FULL PAPERS

Removal of Toxic Metal-Ion Pollutants from Water by Using Chemically Modified Carbon Powders**

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Abstract: The thermodynamics of and the kinetic parameters controlling the sequestration of the toxic heavy-metal ion Cd[II] from aqueous media by using a novel material consisting of glassy carbon microspheres (10–20 μm in diameter) chemically modified with L-cysteine methyl ester are presented. In an effort to reduce the cost and increase the efficiency of toxic-metal-ion removal, this modification strategy was expanded to attach L-cysteine methyl ester to less-expensive graphite powders (2–20 μm in diameter), and the thermodynamic and kinetic parameters of the sequestration of Cd[II], Cu[II], and As[III] toxic metal ions are presented. It was found that the use of chemically modified graphite powder greatly increased both the rate and the amount of metal ions removed from aqueous media. This work has important potential applications to filtration of drinking water and environmental remediation.

Keywords: adsorption · arsenic · cadmium · copper · modified carbon · water detoxification

Introduction

The accumulation and release of toxic substances into the environment, particularly toxic heavy metals, has increased significantly over the past few decades, mainly due to human activities such as mining and the rapid industrialization of countries around the globe, for example, in developing countries such as India and China.[1–7] The environmental impact of mining operations[2,3] and heavy industry[4,5] is leading to the accumulation of high concentrations of toxic heavy-metal ions such as Cu[II], Cd[II], Pb[II], and Hg[II] in lakes and rivers owing to the largely nondegradable and recirculating nature of these pollutants.[7,8,9] The presence of heavy metals in aquatic media and drinking water are potentially dangerous to the health of both humans and aquatic life, depending on the exposure levels and chemical form of the heavy metal.

The potentially damaging impact of heavy-metal release from mining activities was illustrated in 1998 when 5 million cubic meters of acidic waste water containing high concentrations of Pb[II], Cu[II], Zn[II], and Cd[II] was accidentally spilt from a mining reservoir in Andalusia, southwestern Spain. The spill polluted up to 185 000 acres of warm marshland in the Coto de Do'ana National Park, which is home to some 250 species of migratory birds and is a World Heritage Site.[3] The clearest example of the tragic human consequences of heavy-metal pollution is the widespread poisoning of millions of people in countries such as Argentina, China, Mexico, Taiwan, India, and in particular Bangladesh, where up to 60% of the Bangladeshi groundwater contains naturally occurring arsenic concentrations greatly in excess of the World Health Organization (WHO) guidelines of 10 ppb.[10,11]

As many salts of these heavy-metal ions are water-soluble, common physical methods of separation are rendered ineffective. Therefore, there is a pressing need to develop a facile, rapid, and inexpensive method of removing toxic heavy-metal ions from aqueous media for filtration of drinking water and/or environmental cleanup.

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[**] Progress towards an optimized system with L-cysteine methyl ester.

Much of the research efforts of the scientific community have been focused on removing As[III] and As[V] from drinking water. For example, in the recently highlighted work of Al Rmalli et al., powdered water hyacinth roots were found to reduce the concentration of arsenic below the WHO guidelines within one hour of exposure.[12] Holcombe and co-workers demonstrated that polypeptides such as poly-L-histidine,[13] poly-L-aspartic acid,[14] poly-L-glutamic acid,[14] and in particular, poly-L-cysteine are able to chelate metal ions such as Cd[II], Pb[II], Ni[II] and Cu[II];[15–18] this work has been used for trace analysis of these metals. These efforts inspired us to develop a method for the bulk surface modification of graphite powder with poly-L-cysteine (PCcarbon). Subsequently, we showed that this material could remove considerable quantities of Cd[II] ions from aqueous media.[19] However, biohomopolymers are prohibitively expensive and difficult to manufacture on a large scale. To overcome these problems, Gooding and co-workers used monomeric amino acids as well as polypeptides covalently attached to electrode surfaces to detect metal ions such as Cu[II] at sub-ppb levels; however, they have not used this approach for metal-ion sequestration.[20–23] Therefore, we developed a simple and facile technique to attach covalently a monomeric analogue of poly-L-cysteine, namely, L-cysteine methyl ester (CysOMe; MeOOCCH(CH$_2$SH)NH$_2$), onto the surface of glassy carbon microspheres (10–20 μm in diameter, CysOMe-GC). We found that this material was capable of removing similar amounts of Cd[II] ions as PCcarbon, whilst also removing Cu[II] and, most importantly, As[III] ions in a rapid and irreversible manner from real aqueous media such as river water and Bangladeshi well-water samples.[24] Furthermore, CysOMe-GC is considerably less expensive to produce than PCcarbon and proffers the possibility of facile scale-up for mass production on an industrial scale.[24]

To optimize this novel "catch-all" material for real-world applications to the filtration of drinking water in countries such as Bangladesh and environmental remediation, we first need to understand both the thermodynamics and the kinetics of metal adsorption by the CysOMe-GC powder. Our initial investigations used the Cu[II] ion as a model heavy-metal-ion pollutant and allowed us to develop both an understanding of the thermodynamic and kinetic parameters that control the uptake of Cu[II] by CysOMe-GC and a more-general theoretical framework within which we were able to model and simulate mathematically adsorption processes at chemically modified carbon spherical microparticles.[25,26]

Herein, we began by studying the thermodynamics and kinetics of Cd[II] removal by CysOMe-GC powder within our theoretical model before attempting to optimize this novel material further, in terms of both efficiency of metal-ion uptake and cost of the material. To this end, we further developed our method of covalently modifying glassy carbon powder with CysOMe to apply it to the bulk surface modification of less-expensive graphite powder. The resulting material, CysOMe-carbon, was first characterized with X-ray photoelectron spectroscopy (XPS) and combustion analysis before the thermodynamic and kinetic parameters of the

uptake of Cu[II], Cd[II], and As[III] were elucidated by using linear-sweep anodic stripping voltammetric (LSASV) analysis, the accuracy of which was confirmed independently with inductively coupled plasma atomic-emission spectroscopy (ICP-AES) where appropriate. It was found that this optimized material binds irreversibly larger quantities of these toxic metal ions and more rapidly than CysOMe-GC. This discovery has important implications for inexpensive methods of heavy-metal-ion sequestration, particularly in developing countries.

Theory

Thermodynamic Analysis

Adsorption isotherms, such as those obtained in the following sections, represent the ratio of the quantity of adsorbate adsorbed to that remaining in solution at equilibrium at a given, fixed temperature. The earliest and simplest known adsorption-isotherm relationships are those provided by Freundlich[27] and Langmuir.[28] The Langmuir adsorption isotherm is given by Equation (1):

$$N_{ads} = \frac{N_{max} K C_{bulk}}{1 + K C_{bulk}} \tag{1}$$

which, when linearized, gives Equation (2):

$$\frac{1}{N_{ads}} = \frac{1}{N_{max}} + \frac{1}{N_{max} K C_{bulk}} \tag{2}$$

where N_{ads} is the number of moles of metal ion adsorbed per milligram of modified carbon powder, N_{max} is the maximum number of moles that can be adsorbed per milligram of powder under the given conditions, C_{bulk} is the concentration of the metal ion remaining in the solution at equilibrium in mol dm^{-3}, and K is an equilibrium constant relating to the affinity between the adsorbate and adsorbent.

The Freundlich isotherm is an empirically derived isotherm given by Equation (3):

$$N_{ads} = K' C_{bulk}^{1/n} \tag{3}$$

or if linearized, by Equation (4):

$$\log N_{ads} = \log K' + \frac{1}{n} \log C_{bulk} \tag{4}$$

where N_{ads} and C_{bulk} have been defined above and K' and n are Freundlich constants relating to the maximum adsorption capacity (which in some treatments can be thought of as a pseudoequilibrium constant by analogy to the Langmuirian model) and the adsorption intensity, respectively. The larger the value of K' and the smaller the value of n (which typically takes values between 1 and 10), the higher the affinity of the adsorbent towards the adsorbate.

Kinetic Analysis

A general mathematical model that describes the irreversible adsorption of a species at chemically modified microparticles under conditions of transient diffusion, steady-state diffusion, and coupled diffusion/convection mass transport was developed by Chevallier et al.[26] Therefore, only the relevant results are presented herein, and the interested reader is directed to reference [26] for the full theoretical treatment.

The conditions employed throughout this work involve coupled diffusion and convective mass transport of an adsorbate (i.e., the metal ion of interest) to the adsorbent (the CysOMe-modified microparticle). The adsorption flux, η (mol cm^{-2}), to the surface of the modified microparticle is given by Equation (5):

$$\eta = \frac{dC_{bulk}}{dt}\bigg|_{t=0} \times \frac{V}{NA_p} \tag{5}$$

where C_{bulk} is the bulk concentration of adsorbate, V is the volume of solution, N is the number of microparticles suspended in the solution, and A_p is the spherically averaged surface area of the microparticles. Under coupled diffusion/convection conditions, η is related to the rate of adsorption of the adsorbate by the adsorbent microparticle, k_{ads}, by substituting Equation (7) into Equation (6) to produce Equation (8):

$$\eta = k_{ads}C_{surface} \tag{6}$$

$$(k_{ads} + k_{mt})C_{surface} = k_{mt}C_{bulk} \tag{7}$$

$$\eta = \left(\frac{k_{mt}k_{ads}}{k_{ads} + k_{mt}}\right)C_{bulk} \tag{8}$$

where k_{mt} is the mass-transfer coefficient and $C_{surface}$ is the concentration of adsorbate at the surface of the modified microparticle. The minimum value of k_{mt} can be calculated by using the modified Frössling equation, Equation (9):

$$k_{mt} = \frac{D}{d_p}\left(2 + 0.6N_{Re}^{1/2}N_{Sc}^{1/3}\right) \tag{9}$$

where D is the diffusion coefficient of the adsorbate, d_p is the diameter of the microparticle, and N_{Re} and N_{Sc} are the Reynolds and Schmidt numbers ($=$ kinematic velocity/D), respectively. Thus, by measuring the initial rate of change of concentration of metal ion from the concentration–time plot for a given initial bulk concentration, and armed with a knowledge of the average number and size of microparticles suspended in a known volume of solution, we can use Equations (5) and (8) to calculate a minimum value of k_{ads}. This value can be calculated owing to the limitation of Equation (9) in providing the minimum value of k_{mt}, which is then incorporated into Equation (8) to find k_{ads}.

Results and Discussion

Characterization of CysOMe-Carbon Powder

As we seek to extend the modification of carbon surfaces by CysOMe to include modified graphite powder, we must first characterize the CysOMe-carbon made as described in the Experimental Section. To this end, we used the sensitive surface-analysis technique of XPS to determine how much, if any, CysOMe had been successfully attached covalently to the graphite surface. A sample of the CysOMe-carbon powder was mounted in the XPS spectrometer as described in the Experimental Section, and a scan was performed from 0–1200 eV (Figure 1). Peak assignments were carried out with the UKSAF[29] and NIST[30] databases.
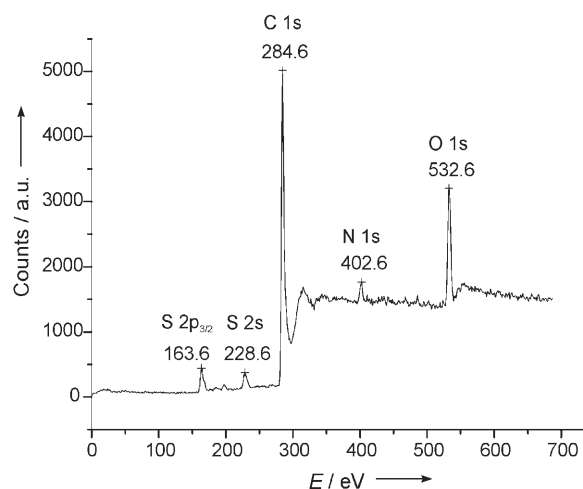

Figure 1. XPS spectrum of L-cysteine methyl ester modified carbon powder.

The percentage surface elemental composition was calculated from the area under each peak in the wide spectrum adjusted by the individual X-ray cross-sectional area of each element. Taking into account the relevant atomic sensitivity factors for the various elements, we found that CysOMe comprises about 10% of the surface elements, with a variation between different sample preparations of $\pm 3\%$. This surface coverage is in good agreement with that obtained with combustion analysis, which gave a surface coverage of CysOMe of 10–14%, and is approximately twice that reported for CysOMe-GC powder.[25]

XPS analysis was also performed on samples of the CysOMe-carbon powder after they were exposed to the highest concentration of Cu^{II}, Cd^{II}, or As^{III} solutions studied (see below) for a period of 30 min. Figure 2 shows the resulting XPS spectrum of CysOMe-carbon after exposure to Cd^{II} over the region where the Cd 3d$_{3/2}$ and 3p$_{3/2}$ and the N 1s and O 1s spectral peaks are observed. The ratio of Cd^{II} to CysOMe (as measured by the nitrogen spectral line areas) were found to be approximately 1:1 after the relative atomic sensitivity factors were taken into account. The XPS results for the other metals studied show a similar stoichometric relationship.
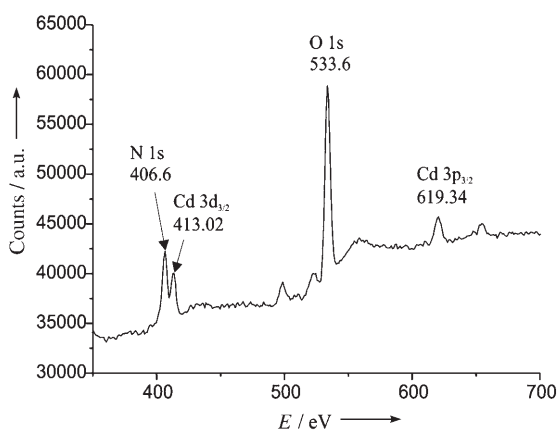
Figure 2. Baseline-corrected XPS spectrum of CysOMe-carbon powder after exposure to Cd^{II}, showing the region of interest from 350 to 700 eV.

Figure 3. Cd^{II} LSASV voltammograms with standard additions of Cd^{II} (0–20 μм, 1 μм increments). Inset: The corresponding standard addition plot.

Thermodynamics and Kinetics of Cd^{II} Removal by CysOMe-GC Powder

To compare the efficacy of CysOMe-carbon powder for both Cu^{II} and Cd^{II}, we must first determine the corresponding parameters for the removal of Cd^{II} by CysOMe-GC powder. The thermodynamic[25] and kinetic[26] parameters that control the sequestration of Cu^{II} by CysOMe-GC powder have already been elucidated as part of our initial investigations.

Previously, we demonstrated that the uptake of Cu^{II}, Cd^{II}, and As^{III} ions by the CysOMe-GC powder is independent of the pH of the solution over pH 1.0–7.0.[26] This pH independence implies that the CysOMe is covalently attached to the carbon surface through the formation of an amide bond rather than a thiol ester bond, and that metal-ion binding occurs through the thiol group. If this were not the case, then, as Gooding and co-workers showed, metal-ion binding to the nitrogen atom would depend strongly on the pK_a of the free amine group within the amino acid.[32] Therefore, for convenience, solutions of cadmium(II) nitrate (Cd-(NO$_3$)$_2$) of varying concentration ($\approx$10, 50, 100, 200, and 500 μм; the exact concentration was determined by LSASV analysis prior to each experiment) were prepared in the same acetate buffer (pH 5.0) as used for the LSASV analysis.

The modified CysOMe-GC powder (25 mg) was stirred in a sample of the solutions of Cd^{II} (25 cm^3) at each concentration studied for various times (2, 5, 10, 20, and 30 min), after which the CysOMe-GC powder was filtered off, and a 10-cm^3 aliquot of the resulting solution of Cd^{II} was analyzed with the LSASV stripping protocol (Figure 3; see Experimental Section) to determine the concentration of Cd^{II} ions remaining in the solution. As shown in Figure 4, within 30 min of exposure to the CysOMe-GC, the Cd^{II} concentration decreased by nearly 70%, which corresponds to an uptake of 88 mg of Cd^{II} per gram of CysOMe-GC. This uptake compares very favorably with that of graphite powder modified with poly-L-cysteine, a vastly more expen-
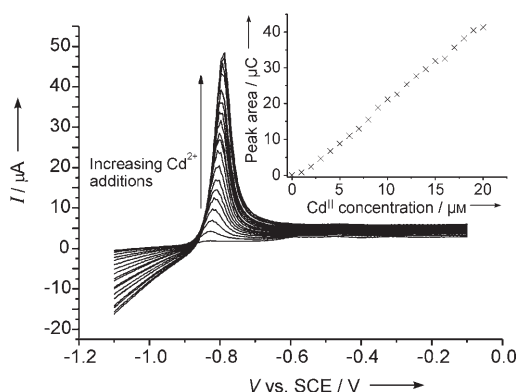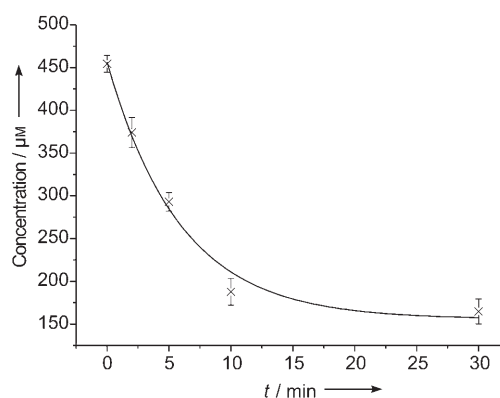

Figure 4. Concentration–time profile for the removal of Cd^{II} (initial concentration $\approx$ 500 μм) by CysOMe-GC.

sive material that requires a complex synthesis, studied under identical conditions.[19]

Concentration–time profiles such as that shown in Figure 4 were constructed for each Cd^{II} concentration studied. In each case, a rapid adsorption of Cd^{II} by the CysOMe-GC powder was observed so that the equilibrium concentration and hence N_{ads} could be determined for each initial value of bulk Cd^{II} concentration, C_{bulk}, studied. The adsorption isotherms were then analyzed with both the Langmuir and the Freundlich model as described earlier. Attempts to fit the experimental data with the linearized Langmuir model [Eq. (2)] resulted in a poor fit that produced physically impossible parameters such as negative values of N_{max}. In contrast, the analysis with a Freundlich isotherm produced an excellent fit to the experimental data (linear least squares regression coefficient = 0.9995) (Figure 5). The values of K' and n were determined to be 0.098 L g^{-1} and 0.90, respectively. When these values are compared with the results obtained for Cu^{II} uptake, where K' and n were found to be 0.18 L g^{-1} and 1.25, respectively, we can see that we have a similar strong affinity for the irreversible adsorption of Cd^{II} by the CysOMe-GC powder and a comparably large uptake.
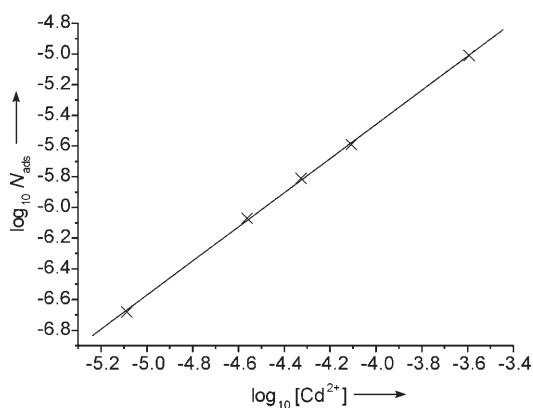
Figure 5. Freundlich plot for the uptake of Cd^{II} by CysOMe-GC.

Thermodynamics and Kinetics of Cu^{II} and Cd^{II} by CysOMe-Carbon Powder

Having established a sufficient understanding of the behavior of CysOMe-GC powder to allow comparisons to be made, we next examined the efficacy of CysOMe-carbon powder in the removal of the model heavy-metal ions Cu^{II}, Cd^{II}, and As^{III} studied so far. Concentration–time profiles were again constructed for the removal of either Cu^{II} from a solution at pH 2.0 or Cd^{II} from a solution at pH 5.0 (for convenience, the pH values used are the same as those for the LSASV analysis as discussed above) by stirring the modified carbon powder (25 mg) in solutions (25 cm^3) of varying concentration for different lengths of time. Again the concentrations used were 5–500 μM, with the exact concentration determined by LSASV analysis prior to commencement of the experiments with graphite powder, and the stirring times were 2–30 min in duration.

Comparison of the concentration–time profiles for the uptake of either Cu^{II} or Cd^{II} between CysOMe-GC and CysOMe-carbon demonstrates that, in every case, the latter removed a greater amount of the metal ions more rapidly (Figure 6). This can be attributed to the greater surface coverage of CysOMe on graphite powder ($\approx$10–14%) compared to glassy carbon powder ($\approx$7%).
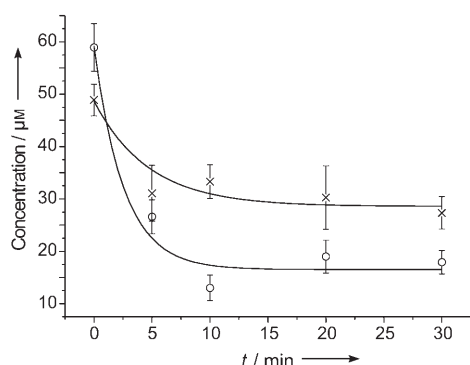

Figure 6. Concentration–time profiles for the removal of Cd^{II} from a solution of Cd(NO$_3$)$_2$ (55 μM) in acetate buffer (pH 5.0), comparing the efficacy of CysOMe-GC and CysOMe-carbon powder adsorbents. × = Treated with CysOMe-GC spheres, ○ = treated with CysOMe-carbon powder.

The experimental data was analyzed with both the Langmuir and the Freundlich isotherm models, and again it was found that the experimental data fitted the Freundlich isotherm model best (Figure 7). A comparison of the thermodynamic parameters obtained for both CysOMe-GC and CysOMe-carbon for Cu^{II} and Cd^{II} uptake is given in Table 1.
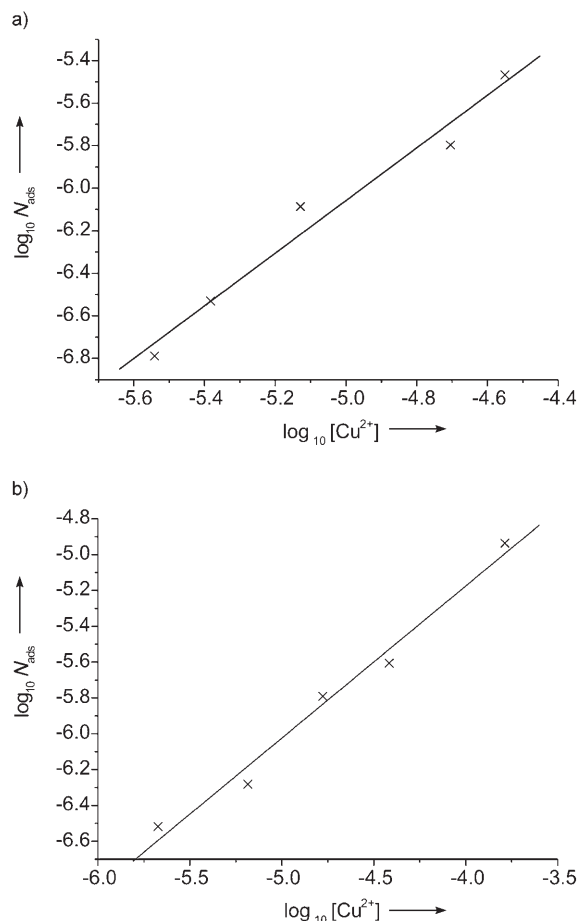

Figure 7. Freundlich plots for the removal of a) Cu^{II} and b) Cd^{II} by CysOMe-carbon powder.

Table 1. A comparison of the thermodynamic parameters derived from the Freundlich isotherm model for the uptake of Cu^{II} and Cd^{II} by both CysOMe-GC and CysOMe-carbon.

Modified carbon powder	Metal ion	K' [Lg^{-1}]	n
CysOMe-GC[a]	Cu^{II}	0.182	1.25
CysOMe-carbon	Cu^{II}	0.136	0.809
CysOMe-GC	Cd^{II}	0.098	0.90
CysOMe-carbon	Cd^{II}	0.167	1.18

[a] Data taken from reference [25].

The rate of metal-ion adsorption by CysOMe-carbon was determined at each concentration studied as described previously by using the initial rate of metal-ion adsorption from the corresponding concentration–time profile. The average adsorption rate constant of both Cu^{II} and Cd^{II} by both CysOMe-GC and CysOMe-carbon is shown in Table 2 for

Table 2. A comparison of the average adsorption rate constant, k_{ads}, measured for the uptake of Cu^{II} and Cd^{II} by CysOMe-GC and CysOMe-carbon powders.

Modified carbon powder	Metal ion	k_{ads} [cm s^{-1}]
CysOMe-GC[a]	Cu^{II}	2×10^{-4}
CysOMe-carbon	Cu^{II}	6×10^{-4}
CysOMe-GC	Cd^{II}	3×10^{-4}
CysOMe-carbon	Cd^{II}	6×10^{-4}

[a] Data taken from reference [25].

comparison. It is apparent that the rate of metal-ion adsorption by CysOMe-carbon is significantly greater than for the CysOMe-GC powder.

The faster adsorption kinetics of CysOMe-carbon compared to the CysOMe-GC powder can be related to the increased surface coverage of CysOMe on the graphite particles, which is approximately double that of the GC microspheres. This implies that for the following equilibrium process [Eq. (10)]:

$$C_{support} - CysOMe_{(s)} + Metal\ ion_{(aq)} \rightleftharpoons$$
$$C_{support} - CysOMe - Metal\ ion_{(s)} \quad (10)$$
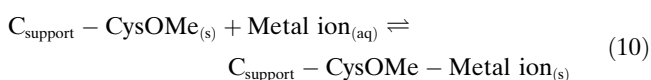
with an overall adsorption rate equation defined as follows [Eq. (11)]:

$$-\frac{d[M^{n+}]_{(aq)}}{dt} = k_{ads}[M^{n+}]_{(aq)}^{a}[CysOMe]_{surf}^{b} \quad (11)$$

the rate of adsorption is approximately first order with respect to the surface concentration of CysOMe.

Control experiments with both unmodified and oxidized graphite powder (treated with HNO$_3$) were carried out and demonstrated that the adsorption of metal ions in these cases was immeasurably small. Having conclusively demonstrated that our novel CysOMe-carbon is a more-effective material for the removal of model divalent cations such as Cu^{II} and Cd^{II} than the CysOMe-GC that we initially developed, we now focused our attention on the ability of CysOMe-carbon to remove large quantities of the priority toxic heavy-metal pollutant As^{III} rapidly and effectively.

Adsorption of As^{III} by CysOMe-Carbon Powder

Previously, it was observed that the adsorption of As^{III} by CysOMe-GC required greater amounts of this material than used for the adsorption of other divalent metal ions, and this probably reflects a more-complex binding mechanism of As^{III} by the CysOMe groups. Therefore, to measure the uptake of As^{III} by CysOMe-carbon, the modified carbon powder (40 mg) was stirred in solutions (20 cm^3) of various concentrations of arsenic (10–150 μM) for times ranging from a few minutes to several hours. After that, the powder was filtered off, and the solution was analyzed by LSASV to determine the concentration of As^{III} remaining (see Experimental Section). A set of samples that were analyzed by the LSASV method was also sent for analysis of their As^{III} con-

centration with ICP-AES. Reassuringly, the results of the ICP-AES analysis were found to be in good agreement (within 5%) with those obtained by LSASV, thereby demonstrating that the electroanalytical protocol produced accurate and reliable results. Again thermodynamic and kinetic analyses were performed as described above. The uptake of As^{III} by CysOMe-carbon was found to obey a Freundlich isotherm model with values of K' and n of 2.8×10^{-3} L g^{-1} and 1.25, respectively. It is clear that whilst the affinity or binding strength of CysOMe for the arsenite ion is as strong as for other metal ions ($n = 1.25$), the maximum adsorption or pseudoequilibrium constant for the removal of As^{III} is considerably smaller. Thus, whilst the adsorption of As^{III} by CysOMe-carbon remains strongly irreversible, greater amounts of the material are required to remove a comparable amount of As^{III} than other solvated divalent metal ions such as Cu^{II} or Cd^{II} from the same volume of solution, as was observed. The kinetic adsorption rate constant was found to be about 2×10^{-5} cm s^{-1}, which is an order of magnitude slower than for the adsorption of the divalent metal ions studied.

Removal of Trace Amounts of As^{III} to Below the WHO Limit

Next, we investigated whether CysOMe-carbon is capable of rapidly lowering the concentration of arsenic in solution from a typically high level of 50–100 ppb to below the WHO-recommended maximum limit of 10 ppb.[10] This is an important requirement of any effective arsenic-removal methodology. CysOMe-carbon (40 mg) was stirred in a solution (20 cm^3), whose initial As^{III} concentration was determined to be about 70 ppb, for various times up to 30 min, and the concentration of As^{III} remaining in the solution was monitored with the LSASV trace-analysis protocol described in the Experimental Section (Figure 8). Figure 9
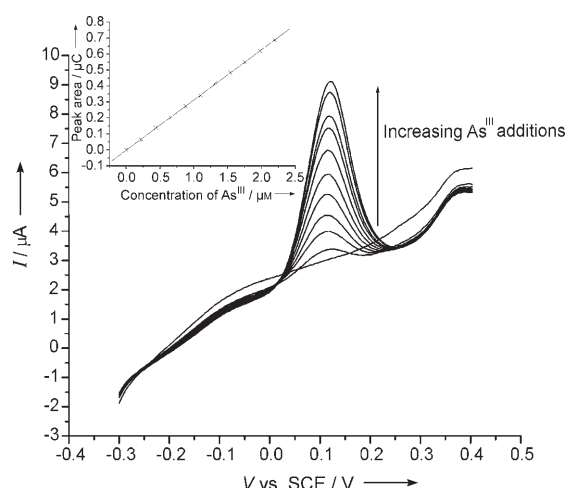

Figure 8. As^{III} LSASV voltammograms with standard additions of As^{III} (0–2.2 μM, 0.22 μM increments). Inset: The corresponding standard addition plot.
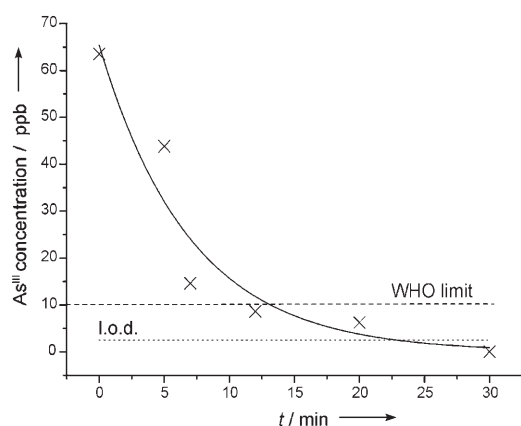
Figure 9. Concentration–time profile for the removal of trace amounts of As[III] to below the WHO-recommended limit of 10 ppb.

shows the resulting concentration–time profile. Remarkably, the initial concentration of As[III] was decreased to below the WHO limit within 10 min of exposure to the small amount of CysOMe-carbon, and was further lowered beyond the limit of detection (l.o.d.) of this methodology after 20 min of exposure. By comparison, 200 mg of CysOMe-GC in 25 cm^3 of a 120-ppb solution was only able to reduce the As[III] concentration to below the Bangladeshi legal limit of 50 ppb.[24] The cost of materials required to produce 1 g of PCcarbon and CysOMe-GC powders was estimated from catalogue prices to be less than £100 and £5, respectively, which prohibits their use in drinking-water filtration systems in poor rural areas of developing countries worst affected by arsenic poisoning. Not only is the cost of materials required to produce CysOMe-carbon vastly reduced at around £1 per gram, we have also demonstrated that this material is much more effective at removing toxic metal ions, particularly As[III], than either of our previous efforts with PCcarbon and CysOMe-GC, or indeed some of the most-recent and effective methods of removing As[III] published in the literature, such as the method of Al Rmalli et al. with dried hyacinth roots.[12]

Conclusions

The thermodynamics and kinetics of uptake of various model toxic metal-ion pollutants, notably As[III], by CysOMe-carbon powder have been elucidated. The adsorption process was found to obey a Freundlich isotherm with strong irreversible binding observed in all cases, and rapid adsorption kinetics of the order of 10^{-4} cm s^{-1} in the case of Cu[II] and Cd[II] and 10^{-5} cm s^{-1} for As[III]. Significant improvements in both the efficiency and the cost of producing the CysOMe-carbon powder were demonstrated over previous materials developed in our laboratory, namely, CysOMe-GC and PCcarbon. CysOMe-carbon was able to reduce the concentration of As[III] in aqueous solutions to below the WHO maximum permissible limit of 10 ppb rapidly, with far less

material than would be required if CysOMe-GC powder were used. The performance of this material leads us to believe that it could offer a low-cost and highly effective method of removing toxic metal ions for environmental remediation and/or filtration of drinking water in countries such as Bangladesh, where drinking water is heavily contaminated with toxic metals, particularly arsenic, and provide obvious health benefits to a vast number of affected people around the world. Alternatively, this material could find application in heavily polluting industries such as mining, thus preventing the routine or accidental release of such toxic heavy-metal pollutants into the environment.

Laboratory standard solutions were used throughout this work; this allowed us to determine the thermodynamic and kinetic parameters for ideal generic cases, which can then be used as a guide to optimize systems in the field. Real effluent samples are well-known to vary wildly in composition and nature; therefore, it would have been necessary to determine the optimum parameters for each and every effluent system, which would require a huge amount of resources and would not be practical or very informative in terms of general information gleaned.

Before novel modified carbon materials such as CysOMe-carbon can be used in real-world applications, many questions still have to be answered, including whether or not these materials can also effectively bind other forms of arsenic, such as organic arsenic compounds and indeed inorganic and organic compounds of As[V]. The exact details of the mechanism by which CysOMe-carbon is able to bind, for example, the AsO_2^- ion remain unclear. Finally, because of the strong binding of metal ions by the CysOMe groups, much work is still required to find a method of regenerating the CysOMe-carbon after exposure to pollutants, with minimal cost and environmental impact. Finding solutions to these problems forms part of our ongoing research activities into this novel material.

Experimental Section

Reagents and Equipment

Graphite powder (2–20 μm, synthetic, 98%) and all reagents were purchased from Aldrich (Gillingham, UK), with the exception of the glassy carbon microspherical powder (Alfa Aesar, Karlsruhe, Germany, Type I, diameter 10–20 μm) and potassium chloride (Reidel de Haen, Seelze, Germany), were of the highest grade commercially available, and were used without further purification. All aqueous solutions were prepared with deionized water with a resistivity of not less than 18.2 MΩ cm (Vivendi Water Systems, UK). pH measurements were performed with a Hanna Instruments pH213 pH meter.

Electrochemical measurements were performed with a μ-Autolab computer-controlled potentiostat (EcoChemie, Utrecht, Netherlands). A three-electrode cell with a solution volume of 10 cm^3 was used throughout. The working electrode consisted of either a glassy carbon (GC; 3 mm diameter, BAS, Indiana, USA), a square boron-doped diamond electrode (BDD; 3 mm×3 mm, Windsor Scientific Ltd, UK), or a gold (1 mm diameter, GoodFellow, Cambridge, UK) macrodisc electrode. A bright platinum wire (99.99%, GoodFellow, Cambridge, UK) acted as the counterelectrode, and either a silver wire pseudoreference electrode (99.99%, GoodFellow, Cambridge, UK) or a saturated calomel electrode

reference electrode (SCE; Radiometer, Copenhagen, Denmark) completed the three-electrode assembly. All solutions were degassed with pure N_2 (BOC Gases, Guildford, UK) for 20 min prior to any electrochemical experiment being performed.

XPS was performed with a VG clam 4 MCD analyzer system at the OCMS Begbroke Science Park, University of Oxford, UK, with X-ray radiation from the $Al_{K\alpha}$ band ($h\nu = 1486.7$ eV). All XPS experiments were recorded with an analyzer energy of 100 eV and a takeoff angle of 90°. The base pressure in the analysis chamber was maintained at no more than 2.0×10^{-9} mbar. Each sample of carbon powder was mounted on a stub with double-sided adhesive tape and then placed in the ultrahigh-vacuum analysis chamber of the spectrometer. To prevent samples becoming positively charged when irradiated due to emission of photoelectrons, the sample surface was bombarded with an electron beam (10 eV) from a "flood gun" within the analysis chamber of the spectrometer. The peak positions reported were not corrected relative to the literature value for C 1s of 286.6 eV, to account for the effect of the flood gun on the peak positions of the spectral lines. Analysis of the resulting spectra was performed with MicroCal Origin 6.0. Assignment of the spectral peaks was made with the UKSAF[29] and NIST[30] databases.

ICP-AES determination of As^{III} concentration in solution was analyzed with a Perkin–Elmer Optima 5300DV emission ICP instrument. The recommended emission wavelength was 188.979 nm, and axial view is recommended for the best detection. As this is below the 200 nm threshold, the optics were purged at a high flow of argon to minimize any absorption of light by water and air. The As^{III} calibration, with five points (0, 50, 100, 150, 200 ppb), gave a correlation coefficient of 0.9993, and the limit of detection, defined as 3 times the standard deviation of the blank averaged from four blank checks each measured in three replicates, was found to be 9.78 ppb or 0.0098 ppm. The expected value for the Perkin–Elmer instrument is 1–10 ppb for this wavelength, so the sensitivity is acceptable. The blank solutions gave between 2.0 and 4.5 ppb for four checks.

Combustion analysis on samples of CysOMe-carbon was carried out by our inhouse chemical-analysis service within the Inorganic Chemistry Laboratory, University of Oxford. Samples were analyzed for their percentage elemental content of C, N, and S with standard techniques and equipment.

Covalent Modification of GC Spheres and Graphite Powder with L-Cysteine Methyl Ester

The procedure, developed in this laboratory, for covalently coupling L-cysteine methyl ester to carbon surfaces through the formation of an amide bond between the amine group in the L-cysteine methyl ester molecule and surface carboxy groups has been published previously,[24–26] and is described briefly below. First, in the bulk surface modification of glassy carbon microspheres, our method is reliant on the fact that there are sufficient carboxy groups already present on the glassy carbon surface for the reaction to proceed. To develop this methodology further and apply it to the bulk surface modification of graphite powder (2–20 μm average particle diameter), we first need to introduce carboxy moieties onto the graphite surface. To this end, we oxidized the oxygen-containing surface groups (e.g., hydroxy and quinonyl groups), which are known to decorate edge-plane defect sites on the graphite surface, by stirring the graphite powder in concentrated nitric acid (HNO_3) for 18 h. The oxidized graphite powder was then washed with copious quantities of pure water until the washings ran neutral to remove any nitric acid from the powder sample. The modification of glassy carbon powder and its extension to graphite powder was then performed as follows: Glassy carbon microspherical powder or oxidized graphite powder (2 g) was stirred in thionyl chloride ($SOCl_2$; 10 cm³) for 90 min to convert the surface carboxy groups into the corresponding acyl chloride groups. After that, the resulting material was washed with dry chloroform to remove any unreacted thionyl chloride impurities. Next, the powder was suspended in dry chloroform (10 cm³) containing cysteine methyl ester hydrochloride (0.5 g). Dry triethylamine (Et_3N; 0.27 cm³) was added to this suspension dropwise, and the reaction mixture was stirred at room temperature for 12 h under an inert argon atmosphere. Finally, the resulting CysOMe

modified glassy carbon or graphite powder was washed with copious quantities of chloroform, acetonitrile, acetone, and pure water to remove any unreacted species.

Determination of Cd^{II} Uptake with LSASV

The concentration of Cd^{II} remaining in a sample after exposure to CysOMe-GC powder was determined with an LSASV protocol at a BDD electrode developed by Banks et al[31] in sodium acetate buffer (pH 5.0).

The LSASV analysis was carried out on Cd^{II}-containing samples with the following parameters: the BDD electrode was held at a deposition potential of -1.5 V versus SCE for 60 s with stirring. The potential was then swept from -1.2 to -0.1 V versus SCE at a scan rate of 0.1 V s^{-1}. A cadmium stripping peak was observed at about -0.8 V versus SCE (Figure 3). Prior to the analysis of samples with unknown concentrations of Cd^{II}, the linear range was determined with the standard additions method on a sample consisting of blank acetate buffer. The results show that the LSASV analytical protocol produced a linear detection range from 1 to 20 μM with a limit of detection (based on 3σ) of 0.96 μM. Where necessary, samples were diluted prior to analysis so that their Cd^{II} concentration fell within this linear range.

Standard 1 μM Cd^{II} aliquots were then added to the sample being analyzed, and the unknown Cd^{II} concentration was determined by constructing a standard addition plot as shown in Figure 3. The analysis was repeated three times, and the reported concentration of Cd^{II} remaining in the sample was the average of these three results

Determination of Cu^{II} Uptake with LSASV

The Cu^{II} concentration in a sample was determined with the standard addition method described above and an LSASV protocol as followings:[25,26] Cu^{II} analysis was performed in H_3PO_4 (0.1 M, pH 2.0) with a GC working electrode and a Ag pseudoreference electrode to avoid the formation of copper(I) chloride precipitates during the electrodeposition; copper(I) chloride could form if an SCE reference electrode was used and is problematic for the LSASV analysis. A copper stripping peak was observed at about -0.1 V versus Ag. The linear analytical concentration range, with standard additions of Cu^{II} (1 μM), was found to be 2–20 μM; therefore, all samples were diluted to fall within this range where necessary. LSASV was performed with a deposition potential of -1.5 V versus Ag, deposition time 30 s, scan rate 100 mV s^{-1}, and scanning from -1.5 to $+0.8$ V versus Ag.

Determination of As^{III} Uptake with LSASV

LSASV was performed in a solution (10 cm³) of HCl (0.1 M, pH 1.0) with a gold working electrode (diameter 1 mm) and an SCE reference electrode. The LSASV analysis was carried out on samples of relatively high concentration with the following parameters: deposition potential -0.3 V versus SCE, deposition time 60 s with stirring for the first 5 s. Then LSASV voltammetry was performed from -0.3 to $+0.4$ V versus SCE at 100 mV s^{-1}, step potential 5 mV. Standard aliquots (2.2 μM, 5 μL of a 4.4 mM standard solution) were then added, and the unknown sample concentration was determined from a standard addition plot. The linear range for As^{III} detection was found to be 2–20 μM with a limit of detection (based on 3σ) of 1.25 μM. Where necessary, solutions were diluted prior to analysis so that their concentration fell within this range.

For trace analysis, the protocol was modified slightly. The solution was stirred throughout the entire 60-s deposition time with all other parameters identical to those described above. The standard As^{III} solution was diluted so that a 5-μL aliquot added to the analysis sample corresponded to a 0.22 μM standard addition, and the resulting voltammetry is shown in Figure 8. The linear range was determined to be 0–2.2 μM with a limit of detection of 0.03 μM, therefore it was not necessary to dilute the samples prior to analysis.

Acknowledgements

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