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A mercapto based nanoscavenger as promising tool for the dispersion preconcentration of trace elements in contaminated waters

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Abstract

A novel chelating mercapto- nanoscavenger has been developed exploiting the high surface area of monodisperse nano-sized mesoporous silica. The nanoscavenger acts as a solid phase trace metal extractant whilst suspended as a quasi-stable sol in aqueous samples. This mode of extraction requires no external agitation as the particles move naturally through the sample by Brownian motion, convection and slow sedimentation. Careful size selection enables the nanoscavenger to be easily recovered together with the extracted analyte by conventional filtration or centrifugation. The paper describes the successful attachment of chelator mercapto to ca. 136 ± 15 nm high surface area (BET surface area = 1006 m^2 g^{-1}) mesoporous silica particles. The resulting material had a copper capacity of ca. 1.34 ± 0.10 mmol g^{-1} and was successfully applied to the collection of a trace element from water. Essentially complete recovery of Cu (II) has been achieved from freshwater samples giving typical preconcentration factors of 100 from 50 µg/l samples. Data obtained from a nanoscavenger-based extraction of copper from samples were not significantly different to those obtained by using a conventional colorimetric procedure employing complexation/solvent extraction.

Keywords: Heavy metals; mesoporous silica; solid phase extraction; nanoscavenger.

1. Introduction

Extraction and preconcentration are important aspects of many analytical procedures, being employed not only to increase the concentration of an analyte, but also to isolate the analyte from interfering species[1]. Various separation and preconcentration methods have been developed to achieve these goals, amongst which are solvent extraction[2], membrane filtration[3], ion exchange, coprecipitation[4] and solid phase extraction techniques[5-11].

Solid phase extraction has become, over recent years, a powerful and widely used approach to the preconcentration and cleanup of samples in pesticide, drug and trace metal analyses. There are a number of advantages to be derived from the use of liquid-solid partition for the collection of analytes from solution. There are physical difficulties associated with the use of conventional solvent extraction, most notably the requirement for vigorous agitation that makes the enrichment of large numbers of samples and/or enrichment from large sample volumes difficult and the approach frequently runs into problems with emulsion formation. In addition, there are increasing environmental and cost pressures to replace, or at the very least reduce, the volumes of solvents employed in all analytical procedures.

Modified silica has received extensive attention as a solid support for metal extraction due to its excellent thermal and mechanical stability[12, 13], no swelling in various solvents[14] and ease of surface modification[15]. The surface of silica can be modified by organic[16, 17] and inorganic[18] functionalization. In the organic modification the modifying agent is an organic molecule often acting for example, as a chelating ligand. Inorganic modifications can be discrete organometallic molecules or inorganic solids compound such as iron oxides[19]. Most of the inorganic modifications of silica however have poor selectivity to heavy metals[20]. Immobilized chelating groups such as ethylenediamine and its derivatives[21], 1,8-dihydroxyanthraquinone[22], dithiocarbamate [23], 2-mercaptopyridine[24], 3(1-imidazolyl)propyl-[25], formylsalicylic acid[26], methylthiosalicylate[27], triethylenetetramine[14] and aminothioamidoanthraquinone [28] on the silica surface have all been successfully employed for the preconcentration and extraction of metal ions.

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Over recent years there have been major developments in nanoscience and syntheses of particles with nanometre dimensions have been reported for many substances [29-37]. These particles fall within the colloidal range, exhibiting typical colloidal properties such as the long-term stability of their sols. Monodisperse populations of colloidal silica spheres can be produced by the hydrolysis of tetraalkoxysilanes in ammoniacal alcohol solution[38] with the subsequent condensation of monomeric species[39-44] into high density spherical particles. With careful control of synthetic conditions the size of these particles can be controlled over a wide range (*ca.* 5 to 5000 nm), the morphology and size of the particles depending strongly on solvent choice and concentration[40, 45-47].

Since the discovery of mesoporous silicas by Mobil Oil Company scientists in 1992[48, 49], this class of material has been the basis of many developments in catalysis, adsorption and separation. Their large surface area and well-defined pore structures make them an excellent choice of supporting material for solid phase extraction[50]. By modifying the available surface of mesoporous silica with chelating agents, solids can be developed to selectively remove metal ions from water[51-56]. In recent years there have been a few reports of organofunctionalized mesoporous silicas having been used for the preconcentration / extraction of some heavy metals. Examples of silica modifications include 3-(2-aminoethylamino) propyl-mesoporous silica for the extraction of inorganic arsenic species[50], chitosanmesoporous silica for the preconcentration of V, Cu, Pb, Cd and Hg[57] and 2-mercaptopyridine meoporous silica for the extraction of Cr (VI)[58].

In previous work[59], mesoporous silica of 250 nm size was modified with different organic groups for preconcentration of organic and inorganic analytes from water. The drawback of using modified mesoporous silica with 250 nm size was the rapid sedimentation which affect the extraction ability of the particles. Therefore, the size of mesoporous silica particles in this work was reduced to 136 nm and these particles were modified with new chelating group to improve the dispersion of the particles in water and avoided rapid sedimentation leading to excellent recovery results of the analytes. This paper extends conventional column based solid phase extraction approaches to a more convenient nanoscavenger based dispersion extraction procedure. The development of a mercapto solid phase nanoscavenger is based on 136 nm spherical mesoporous silica particles modified with a mercapto-silane.

These particles suspend well in aqueous systems, moving naturally through the sample as a result of Brownian motion, convection and sedimentation. Continuous physical agitation is not therefore required. The particles can be recovered from the sample by filtration or centrifugation and the collected metals can be released into acid.

2. Experimental

2.1 Materials

Tetramethoxysilane (98%), sodium diethyldithiocarbamate, dodecyltrimethylammonium bromide (99 %), (3-mercaptopropyl)trimethoxysilane (95 %) and hydrochloric acid (37 % (w/v) were obtained from Aldrich (U.K.) .Nitric acid was obtained from BDH limited (U.K.), ethylene glycol, toluene and ethanol were reagent grade. Water (>14 Mohm.cm) was purified by reverse osmosis followed by deionisation using an Elga Option 4 system. Whatman cellulose nitrate membrane filters (47 mm diameter, pore size 0.1 µm) were supplied by Fisher, U.K. All apparatus was soaked in nitric acid (5 % V/V) and rinsed with deionised water before use. Tris buffer solutions were prepared by dissolving 12.1 g of tris(hydroxymethyl)-aminomethane in 1L of water and adjusting the pH to 7.0 or 9.0 using concentrated hydrochloric acid. Stock standard solutions of the metal (containing 1000 µg/mL of copper ion) was prepared by dissolving a known amount of a copper salt in deionised water to give 100 mL of solution. For preparation of modified mesoporous silica and investigation of its ability as an analytical tool, I followed the procedures described in previous work with making necessary changes in the experimental methods [59-61].

The extracted metals were measured by flame atomic absorption spectroscopy using a Perkin-Elmer instrument, calibrated over the range 0 to 5 µg mL^{-1} and employing conditions specified by the instrument manufacturer.

2.2 Synthesis of 136 nanometer mesoporous silica particles.

Mesoporous silica was prepared as described in previous works [59-61] with changes in molar concentration of reaction recipe to get the desirable particle size. Ethylene glycol (100 mL), deionised water (300 mL), sodium hydroxide solution (3 mL, 1M), and dodecyltrimethylammonium bromide (C_{12}TMABr) (1.70 g) were transferred into a conical flask (1000 mL). The mixture was stirred vigorously for 15 minutes at 20 ºC. Tetramethoxysilane (TMOS) (2.00 mL) was then slowly added and the reaction was left to proceed for 8 h under vigorous stirring. The mixture was then aged overnight. The white solid was isolated by centrifugation (10000 rpm) for 30 minutes, rinsed with water five times and one additional time with ethanol, and then dried at 45 ºC for two days. The white powder was calcinated at 550 ºC for 12 h, increasing the temperature from room temperature at 2 ºC / minunte.

2.3 Mercapto modification of the silica

Dry toluene (200 mL) was transferred to a three

necked round-bottomed flask (500 mL) fitted with a reflux condenser, dropping funnel and continuous slow nitrogen bleed. Mesoporous silica (4.00 g, dried in an oven at 180 ºC overnight) was added to the toluene. The mixture was stirred using a magnetic stirrer for 15 min and then heated at 100 ºC, whilst maintaining the stirring. (3-Mercaptopropyl)trimethoxysilane (6 mL, dissolved in 50 ml of dried toluene) was slowly added to the flask through the dropping funnel once the temperature had stabilized. After 8 h, the reaction mixture was allowed to cool, the product isolated by centrifugation, rinsed thoroughly with dried toluene six times and three additional times with ethanol. The solid was then dried for five hours under continuous vacuum.

2.4 Measurnemt of Copper Capacity

A mercapto nanoscavenger ($SH@SiO_2$) (12 mg) was transferred to a tube (10 mL). A solution of Cu (II) (5 mL) was added to the tube. The mixture was left for two minutes and it was then shaken for 4 minutes. The solid material was isolated by centrifugation and the supernatant was discarded. The solid material was rinsed 10 times with deionised water to remove unattached Cu (II). A solution of HCl (10 mL, 6 M) was added to the tube and it was shaken; the acidic solution was isolated by centrifugation and was then transferred to a volumetric flask (100 mL) and this step was repeated for one more time. The volumatric flask was made up to the mark using deionised water. The measurement of the copper ion was carried out using flame atomic absorption spectroscopy at 324.7 nm**.**

2.5 *Extraction of Cu^{2+} using the mercapto nanoscavenger ($SH@SiO_2$)*

Deisonised water (1000 mL), a tris buffer (5 mL , pH = 7, 1M) and pre-dispersed $SH@SiO_2$ (200 mg) were transferred to bottle and Cu^{2+} (5 mL, 10 µg mL^{-1}) was then spiked. The bottle was left for 1 h without agitation. The solid material was isolated using a 0.1 µm cellulose nitrate membrane filter. The filter was transferred to a tube. A mixture of HCl and HNO_3 (1:1, 5 mL) was added to the tube and heated to 45 ºC for 1 h using a water bath. The acidic solution was isolated using centrifugation and it was transferred to a volumetric flask (10 mL). To the tube, deionised water (5 mL) was added, shaken and centrifuged, then added to the volumetric flask. The volume was made up to the mark using deionised water. The concentration of copper ion was measured by FAAS. This experiment was replicated five times.

2.6 Rate of copper ion uptake by the $SH@SiO_2$

$SH@SiO_2$ nanoscavenger (250 mg) was dispersed in 5 ml of tris-buffer (pH = 7, 1M) and transferred to bottle (1000 mL). Deionized water (1000 mL) was then added to the bottle . The bottle was shaken and 1 ml of a solution containing 50 µg mL^{-1} of Cu (II) was added to the bottle. The solution was left for different equilibrium times (1 min, 30 min, 1 h, 3 h, 6 h, 15 h and 24 h) prior to filtration through a 0.1 µm cellulose nitrate membrane filter. The filter was then transferred to a tube (10 mL) and a mixture of HCl and HNO_3 (1:1, 5 mL) was added to each tube. The tube was heated to 45 ºC for 1 h using a water bath, then centrifuged for 30 minutes and the acidic solution was transferred to a volumetric flask (10 mL). Deionised water (5 mL) was added to each tube, shaken for 2 minutes and centrifuged; the aqueous solution was added to the volumetric flask. The volume of the volumetric flask was made up to the mark using deionised water and the copper ion concentration was measured by FAAS.

2.7 Effect of pH on copper ion extraction efficiencies

Deionised water (100 mL) and $SH@SiO_2$ nanoscavenger (ca. 100 mg) was transferred to bottle (125 mL) and the mixyure was sonicated for 5 minutes. Cu (II) (1 mL, 20 µg ml^{-1}) was then spiked to the bottle. The pH of the bottle mixture was changed to the desired pH (to pH = 4 using acetate buffer or to pH 7 or 9 using tris buffer). The bottle was shaken and then left for 30 minutes prior to filtration using a 0.1 µm cellulose nitrate membrane filter. The filter was moved to a centrifuge tube (10 mL) and a mixture of HCl and HNO_3 (1:1, 5 mL) was added. The tube was left for 1 h on a water bath at 45 ºC. The mixture was centrifuged, the acidic solution was transferred to a volumetric flask and deionised water (5 mL) was added to the tube. After shaking the tube for 2 minutes and centrifuging the resulting aqueous solution was added to the volumetric flask. The volume was made up to the mark using deionised water and FAAS was used to measure the Cu (II) concentration.

2.8 Colorimetric determination of copper as its dithiocarbamate complex

Colorimetric method was used to determine copper ion after solvent extraction of its diethyldithiocarbamate complex into chloroform (HPLC grade). To separating funnel (500 mL), a tap water sample (200 mL) was transferred and the pH was altered to 7.0 using a tri-ammonium citrate (10 % w/v) solution. Sodium diethyldithiocarbamate (2 mL, 1 mg mL^{-1}) was added to the funnel and the mixture was shaken for 5 minutes and chloroform (10 mL) was then added. The funnel was shaken vigorously for 2 minutes and the organic layer was collected into a volumetric flask (20 mL). The last step was repeated again, the organic layer was added to the volumetric flask and the volume was made up to the mark using chloroform. The absorbance was measured at 435 nm and the concentration was calculated based on a calibration curve derived from the extraction of standard copper solutions.

2.9 SH@SiO_2 extraction of Cu^{2+} from tap water

A tap water (200 mL) was transferred to a bottle (250 mL) and the pH was altered to 7 using tri-ammonium citrate (10 mL, 10 % w/v) solution. Pre-dispersed SH@SiO_2 nanoscavenger (100 mg) was added to the bottle and the mixture was shaken for 2 minutes. The solution was left for 1 h and then filtered using a 0.1 µm cellulose nitrate membrane filter. The filter was then transferred to a tube. A mixture of HCl and HNO_3 (1:1, 5 mL) was added to the tube mixture and the tube was heated to 45 ºC for 1 h using a water bath. The acidic solution was transferred to a volumetric flask (20 mL), deionised water (10 mL) was added to the solid material in the tube, shaken for 2 minuntes. The tube mixture was centrifuged and the liquid layer was tranferred to the volumetric flask. The volume of the volumetric flask was made up to the mark using deionised water and the copper ion concentration was measured by FAAS.

2.10 Characterization of the particles

The nanoscavenger particles were characterized using a wide variety of techniques.

The surface area and pore size distribution were measured using a surface area and porosity analyser micromeritics ASAP 2020.

Focused ion-beam micropscopy (FIB) was utilized to measure the particle size and to evaluate the morphology of the particles. Silica particles (10 mg) were dispersed in 10 mL of deionised water (10 mL) by ultrasonication. Drops of the pre-dispersed silica were applied to a glass plate and the water was allowed to evaporate at room temperature. The glass surface was then coated with a thin gold film. The microscopy measurement was carried out using a FEI Helios Nanolab 600i instrument under these conditions: Mode: high vacuum 5 kv, Beam current 0.17 nA and detector: Secondary Electron (SE).

The settling time of a colloidal suspension of the nanoscavenger was measured using a Perkin Elmer Lambda 3 spectrophotometer. The silica suspension was prepared by dispersing the silica particles (10 mg) in deionised water (10 mL). The light transmission through the dispersion held in a 1 cm pathlength quartz cuvette (at 600 nm) was measured over time.

3. Results and Discussion

3.1 Mesoporous silica

Dithiocarbamate groups were loaded on the surface of 250 nm spherical silica particles (Stöber type) to prepare a dithiocarbamatenanoscavenger. One of the main disadvantages of this kind of silica particle is its low surface area of around 20 m^2 g^{-1} and its easily sedimented [23]. Therefore increasing the surface area of the silica particle was at the top of my priorities

Mesoporous silica has a much higher surface area and is one of the best solid phase supports in which to immobilize chelating agents to prepare nanoscavengers. Spherical mesoporous silica particles have been successfully synthesized from TMOS using a C_{12}TMABr template. SEM imaging of the particles showed them to be spherical with a mean diameter of 136 nm (Figure 1) and this small size of the particles make them last for long time. In our previous work some chelating agents such as mercaptobenzamide has successfully loaded to 250 mesoporous silica particles to produce nanoscavengers . These nanoscavengers were applied to preconcentrate some metal ions (Cu^{2+}, Cd^{2+}, Ni^{2+}, Pb^{2+}, Co^{2+}, Cr^{3+}, Mn^{2+} and Zn^{2+}) from water and recovery results were more than 90 % for most of metal ions [59]. There were some drawbacks such as rapid sedimentation of modified particles, therefore shaking sometime was required during preconcentration process. In this work the size of mesoporous silica particles was reduced to nanosized to improve particles dispersion and avoid any rapid sedimentation for some particles which can reduce nanoscavenger ability to preconcentrate metal ions.

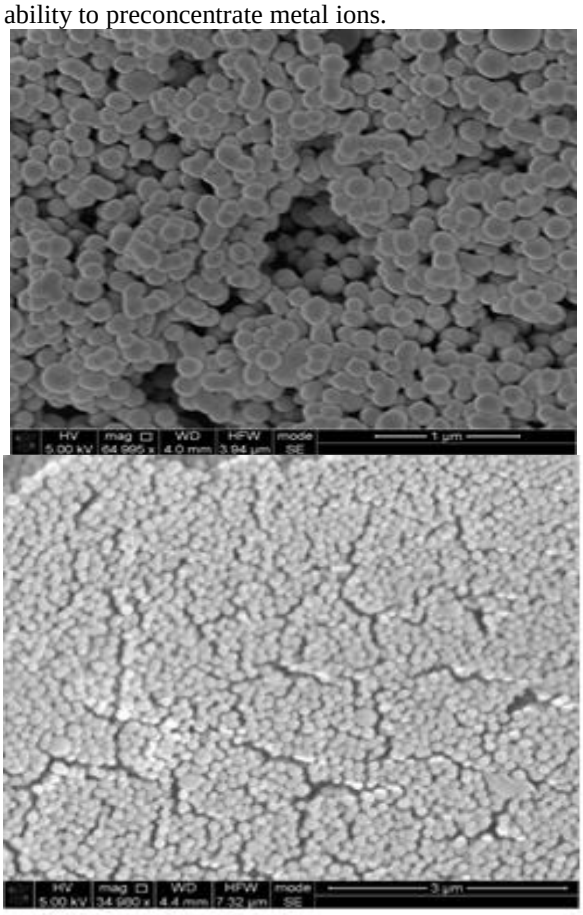

Fig. 1. Sub-micron silica particles a) SEM image of mesoporous silica (64995 X magnification) b) SEM image of SH@SiO2 (34980 X magnification)

FT-IR spectroscopy studies of the silicas before and

after combustion confirm the removal of the surfactant from the silica. The FT-IR result shows the CH_2 and CH_3 stretching peaks at 2947 and 2859 cm^{-1} were completely removed after burning off the organic species. Removal of the surfactant using combustion gives a better result than using a Soxhlet extraction technique in which the two peaks of the alkyl groups were not completely removed. Therefore combustion was applied to remove the organic species from the silica structure.

To provide additional proof of the removal of the surfactant from the silica, thermogravimetric analyses were carried out from 30 to 800 ºC. Figure 2A shows a 35 % weight loss between 162 ºC and 343 ºC. This weight loss disappeared from the TG trace following combustion (Figure 2B).

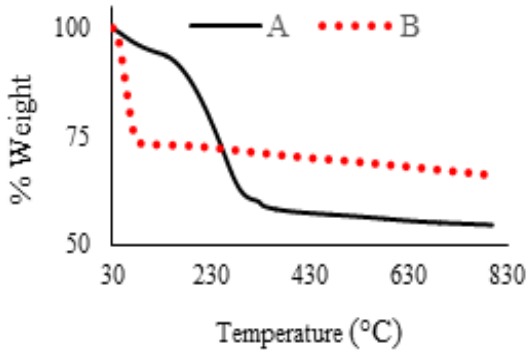

Fig. 2. Thermal analysis of silica (in air): A) before burning off the surfactant and B) after burning off the surfactant.

The surface area of the mesoporous silica was determined using a Brunaure-Emmett-Teller (BET) method[62] based on a N_2 adsorption isotherm. The N_2 adsorption isotherm measurement shows a high surface area (1006 m^2 g^{-1}). In figure 3 the relative pressure (P/P^o) is shown for both the adsorption and desorption processes. The isotherm curve shows the characteristics of a type IV [63, 64] materials in the IUPAC classification. According to the IUPAC classification of adsorption isotherms, type IV occurs when the material is mesoporous (pore widths between 2 and 50 nm)[63]. Similar nitrogen adsorption isotherms have been reported by Yamada and Yano[65] for their synthesis of monodispersed mesoporous spherical particles prepared using TMOS and C_{12}TMABr. They obtained an N_2 adsorption isotherm shape analogous to the one drawn in figure 3. The adsorption/desorption isotherm curve reveals a reversible isotherm for both branches (adsorption and desorption) (Figure 3)[66]. The absence of a hysteresis loop is due to the amount of adsorbed gas being almost equal to the amount of desorbed gas.

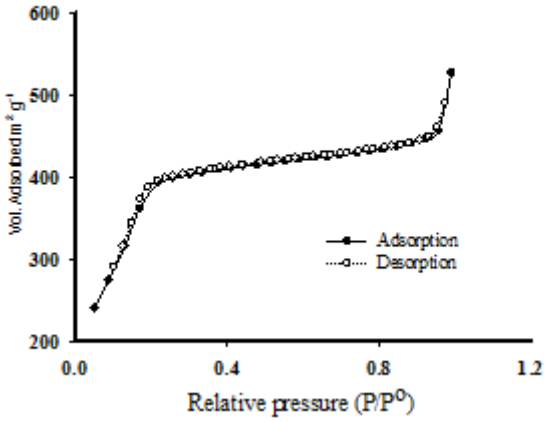

Fig. 3. N_2 adsorption isotherm of mesoporous silica

3.2 Synthesis of mercaptonanoscavenger ($SH@SiO_2$

In this material the 3-mercaptopropyl- group was anchored to the surface of mesoporous silica particles by a condensation mechanism in dried toluene medium. The reaction medium was extremely dry to avoid hydrolysis and polymerization of 3-mercapto-propyl on the silica surface. Modification of the silica surface was confirmed by thermogravimetric analysis. There were in general three regions of weight loss on the TG traces. The first change between 30 ºC and 124ºC was a 4% of weight loss believed to be adsorbed water and residual solvent[67] . A 2.43 % weight loss between 126 and 342 ºC, and another 9 % loss between 326 and 773 ºC were due to oxidation of organic material [68]. In the FT-IR shows a weak band at 2550 cm^{-1} that are characteristic of the thiol (–SH) and the presence of –CH stretching vibration bands (2850–3000 cm^{-1}) mainly associated with the propyl group introduced by the functionalization of mesoporous silica surface with 3-mercaptopropyl- . Furthermore, the colour of the particles turned blue when dispersed in a Cu (II) solution indicating the formation of a copper mercapto- complex. The copper capacity of the 3-mercaptopropyl silica was 1.34 ± 0.10 mmol g^{-1}.

3.3 Settling of the $SH@SiO_2$ from an aqueous suspension

Stability of the nanoscavenger particles in the aqueous suspension is an essential factor of the nanoscavenger concept of solid phase dispersion extraction (SPDE) as the particles must remain dispersed in the solution for a significant time period. This allows the particles to move naturally throughout the sample solution without external agitation. The stability of a $SH@SiO_2$ suspension was therefore assessed by measuring the settling rate of the particles over an extended time period. Light transmission remained essentially constant for more than 10 hours, demonstrating extremely low sedimentation.

3.4 Extraction of copper ions from water

The ability of $SH@SiO_2$ to enrich metal ions from water was tested by spiking aliquots of metal ions into water. To (1000 mL) water samples was added 50 µg of metals Cu^{2+}. The $SH@SiO_2$ (50 mg) was dispersed in water sample and the complexed metal was collected on the filter. Copper ion cannot release from the nanoscavenger by deionised water. Therefore copper ion was released from the nanoscavenger by acidification and oxidation using mixture of HCl and HNO_3 (1:1). The recovery result of the Cu^{2+} was 99 ± 1 %. It seemed that the size of particles improve the dispersion and increase the extraction as result of that. The preconcentration factor of 100 can be improved by decreasing the final volume of extracted metals.

3.5 Rate of copper ion uptake from dilute solution

The equilibrium between the metal and the $SH@SiO_2$ was assessed by following the extraction of metals over time. Tri buffer was added to adjust the pH to 7 and to avoid any change on the pH during the preparation of the sample. The time had no effect on the Cu (II) ion uptake as it reached maximum recovery within one minute and no further change was observed afterwards (Figure 4).

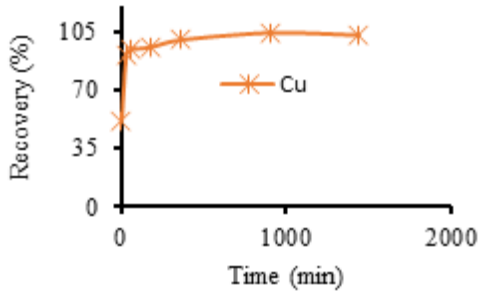

Fig. 4. Effect of time on the copper ions uptake by $SH@SiO_2$

3.6 Effect of pH on the copper enrichment

The pH of the sample solution is an important factor in the extraction of metals from solution. Buffers were added to the sample solution to maintain accurate pHs between 4 and 9. Strong acid or bases were avoided because of potential decoupling of the chelating groups from the surface of the nanoscavenger and potential dissociation of the silica. Acetate buffer were used to adjust the pH of sample solution to 4 and Tris buffer to adjust the sample solution to 7 and 9. The recoveries of the cupper ion from different pH media have been slightly influenced much by changing the pH. The lowest recovery results (92 ± 4) were obtained at low pH . However, the recoveries increased with increasing pH. The reason for low extraction of Cu (II) at lower pH is the increasing tendency for replacement of the copper from the chelate by hydrogen ions[69].

3.7 A comparison of Cu (II) determinations using a $SH@SiO_2$ and a conventional colorimetric procedure

The performance of a $SH@SiO_2$ solid phase extraction procedure was evaluated by comparing it against a standard procedure based on solvent extraction. In this experiment the water samples were collected from variety of tap water. The first method was a colorimetric procedure involving solvent extraction of the Cu diethyldithiocarbamate complex into chloroform. The Cu was determined by measurement of the absorbance at 435 nm**.** The concentration of Cu was calculated based on calibration with standard solutions. The second method employed the $SH@SiO_2$ to extract the Cu ion from tap water with subsequent measurement of the extracted Cu ion by FAAS. The concentration of Cu formed using the solid phase dispersion extraction (SPDE) method was plotted against the concentration measured using the colorimetric method. The slope correlation of the approaches was 1.0187, indicating that the concentration of Cu attained from the two methods was indistinguishable. The good agreement of the results attained from both methods suggests that the $SH@SiO_2$ procedure is a promising new method for the extraction of metals from water. The Cu concentration on the tap water samples was found to range from 0.023 to 0.97 ppm.

4. Conclusions

The preconcentration of metal ions from water can be carried out using a variety of different techniques ranging from solvent extraction to solid phase microextraction. Choosing between methods involves a careful matching of method performance to the sample type and available instrumentation. Nowadays using organic solvents for the enrichment of metals from water is to be avoided due to environmental issues and cost implications. The new nanoscavenger approach is simple to apply and applicable to the processing of large batches of samples. Once dispersed in the water sample, the modified solid phase extractant (nanoscavenger) requires no further physical intervention until it is time for the nano-scavenger to be recovered from the sample having bound the analyte metal. This nanoscavenger recovery can be achieved by simple filtration or centrifugation and the analyte can be determined following metal release into solution by treatment with acid and determination by a suitable solution based procedure such as FAAS. Whilst not investigated in this study, the direct measurement of the analyte on the solid nanoscavenger should also be possible by techniques such as X-ray fluorescence, thereby removing the

release stage from the analytical procedure.

In this paper we have described the synthesis of an SH-nanoscavenger based on spherical mesoporous silica (136 nm particles). The size of the SH@SiO_2 was chosen to be 136 nm as particles with this particular size move naturally when suspended in water due to Brownian motion yet are very slow to sediment. Mechanical agitation is therefore not required during the extraction. The size of the particles are neither too small to make them difficult to recover, nor are they too big to sediment rapidly.

The stage linking procedure employed in this study involved solid modification with 3-mercaptpropyl-trimthoxysilane. The resulting 136 nm SH@SiO_2 particles remained suspended for over 10 hours; more than enough to quantitatively attach the metals to the solid. 136 nm particles with a narrow size distribution make their recovery by filtration easy.

The SH@SiO_2 nanoscavenger was applied to the enrichment of Cu (II) with recovery greater than 99 % with a 100-fold of preconcentration factor. The procedure was then applied to the preconcentration Cu (II) from tap water samples and the new technique was found to compare favourably with a well accepted solvent extraction of the copper dithiocarbamate complex followed by colorimetry.

The nanoscavenger extraction approach offers a number of important advantages over conventional procedures. Not only is solid phase dispersion extraction one of the 'greenest' techniques for the preconcentration of analytes from water due to its low reagent use, it requires little human intervention during the analytical procedure. Routine water analysis laboratories are often required to perform very large numbers of analyses within a very short time period dictated by customer demand and rapid sample degradation. The nanoscavenger approach allows analyte stabilization to be initiated at the point of sampling either after filtration, or if appropriate to the analytical requirements, by the addition of the nanaoscavenger to a measured volume of sample scheme without pretreatment. In this latter case the analytical results obtained after digestion of the filter material would be expressed as a 'total' measurement; particulate material from the sample would be included together with the recovered nanoscavenger.

Addition of the nanoscavenger to samples at the sampling site permits large numbers of samples to be stabilized at the time of collection reducing pressure on the analyst to further process the samples due to their degradation in the untreated state. The metal extractions then take place as the samples return to the laboratory and during storage. Multiple rapid filtrations carried out in parallel followed by parallel metal recoveries permit the efficient subsequent processing of the samples. Overall, the nanoscavenger extraction approach can offer significant analytical and operational advantages over many commonly employed alternative approaches.

Conflicts of interest

The author have no Conflicts to declare.

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References

[1] A.G. Howard, P.J. Statham, Inorganic Trace Analysis: Philosophy and Practice, John Wiley & Sons, Chichester, 1993.

[2] R. Saran, T.S.B. Baul, P. Srinivas, D.T. Khathing, SIMULTANEOUS DETERMINATION OF TRACE HEAVY-METALS IN WATERS BY ATOMIC-ABSORPTION SPECTROMETRY AFTER PRECONCENTRATION BY SOLVENT-EXTRACTION, Analytical Letters, 25 (1992) 1545-1557.

[3] U. Divrikli, A.A. Kartal, M. Soylak, L. Elci, Preconcentration of Pb(II), Cr(III), Cu(II), Ni(II) and Cd(II) ions in environmental samples by membrane filtration prior to their flame atomic absorption spectrometric determinations, Journal of Hazardous Materials, 145 (2007) 459-464.

[4] V.N. Bulut, C. Duran, A. Gundogdu, M. Soylak, N. Yildirim, L. Elci, A new approach to separation and pre-concentration of some trace metals with co-precipitation method using a triazole, Talanta, 76 (2008) 469-474.

[5] Y. Yamini, L. Hejazi, D.E. Mohammadi, Solid phase extraction and simultaneous spectrophotometric determination of trace amounts of copper and iron using mixture of ligands, Microchimica Acta, 142 (2003) 21-25.

[6] M.M. Osman, S.A. Kholeif, N.A. Abou Al-Maaty, M.E. Mahmoud, Metal sorption, solid phase extraction and preconcentration properties of two silica gel phases chemically modified with 2-hydroxy-1-naphthaldehyde, Microchimica Acta, 143 (2003) 25-31.

[7] O. Dalman, S. Karabocek, Solid phase extraction of copper(II) by modified octadecyl silica membrane disks with OXIME, Turkish Journal of Chemistry, 27 (2003) 649.

[8] M.E. Mahmoud, A.A. Soayed, O.F. Hafez, Selective solid phase extraction and pre-concentration of heavy metals from seawater by physically and chemically immobilized 4-amino-3-hydroxy-2-(2-chlorobenzene)-azo-1-naphthalene sulfonic acid silica gel, Microchimica Acta, 143 (2003) 65-70.

[9] V. Camel, Solid phase extraction of trace elements, Spectrochimica Acta Part B: Atomic Spectroscopy, 58 (2003) 1177-1233.
[10] M. Sarkar, M. Das, P.K. Datta, Solid-phase extraction for the decontamination of alkali metal, alkaline earth metal, and ammonium salts from heavy metal ions, Journal of Colloid and Interface Science, 246 (2002) 263-269.
[11] S.A.M. Fathi, M.R. Yaftian, Enrichment of trace amounts of copper(II) ions in water samples using octadecyl silica disks modified by a Schiff base ionophore prior to flame atomic absorption spectrometric determination, Journal of Hazardous Materials, 164 (2009) 133-137.
[12] R.J. Qu, M.G. Wang, C.M. Sun, Y. Zhang, C.A. Ji, H. Chen, Y.F. Meng, P. Yin, Chemical modification of silica-gel with hydroxyl- or amino-terminated polyamine for adsorption of Au(III), Applied Surface Science, 255 (2008) 3361-3370.
[13] M. Zhu, Y. Zhu, B. Ni, N. Xie, X. Lu, J. Shi, Y. Zeng, X. Guo, Mesoporous Silica Nanoparticles/Hydroxyapatite Composite Coated Implants to Locally Inhibit Osteoclastic Activity, Acs Applied Materials & Interfaces, 6 (2014) 5456-5466.
[14] M. Imamoglu, V. Gunes, Column solid phase extraction of copper and nickel on triethylenetetramine bonded silica gel for their atomic absorption spectrometric determination, Instrumentation Science & Technology, 36 (2008) 105-116.
[15] W. Ngeontae, W. Aeungmaitrepirom, T. Tuntulani, A. Imyim, Highly selective preconcentration of Cu(II) from seawater and water samples using amidoamidoxime silica, Talanta, 78 (2009) 1004-1010.
[16] E.L. da Silva, A.O. Martins, A. Valentini, V.T. de Favere, E. Carasek, Application of silica gel organofunctionalized with 3(1-imidazolyl)propyl in an on-line preconcentration system for the determination of copper by FAAS, Inaugural Conference on Southern and Eastern Africa Network of Analytical Chemists (SENAC), Elsevier Science Bv, Gaborone, BULGARIA, 2004, pp. 181-189.
[17] M.A.A. Akl, I.M.M. Kenawy, R.R. Lasheen, Organically modified silica gel and flame atomic absorption spectrometry: employment for separation and preconcentration of nine trace heavy metals for their determination in natural aqueous systems, Microchemical Journal, 78 (2004) 143-156.
[18] H.F. Maltez, E. Carasek, Chromium speciation and preconcentration using zirconium(IV) and zirconium(IV) phosphate chemically immobilized onto silica gel surface using a flow system and F AAS, Talanta, 65 (2005) 537-542.
[19] F. Unob, B. Wongsiri, N. Phaeon, M. Puanngam, J. Shiowatana, Reuse of waste silica as adsorbent for metal removal by iron oxide modification, Journal of Hazardous Materials, 142 (2007) 455-462.
[20] A. Scheidegger, M. Borkovec, H. Sticher, COATING OF SILICA SAND WITH GOETHITE - PREPARATION AND ANALYTICAL IDENTIFICATION, Geoderma, 58 (1993) 43-65.
[21] D.E. Leyden, G.H. Luttrell, PRECONCENTRATION OF TRACE-METALS USING CHELATING GROUPS IMMOBILIZED VIA SILYLATION, Analytical Chemistry, 47 (1975) 1612-1617.
[22] A. Goswami, A.K. Singh, 1,8-dihydroxyanthraquinone anchored on silica gel: synthesis and application as solid phase extractant for lead(II), zinc(II) and cadmium(II) prior to their determination by flame atomic absorption spectrometry, Talanta, 58 (2002) 669-678.
[23] A.G. Howard, N.H. Khdary, Nanoscavenger based dispersion preconcentration; sub-micron particulate extractants for analyte collection and enrichment, Analyst, 130 (2005) 1432-1438.
[24] D. Perez-Quintanilla, I. del Hierro, M. Fajardo, I. Sierra, Mesoporous silica functionalized with 2-mercaptopyridine: Synthesis, characterization and employment for Hg(II) adsorption, Microporous and Mesoporous Materials, 89 (2006) 58-68.
[25] J.C. Moreira, Y. Gushikem, PRECONCENTRATION OF METAL-IONS ON SILICA-GEL MODIFIED WITH 3(1-IMIDAZOLYL)PROPYL GROUPS, Analytica Chimica Acta, 176 (1985) 263-267.
[26] M.E. Mahmoud, E.M. Soliman, Silica-immobilized formylsalicylic acid as a selective phase for the extraction of iron(III), Talanta, 44 (1997) 15-22.
[27] P.C. Rudner, J.M.C. Pavon, F.S. Rojas, A.G. de Torres, Use of flow injection cold vapour generation and preconcentration on silica functionalized with methylthiosalicylate for the determination of mercury in biological samples and sea-water by inductively coupled plasma atomic emission spectrometry, Journal of Analytical Atomic Spectrometry, 13 (1998) 1167-1171.
[28] W. Ngeontae, W. Aeungmaitrepirom, T. Tuntulani, Chemically modified silica gel with aminothioamidoanthraquinone for solid phase extraction and preconcentration of Pb(II), Cu(II), Ni(II), Co(II) and Cd(II), Talanta, 71 (2007) 1075-1082.
[29] R. Alexandrescu, F. Dumitrache, I. Morjan, I. Sandu, M. Savoiu, I. Voicu, C. Fleaca, R. Piticesu, TiO2 nanosized powders by TiCl4 laser pyrolysis, Nanotechnology, 15 (2004) 537-545.
[30] W.J. Stark, A. Baiker, S.E. Pratsinis, Nanoparticle opportunities: Pilot-scale flame synthesis of

vanadia/titania catalysts, Particle & Particle Systems Characterization, 19 (2002) 306-311.
[31] R.P. Das, S. Anand, Preparation of fine particles through aqueous processing route, Indian Journal of Physics and Proceedings of the Indian Association for the Cultivation of Science-Part A, 78A (2004) 165-174.
[32] K. Okuyama, I.W. Lenggoro, Preparation of nanoparticles via spray route, Chemical Engineering Science, 58 (2003) 537-547.
[33] E. Hosono, S. Fujihara, T. Kimura, H. Imai, Non-basic solution routes to prepare ZnO nanoparticles, Journal of Sol-Gel Science and Technology, 29 (2004) 71-79.
[34] P. Tartaj, L.C. De Jonghe, Preparation of nanospherical amorphous zircon powders by a microemulsion-mediated process, Journal of Materials Chemistry, 10 (2000) 2786-2790.
[35] A. Rahman, D. Seth, S.K. Mukhopadhyaya, R.L. Brahmachary, C. Ulrichs, A. Goswami, Surface functionalized amorphous nanosilica and microsilica with nanopores as promising tools in biomedicine, Naturwissenschaften, 96 (2009) 31-38.
[36] M.K. Bruska, K. Szacilowski, J. Piechota, Adsorption of selected ions on the anatase TiO2 (101) surface: a density-functional study, CCP5 Annual Conference on Surfaces and Interfaces, Taylor & Francis Ltd, London, ENGLAND, 2009, pp. 567-576.
[37] Y.Q. Zhang, L.B. Shan, Z.Y. Tu, Y.H. Zhang, Preparation and characterization of novel Ce-doped nonstoichiometric nanosilica/polysulfone composite membranes, Separation and Purification Technology, 63 (2008) 207-212.
[38] W. Stober, A. Fink, E. Bohn, Controlled growth of monodisperse silica spheres in the micron size range, Journal of Colloid and Interface Science, 26 (1968) 62-69.
[39] A. Vanblaaderen, J. Vangeest, A. Vrij, Monodisperse Colloidal Silica Spheres from Tetraalkoxysilanes - Particle Formation and Growth-Mechanism, Journal of Colloid and Interface Science, 154 (1992) 481-501.
[40] T. Matsoukas, E. Gulari, Dynamics of Growth of Silica Particles from Ammonia-Catalyzed Hydrolysis of Tetra-Ethyl-Orthosilicate, Journal of Colloid and Interface Science, 124 (1988) 252-261.
[41] C.F. Zukoski, J.L. Look, G.H. Bogush, Formation of Uniform Precipitates from Alkoxides, in: H.F. Bergna (Ed.) The Colloid Chemistry of Silica, Oxford University Press, Oxford, 1994, pp. 451-465.
[42] C.F. Zukoski, G.H. Bogush, J.L. Look, Uniform Particle Formation from Alkoxides - Mechanisms of Growth, Abstracts of Papers of the American Chemical Society, 200 (1990) 261-COLL.
[43] T. Tsoncheva, I. Genova, M. Stoyanova, M.-M. Pohl, R. Nickolov, M. Dimitrov, E. Sarcadi-Priboczki, M. Mihaylov, D. Kovacheva, K. Hadjiivanov, Effect of mesoporous silica topology on the formation of active sites in copper supported catalysts for methanol decomposition, Applied Catalysis B-Environmental, 147 (2014) 684-697.
[44] L. Tang, Y. Fang, Y. Pang, G. Zeng, J. Wang, Y. Zhou, Y. Deng, G. Yang, Y. Cai, J. Chen, Synergistic adsorption and reduction of hexavalent chromium using highly uniform polyaniline-magnetic mesoporous silica composite, Chemical Engineering Journal, 254 (2014) 302-312.
[45] G.H. Bogush, M.A. Tracy, C.F. Zukoski, Preparation of Monodisperse Silica Particles - Control of Size and Mass Fraction, Journal of Non-Crystalline Solids, 104 (1988) 95-106.
[46] A. Van Blaaderen, J. Van Geest, A. Vrij, Monodisperse colloidal silica spheres from tetraalkoxysilanes: Particle formation and growth mechanism, Journal of Colloid and Interface Science, 154 (1992) 481-501.
[47] S.L. Chen, P. Dong, G.H. Yang, J.J. Yang, Kinetics of formation of monodisperse colloidal silica particles through the hydrolysis and condensation of tetraethylorthosilicate, Industrial & Engineering Chemistry Research, 35 (1996) 4487-4493.
[48] C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli, J.S. Beck, Ordered Mesoporous Molecular-Sieves Synthesized by a Liquid-Crystal Template Mechanism, Nature, 359 (1992) 710-712.
[49] J.S. Beck, J.C. Vartuli, W.J. Roth, M.E. Leonowiez, C.T. Kresge, K.D. Schmitt, C.T. Chu, D.H. Olson, E.W. Sheppard, S.B. Higgins, J.L. Schlenker, mesoporous silica, Journal of American Chemical Society, 114 (1992) 10884.
[50] D.H. Chen, C.Z. Huang, M. He, B. Hu, Separation and preconcentration of inorganic arsenic species in natural water samples with 3-(2-aminoethylamino) propyltrimethoxysilane modified ordered mesoporous silica micro-column and their determination by inductively coupled plasma optical emission spectrometry, Journal of Hazardous Materials, 164 (2009) 1146-1151.
[51] A.M. Burke, J.P. Hanrahan, D.A. Healy, J.R. Sodeau, J.D. Holmes, M.A. Morris, Large pore bi-functionalised mesoporous silica for metal ion pollution treatment, Journal of Hazardous Materials, 164 (2009) 229-234.
[52] S. Pas, S. Bhunia, T. Maity, S. Koner, Suzuki cross-coupling reaction over Pd-Schiff-base anchored mesoporous silica catalyst, Journal of Molecular Catalysis a-Chemical, 394 (2014) 188-197.
[53] T. Ben Amor, I. Dhaouadi, B. Lebeau, M. Tlili, M. Ben Amor, Synthesis, characterization and application of glucamine-modified mesoporous silica type SBA-15 for the removal of boron from natural water, Desalination, 351 (2014) 82-87.
[54] M.R. Awual, M.M. Hasan, T. Ihara, T. Yaita, Mesoporous silica based novel conjugate adsorbent for efficient selenium(IV) detection and removal

from water, Microporous and Mesoporous Materials, 197 (2014) 331-338.
[55] M. Sadia, M.R. Jan, J. Shah, G.M. Greenway, Simultaneous preconcentration and determination of nickel and cobalt using functionalised mesoporous silica spheres by ICP-OES, International Journal of Environmental Analytical Chemistry, 93 (2013) 1537-1556.
[56] H. Aghayan, A.R. Mahjoub, A.R. Khanchi, Immobilization of Tin (IV) molybdophosphate onto mesoporous silica SBA-15 and its application on strontium removal from aqueous solution, Applied Surface Science, 261 (2012) 14-20.
[57] D.H. Chen, B. Hu, C.Z. Huang, Chitosan modified ordered mesoporous silica as micro-column packing materials for on-line flow injection-inductively coupled plasma optical emission spectrometry determination of trace heavy metals in environmental water samples, Talanta, 78 (2009) 491-497.
[58] D. Perez-Quintanilla, I. Del Hierro, M. Fajardo, I. Sierra, Cr(VI) adsorption on functionalized amorphous and mesoporous silica from aqueous and non-aqueous media, Materials Research Bulletin, 42 (2007) 1518-1530.
[59] M.M. Algaradah, The Development of Nano-sized Silicas as Analytical Tools, 2011.
[60] D.P. Ferris, P.R. McGonigal, L.S. Witus, T. Kawaji, M.M. Algaradah, A.R. Alnajadah, M.S. Nassar, J.F. Stoddart, Oxime Ligation on the Surface of Mesoporous Silica Nanoparticles, Organic Letters, 17 (2015) 2146-2149.
[61] I.R. Fernando, D.P. Ferris, M. Frasconi, D. Malin, E. Strekalova, M.D. Yilmaz, M.W. Ambrogio, M.M. Algaradah, M.P. Hong, X. Chen, M.S. Nassar, Y.Y. Botros, V.L. Cryns, J.F. Stoddart, Esterase- and pH-responsive poly([small beta]-amino ester)-capped mesoporous silica nanoparticles for drug delivery, Nanoscale, (2015).
[62] S. Brunauer, H. Emmett, E. Teller, surface area BET, Journal of the American Chemical Society, 60 (1938) 309.
[63] P.B. Balbuena, K.E. Gubbins, Theoretical Interpretation of Adsorption Behavior of Simple Fluids in Slit Pores, Langmuir, 9 (1993) 1801-1814.
[64] V. Rebbin, M. Jakubowski, S. Potz, M. Froba, Synthesis and characterisation of spherical periodic mesoporous organosilicas (sph-PMOs) with variable pore diameters, Microporous and Mesoporous Materials, 72 (2004) 99-104.
[65] Y. Yamada, K. Yano, Synthesis of monodispersed super-microporous/mesoporous silica spheres with diameters in the low submicron range, Microporous and Mesoporous Materials, 93 (2006) 190-198.
[66] S. Zheng, L. Gao, J.K. Guo, Synthesis and characterization of copper(II)-phenanthroline complex grafted organic groups modified MCM-41, Materials Chemistry and Physics, 71 (2001) 174-178.
[67] H. Chen, S.X. Zhou, G.X. Gu, L.M. Wu, Modification and dispersion of nanosilica, Journal of Dispersion Science and Technology, 25 (2004) 837-848.
[68] T. Shamim, M. Gupta, S. Paul, The oxidative aromatization of Hantzsch 1,4-dihydropyridines by molecular oxygen using surface functionalized silica supported cobalt catalysts, Journal of Molecular Catalysis a-Chemical, 302 (2009) 15-19.
[69] A.E. Martell, M. Calvin, Chemistry of the metal chelate compounds, 2nd ed., Prentice-Hall, New York, 1953.