

Electronic Supplementary Information for “Cysteine Methyl Ester Modified Carbon Spheres for Removal of Toxic Heavy Metals from Aqueous Media”

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1. Experimental

1.1 Reagents and Chemicals

All chemicals used were of analytical grade and were used as received without any further purification. These were: sodium (meta) arsenite, (Fluka, +99.0%) and nitric acid (Aldrich, 70%, double distilled PPB/Teflon grade with trace metal impurities in parts per trillion determined by ICP-MS), cadmium (II) nitrate (Aldrich, 99%), copper (II) sulphate (Aldrich, 99%) sodium acetate (Sigma-Aldrich, 3M stock solution, 0.2 µm filtered), phosphoric acid (Aldrich, 85% w/w in water stock solution) potassium chloride (Reidel de Haan, 99%). All solutions were prepared with deionised water of resistivity not less than 18.2 MΩ cm (Vivendi water systems, UK). A sample of drinking water was obtained from Bangladesh and a sample of river water was taken from the River Cherwell, Oxford.

1.2 Cysteine Methyl Ester Coupling Protocol to Glassy Carbon Spherical Powder (Scheme 1)

2g GC spherical powder (10-20 µm diameter, Type I, Alfa Aesar, UK) was stirred with 10 cm³ SOCl₂ for 1 hour after which it was washed with dry CHCl₃. This converts the surface carboxyl groups to acyl-chlorides. This material was then treated with 0.5g of L-cysteine methyl ester hydrochloride (Sigma-Aldrich, UK) in 10 cm³ dry CH₂Cl₂, with stirring and the slow addition of 0.27 cm³ dry Et₃N. The reaction mixture was then stirred for 12 hours (overnight), filtered and washed with copious

amounts of CHCl_3 and then pure water to produce cysteine methyl ester derivatised GC spherical powder (CysOMe-GC).

1.3 Linear Sweep Stripping Protocol for the Detection of Cadmium(II)

The linear sweep voltammetry (LSV) stripping protocol used here is based on a previous detection protocol.¹ A Boron doped diamond electrode (BDD, diameter = 3mm, Windsor Scientific, UK) was used as the working electrode, with a platinum coil and saturated calomel electrode (SCE, Radiometer, Copenhagen, Denmark) acting as counter and reference electrodes respectively. The electrochemical experiments were carried out using a computer controlled potentiostat ($\mu\text{Autolab}$, Utrecht, Netherlands) in pH 5.04 0.05M sodium acetate buffer with 0.1 M KCl added as supporting electrolyte.

LSV detection of Cd(II) was carried out using the following parameters: a 10 μL aliquot of the sample to be tested was added to 10 cm^3 of the sodium acetate buffer. Cadmium was deposited onto the BDD electrode at a potential of -1.5 V vs. SCE, for 60 s with stirring. The potential was then swept at 100 mVs^{-1} from -1.1 V to -0.6 V vs. SCE with a cadmium stripping peak observed at *ca.* -0.780 V vs. SCE. Standard additions of 0.1 μM Cd(II) were then added over the range 0.1-1.0 μM and a corresponding addition plot was constructed and used to calculate the background Cd(II) concentration in the original sample. A control experiment was performed before each sample was exposed to the carbon powder to ensure the concentration of Cd(II) determined by the standard additions method was correct to within the detection limits of the procedure.

1.4 Square Wave Stripping Protocol for the Detection of Copper(II)

The square wave voltammetry (SWV) stripping protocol used here is based on a previous detection protocol.² A 50 μm diameter gold disc electrode (<99.99%, Goodfellow, Cambridge, UK) was used as the working electrode, with a platinum coil and saturated calomel electrode (SCE, Radiometer, Copenhagen, Denmark) acting as counter and reference electrodes respectively. The electrochemical experiments were carried out using a computer controlled potentiostat ($\mu\text{Autolab}$, Utrecht, Netherlands) in pH 2.00 0.1 M phosphoric acid (H_3PO_4) buffer with 0.1 M KCl added as supporting electrolyte.

SWV detection of Cu(II) was carried out using the following parameters: Frequency 50 Hz, step potential 2 mV, amplitude 25 mV. A 0.5 cm³ aliquot of the sample to be tested was added to 9.5 cm³ of the phosphoric acid buffer. Copper was deposited onto the working electrode at a potential of -1.5 V vs. SCE, for 15 s with stirring. The potential was then swept -1.0 V to +0.6 V vs. SCE with a copper stripping peak observed at *ca.* -0.05 V vs. SCE. Standard additions of 1.0 μM Cu(II) were then added over the range 1.0-10.0 μM and a corresponding addition plot was constructed and used to calculate the background Cu(II) concentration in the original sample. A control experiment was performed before each sample was exposed to the carbon powder to ensure the concentration of Cu(II) determined by the standard additions method was correct to within the detection limits of the procedure.

1.5 Anodic Stripping Voltammetry for As(III) Detection

Voltammetric measurements were carried out using a μ-Autolab (III) (ECO-Chemie, Utrecht, The Netherlands) potentiostat. All measurements were conducted using a three electrode cell. The working electrode was a gold micro disk electrode (1mm diameter), which was constructed in house by sealing a gold wire into Teflon housing. The counter electrode was a bright platinum wire, with a saturated calomel electrode (Radiometer, Copenhagen, Denmark) as the reference. The gold electrode was polished using a 0.1 μm alumina slurry on a soft lapping pad.

An ultrasonic horn, model CV 26 (Sonics and Materials Inc. USA) operating at a frequency of 20 kHz fitted with a 3mm diameter titanium alloy microtip (Jencons Leyton Buzzard, UK) was used for sonovoltammetric studies. The intensity of the ultrasound was determined calorimetrically³⁻⁵ and was found to be 57 Wcm⁻² at 10%. The working electrode was placed in a face-on arrangement to the ultrasonic horn and the horn was immersed beyond the shoulder of the stepped tip to ensure that ultrasound was efficiently applied to the solution. For arsenic detection the voltammetric curves were baseline corrected using autolab software, which utilises a third-order polynomial correction. A control experiment was performed before each sample was exposed to the carbon powder to ensure the concentration of As(III) determined by the standard additions method was correct to within the detection limits of the procedure.

2. Removal of Cd(II) and Cu(II) from Various “Real” Aqueous Media

2.1 Removal of Cadmium from “Real” Media: River Water

In order to demonstrate that CysOMe-GC was a suitable material for the removal of toxic heavy metal ions in aqueous media we investigated the removal of Cd(II) from “real” samples. The first “real” matrix was a sample of river water taken (untreated) from the River Cherwell in Oxford. A stock solution of this river water was spiked to produce a cadmium(II) concentration of *ca.* 1.5 mM to simulate an environmentally disastrous spillage of toxic cadmium waste. 10 mg of CysOMe-GC powder was then added to 10 cm³ samples of this “real” matrix and stirred for varying times (5, 10, 20 minutes etc.) up to 1 hour. At the end of each sample’s allotted exposure time the sample was filtered and a 10 µL aliquot of the filtrate removed for analysis using the LSV Cd(II) stripping protocol given above. The entire experiment was repeated three times and the results averaged with error bars shown. Figure 2a in the communication shows the resulting Cd(II) concentration profile.

It is apparent that *ca.* 87% of the Cd(II) has been removed from the sample by 10 mg of CysOMe-GC powder. This demonstrates the proof of concept that CysOMe-GC powder could be used as a cheap and highly effective material for use in environmental clean up and/or metal ion sequestration.

2.2 Removal of Cadmium from “Real” Media: Mineral Water

In order to demonstrate the utility of CysOMe-GC powder for drinking water filtration we simulated contamination of drinking water supplies by spiking a stock solution of Evian mineral water Cd(II) to produce a Cd(II) concentration of 50 ppb which is ten times the EPA recommended maximum limit for drinking water. 10 cm³ samples of this “real” matrix were then stirred for varying times with 10 mg CysOMe-GC powder and analysed as in section 1.3. The entire experiment was repeated three times and the results averaged with error bars shown. The resulting removal of Cd(II) is shown in figure 2b in the communication.

Within ten minutes of exposure to CysOMe-GC powder the Cd(II) concentration in the mineral water was below the EPA recommended maximum limit of 5 ppb. Thus we have demonstrated the proof of concept that CysOMe-GC is an excellent material for use in drinking water filtration to remove toxic heavy metals such as Cd(II).

2.3 Removal of Copper from “Real” Media: River Water

A 10 cm³ sample of River Cherwell water (untreated) was analysed using the SWV copper stripping protocol outlined in section 1.4 and found to have a Cu(II) concentration of *ca.* 30 μM which is just above the EPA limit of 1.3 mg L⁻¹ or 20.1 μM and was therefore used without spiking the Cu(II) concentration. Again 10 cm³ samples were exposed to 10 mg of CysOMe-GC balls and analysed at various intervals for one hour to measure the remaining Cu(II) concentration. The entire experiment was repeated three times and the results averaged with error bars shown. Figure 2a in the communication shows the resulting removal of Cu(II) from the sample.

It is apparent that CysOMe-GC is an excellent chelator of Cu(II) ions removing all the detectable Cu(II) from the river water sample.

2.4 As (III) Removal with CysOMe-GC Spherical Powder

2.4.1 High As(III) Concentrations in the mM Region

A 0.98 mM solution of As(III) was prepared from sodium (meta) arsenite dissolved in ultra pure water at pH 5.4, 25 mL of the solution was placed in a stirred flask to which 10 mg of the CysOMe-GC powder was added. At intervals of 10, 20 and 60 minutes, a 50 μL sample was taken from the solution which was then diluted down in 0.1 M nitric acid to trace levels for analysis.

Figure ESI.1 shows the reduction in As (III) concentration over time, after 60 minutes of stirring the concentration of As (III) has dropped from 0.98 mM to 0.7 mM a 29 % decrease. The solution was then left 3 days without further stirring however no further decrease in arsenic concentration was found after this time.

2.4.2 Trace As(III) Levels

Experiments were then carried out at trace levels such that would be expected to be found in drinking water from areas such as Bangladesh⁷. A sample was prepared to an As (III) level of 200 ppb (2.66 μM) 4 times greater than the Bangladesh limit of 50 ppb. 200 mg of CysOMe-GC powder was then placed in 25 mL of the sample which was then stirred for a specified length of time before filtration of the CysOMe-GC powder using filter paper in order to stop the complexation of As (III) by cysteine. The sample was then diluted 1:1 into a 0.1 M nitric acid solution for analysis.

Figure ESI.2 shows that after only ten minutes the arsenic concentration has been significantly reduced by the balls from 200 ppb to 77 ppb, after 30 minutes the level has dropped to 55 ppb. Analysis at 60 minutes shows that the concentration of arsenic has remained constant at this level; a 73 % decrease.

2.4.3 Bangladesh Well Water Sample

A real sample was then used to test the ability of the CysOMe-GC powder to complex arsenic in an authentic Bangladesh well water sample. The sample was first tested by our ASV method to determine the concentration of As (III) present. However the concentration of As (III) was found to be below the detectable limit (1×10^{-8} M), therefore the water sample was spiked to a value of 120 ppb for use in the experiments. As in the previous experiments 200 mg of the CysOMe-GC powder was added to 25 mL of the water sample which was then stirred for a specified time (5, 10, 30 and 45 minutes), before being filtrated to remove the powder from the solutions. Once again the sample was diluted 1:1 into 0.1 M nitric acid for the analysis experiments.

Figure 1 in the communication shows the results of the analysis fitted to a 1st order exponential decay. After only 5 minutes of stirring the concentration of arsenic present has dropped by 47% to 64 ppb, at 10 minutes the concentration is found to have dropped further by 69% to 38 ppb – 12 ppb below the Bangladesh safe drinking limit. After 45 minutes the drop in concentration has levelled off at 34 ppb, or 28 % of the original value. As the analysis was conducted in a real sample rather than pure water the experiment was exposed to many trace metals generally found in Bangladesh water supplies (Copper, Lead, Mercury etc.).⁷ Figure ESI.4 shows the ASV plots from the analysis of the 30 minute sample, a large stripping wave can be seen at approximately 0.4 V vs. SCE, due to one of these contaminants.

3. Figures

Figure ESI.1

Concentration of As (III) remaining after exposure to 10mg of CysOMe-GC spherical powder, stirred for specified lengths of time. The curve shows a 1st order exponential decay fitted to the data.

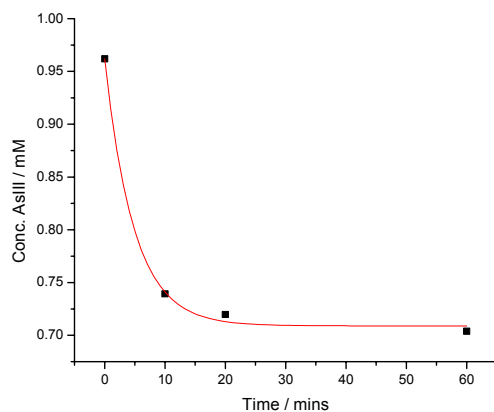


Figure ESI.2

Concentration of As (III) remaining after exposure to 200mg of CysOMe-GC spherical powder to a 200ppb As II solution, stirred for specified lengths of time. The curve shows a 1st order exponential decay fitted to the data.

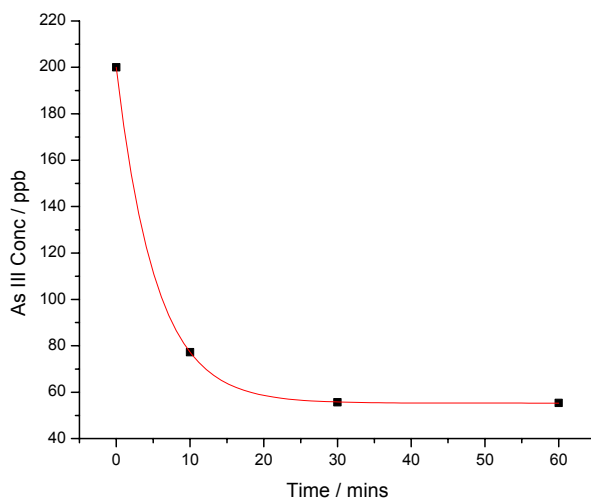


Figure ESI.3

Concentration of As (III) remaining after exposure to 200mg of CysOMe-GC spherical powder to a 120ppb As (III) solution in a Bangladesh water sample, stirred for specified lengths of time. The curve shows a 1st order exponential decay fitted to the data.

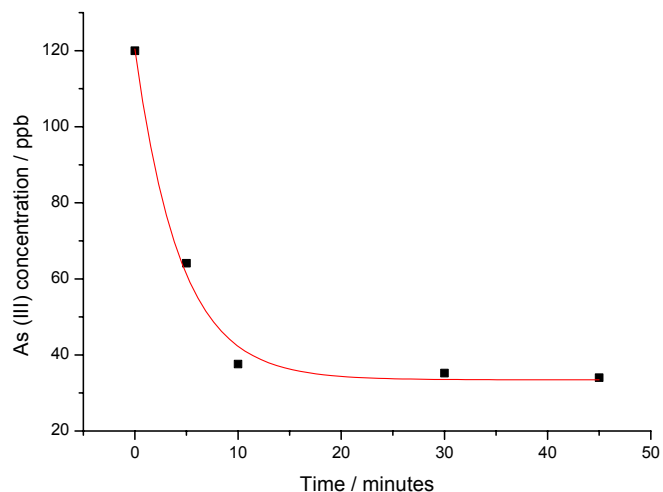
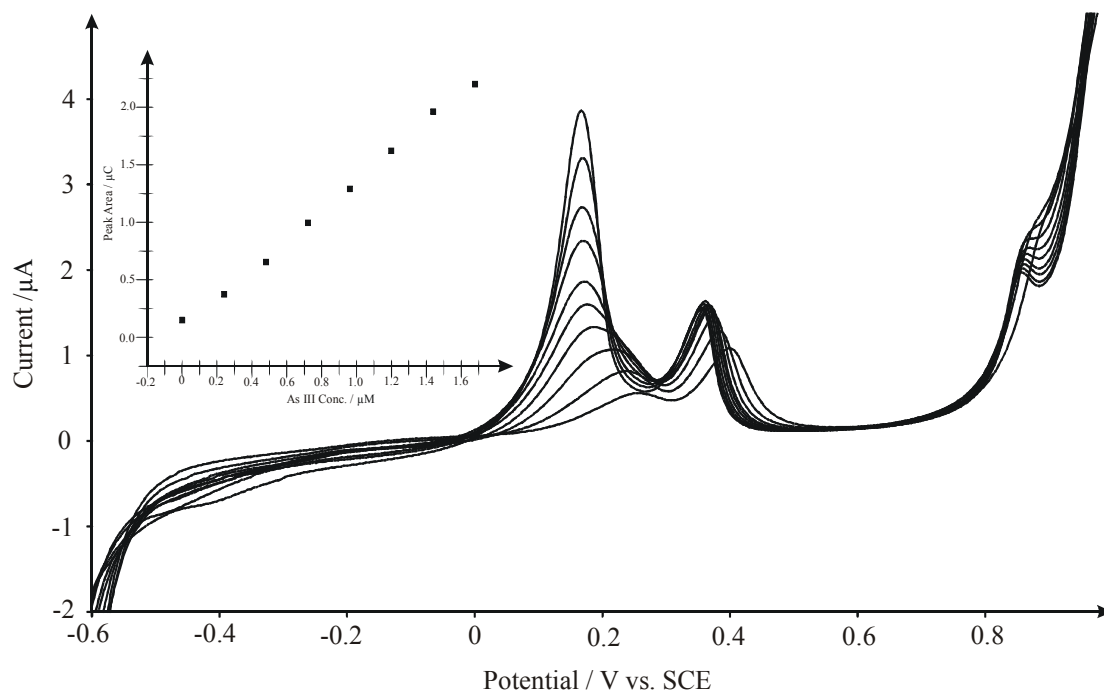


Figure ESI.4



Anodic Stripping Voltammograms of a 120ppb As (III) Bangladesh water sample exposed to 200mg of CysOMe-GC spherical powder and stirred for 30 minutes. LSV performed at 100mV/s, standard additions of 2.4×10^{-7} M used.

4. References

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