine functionalisation reduces the pore diameter and pore volume by significantly more than the thiol treatment. This is consistent with the significantly greater length of the hydrocarbon chain of the amine species. The combined functionalised system has the lowest effective pore diameter, pore volume and surface area.

Table 1
Physiochemical data recorded for the SiO$_2$, Si—NH, Si—SH and Si—NH—SH samples (values based on three batch products)

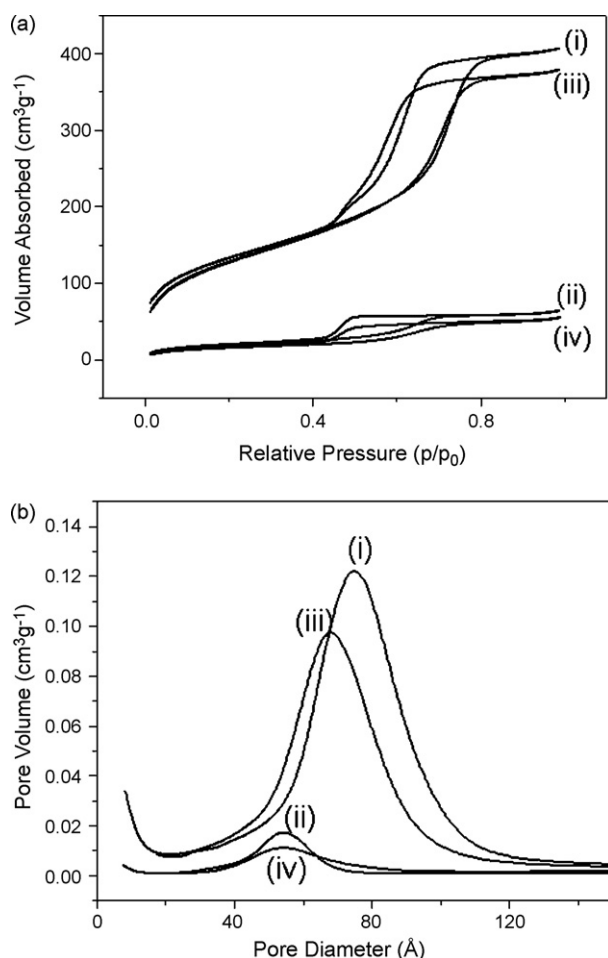|	Pore size (Å)	d-Spacing[a] (Å)	Pore volume (cm^3 g^{-1})	Surface area (m^2 g^{-1})	P/P_0
SiO$_2$	76.0 ± 13	68	0.629	706	0.451
Si—NH	52.5 ± 8	55	0.130	119	0.411
Si—SH	67.0 ± 13	58	0.586	703	0.414
Si—NH—SH	50.0 ± 13	48	0.085	85	0.405

[a] As calculated from XRD analysis.

Fig. 3. (a) BET isotherm patterns of the (i) SiO$_2$, (ii) Si—NH (iii) Si—SH and (iv) Si—NH—SH samples (b) BET pore size distribution patterns of the (i) SiO$_2$, (ii) Si—NH, (iii) Si—SH and (iv) Si—NH—SH samples.

Elemental analyses of the silica samples after functionalising were used to further quantify the bonding and uptake of amine (—NH) and thiol (—SH) moieties grafted to the silica following functionalisation. Table 2 compares the %C, %H, %N and %S (by weight) values measured for the original parent mesoporous sample with the aminopropyl and mercatopropyl functionalised samples. For the thiol functionalised samples the C:H:S ratio was determined

Table 2
Elemental analysis data recorded for the SiO$_2$, Si—NH, Si—SH and Si—NH—SH (values based on three batch products)

	% Carbon	% Hydrogen	% Nitrogen	% Sulphur
SiO$_2$	0.35	0.11	0	0
Si—NH	11.31	1.98	3.7	0
Si—SH	3.44	0.67	0	2.71
Si—NH—SH	14.38	2.55	3.86	2.74

as 3:7.8:0.98 close to that expected by loss of the three terminal methoxy groups and bonding to the surface as shown in Fig. 1. The C:H:N ratio determined for the amine functionalised material is 10.3:22.5:3 consistent with bonding to the surface through the methoxy group, also described in Fig. 1. Importantly, the co-functionalisation does not alter the elemental compositions (within experimental error) suggesting that the additions are purely additive. This is consistent with the decreases in pore volume and surface area determined above.

The bonding of the functional groups to the surface is through reaction with surface silanol groups. Fig. 4 shows the IR spectra for each of the samples. For the silica sample a sharp absorption band is identified at 3745 cm^{-1} due to free SiOH groups while the broad absorption band at 3410 cm^{-1} is assigned to hydrogen bonded SiOH groups [14]. Both these bands are strongly attenuated by functionalisation. For the amine functionalised materials isolated silanol groups are not observed but a broad band is distinguished at 3250 cm^{-1} which we assign to hydrogen bonded species associated with the remaining methoxy groups. New features can also be seen at 2700–2900 cm^{-1}, 1625 cm^{-1} and 1460 cm^{-1} which can be assigned to C=O and C—OH stretches of the methoxy group [19]. There is another just resolvable feature around 1300 cm^{-1} which can be assigned to C—H bending of the methoxy groups. The thiol functionalised materials show almost complete loss of the silica silanol groups at 3740 cm^{-1} and attenuation of the hydrogen bonded SiOH groups (3440 cm^{-1}). The feature observed at 3627 cm^{-1} can be attributed to a weak ν (S—H) vibration [19].

4. Metal ion sorption results

4.1. Single metal ion extraction results

Each sorbent (Si—NH, Si—SH and Si—NH—SH) synthesised was tested for sorption performance to Cr^{6+}, Ni^{2+}, Pd^{2+}, Fe^{2+} and Mn^{2+}
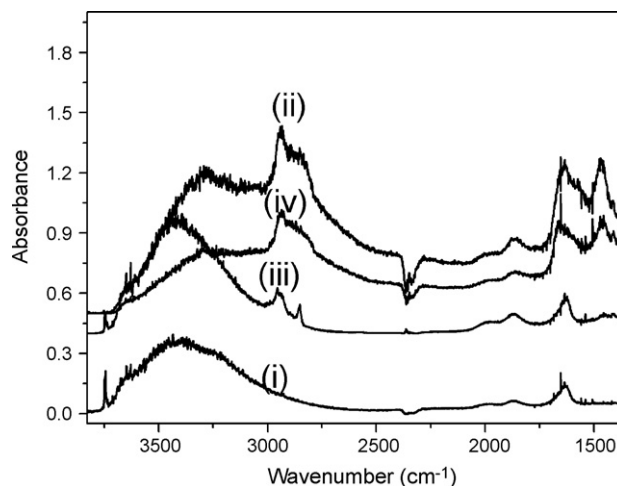

Fig. 4. FTIR spectra of (i) SiO$_2$, (ii) Si—NH, (iii) Si—SH and (iv) Si—NH—SH samples. Peak assignment as described in text.

Table 3

Sorption capacity (μmol g^{-1}) of Si—NH of metal ions at varying pH and as prepared (i.e. no buffer) solutions

Metal	pH 4	pH 7	pH 10	H$_2$O
Ni	76 ± 0.7	340 ± 3	340 ± 3	340 ± 3
Cr	354 ± 3	322 ± 3	384 ± 4	360 ± 4
Fe	0	358 ± 4	358 ± 4	358 ± 4
Mn	0	364 ± 4	364 ± 4	364 ± 4

Values are based on an average of three extraction results.

at variable buffered solutions with pHs of 4, 7 and 10. Sorption tests were also carried in non-buffered H$_2$O in an attempt to model the extraction profile of the sorbent working under natural environmental conditions. A control experiment using the parent SiO$_2$ as an extraction material indicated zero uptake of metal ions within our characterisation sensitivity limits. Tables 3–5 below outline the results of single metal extraction studies using the sorbents Si—NH, Si—SH and Si—NH—SH.

As expected the Si—NH (shown in Table 3) materials show a large capacity for Fe, Mn, Ni, Cr, with increasing uptake noticeable at the higher pH values. This increased sorption performance can be attributed to formation of hydroxy species when the pH of the solution is increased and this is consistent with previously reports [17,20,21]. Extracted metal ion loadings of approximately 350 μmol g^{-1} compare very well to industrial sorbents. Indeed, literature values for aminopropyl functionalised small pore mesoporous silicas give nickel loading capacities of only 150 μmol g^{-1} [14]. Control experiments carried out for Pd^{2+} sorption using amine-modified surfaces showed no affinity for Pd as might be expected due to the soft nature of the Pd ion.

Table 4 shows the sorption capacities of thiol-modified mesoporous silica. As might be expected significant quantities of Pd are extracted, 187 μmol g^{-1}. Preliminary experiments showed no significant uptake for the 'hard' metal ions Fe^{2+}, Cr^{6+}, Ni^{2+} or Mn^{2+}.

Table 5 shows the sorption capacities for the bi-functionalised silica sample (Si—NH—SH). Significant loading of both hard and soft metallic ions are noticeable. Similar metal ions loading to singly functionalised samples are achieved as might be expected from the elemental analysis which shows similar thiol and amine content in the bi-functionalised materials as in the single-functionalised systems. Sorption for each of the metal ions by the Si—NH—SH material is quantified for; Ni^{2+}: 340 μmol g^{-1}, Cr^{6+}: 362 μmol g^{-1}, Fe^{2+}: 358 μmol g^{-1}, Mn^{2+}: 152 μmol g^{-1} and

Table 4

Sorption capacity (μmol g^{-1}) of Si—SH of metal ions at varying pH and as prepared (i.e. no buffer) solutions

Metal	Pd
pH 4	186 ± 2
pH 7	187 ± 2
pH 10	115 ± 1
H$_2$O	187 ± 2

Values are based on an average of three extraction results.

Table 5

Sorption capacity (μmol g^{-1}) of Si—NH—SH of metal ions at varying pHs and extraction results under neutral (H$_2$O) conditions (values based on three extraction results)

Metal	pH 4	pH 7	pH 10	H$_2$O
Ni	114 ± 1	340 ± 3	340 ± 3	340 ± 3
Cr	258 ± 2	258 ± 2	278 ± 3	362 ± 4
Fe	117 ± 1	358 ± 4	358 ± 4	358 ± 4
Mn	0	364 ± 4	364 ± 4	152 ± 2
Pd	188 ± 2	188 ± 2	188 ± 2	188 ± 2

Table 6

Physiochemical data recorded for the metal–silica composites post-extraction

	Pore size(Å)	Pore volume (cm^3 g^{-1})	Surface area (m^2 g^{-1})	P/P_0
Si—NH—Ni	50.5 ± 13	0.102	61.3	0.410
Si—NH—Cr	48.1 ± 9	0.276	105.3	0.412
Si—NH—Fe	51.7 ± 12	0.012	12.7	0.112
Si—NH—Mn	50.1 ± 8	0.087	56.4	0.361
Si—SH—Pd	44.6 ± 10	0.018	3.2	0.312

Pd^{2+}: 188 μmol g^{-1} when extracted from non-buffered H$_2$O solutions.

Table 6 illustrates the physiochemical properties of the sorbents after the extraction procedure. In all cases the surface area, pore volume and pore diameter are reduced following exposure to metal ion solutions. These data yield further evidence that the metal ions are attached within the pore of the chosen functionalised silica. Significant decreases in surface area are noticeable after the extraction.

4.2. Mixed metal ion extraction results

Each sorbent was tested for sorptive performance towards mixed metal ion solutions. This test was carried out on a complex aqueous non-buffered solution to provide the most demanding test of the materials. Non-buffered solution mimics 'real life' conditions. This mixture of metal ions was chosen to mimic the array of species found in acid pickling waste from the steel industry [22]. Note here the use of a column filtration system (described in Section 2). Table 7 shows the sorption capacities for the mono-functionalised and bi-functionalised materials used for the 1 ppm standard mixed metal solutions.

As expected each metal ion has varying response to the different mono-functionalised mesoporous silica. The Si—NH material shows large extraction capacities for zinc, lead, cadmium, nickel, iron, chromium, manganese and copper, whereas the Si—SH material shows increased extraction of magnesium, vanadium and calcium. On the basis of these results one might expect that the use of the bi-functionalised mesoporous silica would have most relevance in assessing the applicability of this methodology. When Si—NH—SH material was used as a sorbent for the mixed metal ion solutions it shows a higher affinity with each of the metals when compared to the mono-functionalised mesoporous silica. The results show that environmental samples containing relatively high concentrations of mixed metal ions can be reduced to low concentration levels by a simple procedure. These results suggest that the sorbent materials developed here may have

Table 7

ICP-AES concentration data recorded before and after passage of test solution through the filter bed

	Initial concentration (μmol g^{-1})	Si—NH (μmol g^{-1})	Si—SH (μmol g^{-1})	Si—NH—SH (μmol g^{-})
Zn	152.9 ± 0.2	0.6 ± 0.4	30.8 ± 5.1	1.3 ± 1.0
Pb	48.3 ± 0.1	0.0 ± 1.1	7.7 ± 1.8	1.3 ± 0.8
Cd	88.9 ± 0.1	0.8 ± 0.3	13.1 ± 1.0	0.1 ± 0.3
Ni	170.4 ± 0.2	16.0 ± 3.7	30.1 ± 4.1	2.4 ± 3.1
Fe	179.1 ± 0.2	1.6 ± 2.2	17.3 ± 3.9	0.2 ± 0.1
Cr	192.3 ± 0.3	18.9 ± 0.9	26.5 ± 1.4	3.2 ± 2.8
Mg	411.4 ± 0.5	338.1 ± 88.1	75.2 ± 12.1	0.0 ± 0.2
V	196.3 ± 0.3	7.0 ± 4.2	6.7 ± 1.6	0.0 ± 0.3
Mn	182.0 ± 0.3	3.5 ± 4.7	27.6 ± 1.0	0.0 ± 0.1
Ca	249.5 ± 0.4	93.0 ± 24.2	25.0 ± 2.1	3.8 ± 1.2
Cu	157.4 ± 0.2	0.0 ± 1.8	0.0 ± 0.3	0.0 ± 0.2

Si—NH, Si—SH and Si—NH—SH samples were investigated. Extraction was carried out in a non = buffered H$_2$O solution (values based on an average of three extraction results).

significant applicability in the area of environmental mitigation strategies.

In conclusion, a facile procedure for mono-functionalising and bi-functionalising mesoporous silica with both aminopropyl and mercatopropyl ligands is reported here. Comparison of the physiochemical properties of the mono-functionalised and bi-functionalised materials (as studied by N_2 physisorption and elemental analysis) show that the uptake of thiol and amine is not compromised in the bi-functionalised material compared to the mono-functionalised case. Although pore diameter is reduced by the amine/thiol grafting there is no pore blockage observed but pore volume does reduce due to the size of the grafted species. The sorption capacities of these mono-functionalised and bi-functionalised mesoporous silicas were tested on single metal ion solutions using pH 4, 7, 10 and non-buffered H_2O as solvents to identify the optimum extraction parameters (over all data not just the selected set of data reported here). The maximum sorptive capacities were determined to be $384\,\mu mol\,g^{-1}$ for Cr, $340\,\mu mol\,g^{-1}$ for Ni, $358\,\mu mol\,g^{-1}$ for Fe, $364\,\mu mol\,g^{-1}$ for Mn and $188\,\mu mol\,g^{-1}$ for Pd using various tailored sorptive materials. For more appropriate tests, relevant to water clean-up applications, mixed metal ion solutions were applied to each sorbent via a simple column filtration system. ICP-AES analysis was used to measure the metal content in the mixed metal ion solution prior to and following column filtration. These experiments show that the mono-functionalised materials have specific responses to the metal ions. It is specifically shown that the use of the bi-functionalised mesoporous silica is highly effective in reducing a wide array of metal ions (from high concentration mixed metal ion solutions) to trace (>ppb) levels. Although solvent washing and recovery of the mesoporous silica was explored we have not yet found conditions where recovery would be cost or ecologically effective.

Acknowledgments

References

[1] A. Celik, A. Demirba, Removal of heavy metal ions from aqueous solutions via adsorption onto modified ligand from pulping wastes, Energy Sources 27 (2005) 1167–1177.
[2] R. Say, E. Birlik, A. Denizli, A. Ersoz, Removal of heavy metal ions by dithiocarbamate-anchored polymer/organosmectite composites (2005).
[3] M. Ajay Kumar, G.K. Mishraa, P.K. Raia, C. Rajagopala, P.N. Nagarb, Removal of heavy metal ions from aqueous solutions using carbon aerogel as an adsorbent (2005).
[4] F. Ekmekyapara, A. Aslanb, Y.K. Bayhana, A. Cakicia, Biosorption of copper(II) by nonliving lichen biomass of *Cladonia rangiformis hoffm* (2006).
[5] EPA. Environment in Focus 2006 (2000).
[6] C. Namasivayam, K. Ranganathan, Removal of Pb(II), Cd(II) and Ni(II) and mixture of metal ions by adsorption onto waste Fe(III)/Cr(III) hydroxide and fixed bed studies, Environ. Technol. 16 (1995) 851–860.
[7] R.J. Kiffs, D. Barnes, C.F. Forster, S.E. Hrudey, Surveys in industrial wastewater treatment, Manufacturing and Chemical Industries, 3 (1987) 377–399.
[8] H. Irving, R.J.P. Williams, The stability of transition–metal complexes, J. Am. Chem. Soc. 13 (1953) 3192–3210.
[9] S. Ahrland, J. Chatt, N.R. Davies, The relative affinities of ligand atoms. for acceptor molecules and ions, Quart. Rev. Chem. Soc. 12 (1958) 265.
[10] R.G. Pearson, Hard and soft acids and bases, J. Am. Chem. Soc. 85 (1963) 3533.
[11] G.E. Fryxell, X. Feng, L.-Q. Wang, A.Y. Kim, J. Liu, K.M. Kemner, Functionalised monolayers on ordered mesoporous supports, Science 276 (1997) 923–926.
[12] L. Mercier, T. Pinnavaia, Heavy metal ion adsorbents formed by the grafting of a thiol functionality to mesoporous silica molecular sieves: factors affecting Hg(II) uptake, Am. Chem. Soc. 32 (1998) 2749–2754.
[13] A. Mehdi, S. Dourdain, J.-F. Bardeau, C. Reye, R.J.P. Corriu, A. Gidaud, First direct synthesis of highly ordered bi-functionalized mesoporous silica thin films, J. Nanosci. Nanotechnol. 6 (2006) 377–381.
[14] L. Bois, A. Bonhomme, A. Ribes, B. Pais, G. Raffin, F. Tessier, Functionalised silica for heavy metal ions adsorption, Colloids Surf. A: Physiochem. Eng. Aspects 221 (2003) 221–230.
[15] T.-W. Kim, R. Ryoo, M. Kruk, K. Gierzal, M. Jaroniec, S. Kamiya, O. Terasaki, Tailoring the pore structure of SBA-16 silica molecular sieve through the use of copolymer blends and control of synthesis temperature and time, J. Phys. Chem. B 108 (2004) 11480–11489.
[17] S. Bhattacharjee, S. Chakrabarty, S. Maity, S. Kar, P. Thakur, G. Bhattacharyya, Removal of Lead from contaminated water bodies using sea nodules, Water Res. 37 (2002) 3654–3966.
[18] G. Zhu, Q. Yang, D. Jiang, J. Yang, L. Zhang, Y. Li, C. Li, Synthesis of bifunctionalised mesoporous organosilica spheres for high performance liquid chromatography, J. Chromatogr. A 1103 (2005) 257–264.
[19] G. Socrates, Infrared Characteristic Group Frequencies, Tables and Charts, Wiley, U.S., 1994.
[20] K. Parida, P.K. Satapathy, N. Das, Studies on Indian manganese nodules adsorption of some bivalent heavy metal ions onto ferromanganese nodules, J. Colloid Interf. Sci. 181 (1996) 456–462.
[21] M. Horsfall, A.A. Abia, Sorption of cadmium (II) and zinc (II) ions from aqueous solutions by cassava waste biomass, Water Res. 37 (2002) 4913–4923.
[22] I. Ali, H.Y. Aboul-Enein, Instrumental methods in metal ion speciation, in: T. Francis (Ed.), Chromatographic Science Series, Vol. 96.