Available online at www.sciencedirect.com
SCIENCE DIRECT®
Analytica Chimica Acta 502 (2004) 207–212
ANALYTICA CHIMICA ACTA
www.elsevier.com/locate/aca

Simultaneous detection of cadmium, copper, and lead using a carbon paste electrode modified with carbamoylphosphonic acid self-assembled monolayer on mesoporous silica (SAMMS)

Wassana Yantasee, Yuehe Lin*, Glen E. Fryxell, Brad J. Busche

Pacific Northwest National Laboratory (PNNL), Environmental Technology, 902 Battelle Boulevard, Richland, WA 99352, USA

Received 10 March 2003; received in revised form 30 September 2003; accepted 1 October 2003

Abstract

A new sensor was developed for simultaneous detection of cadmium (Cd^{2+}), copper (Cu^{2+}), and lead (Pb^{2+}), based on the voltammetric response at a carbon paste electrode modified with carbamoylphosphonic acid (acetamide phosphonic acid) self-assembled monolayer (SAM) on mesoporous silica (Ac-Phos SAMMS). The adsorptive stripping voltammetry (AdSV) technique involves preconcentration of the metal ions onto Ac-Phos SAMMS under an open circuit, then electrolysis of the preconcentrated species, followed by a square wave potential sweep towards positive values. Factors affecting the preconcentration process were investigated. The voltammetric responses increased linearly with the preconcentration time from 1 to 30 min or with metal ion concentrations ranging from 10 to 200 ppb. The responses also evolved in the same fashion as adsorption isotherm in the pH range of 2–6. The metal detection limits were 10 ppb after 2 min preconcentration and improved to 0.5 ppb after 20 min preconcentration.
© 2003 Published by Elsevier B.V.

Keywords: Adsorptive stripping voltammetry; Self-assembled monolayer; Chemically modified electrode; Carbamoylphosphonic acid; Carbon paste electrode

1. Introduction

Currently, quantification of heavy metals at subsurface hazardous waste sites relies upon collection of liquid discrete samples for subsequent laboratory analysis using techniques such as ICP-MS and AAS. Analysis by off-site governmental or commercial laboratories often results in lengthy turnaround times. Sensors for obtaining real-time ppb-level heavy metal concentrations would reduce time and costs associated with the characterization and treatments of hazardous waste sites. Electrochemical sensors based on stripping voltammetry appear to be a promising technique for determining aqueous heavy metal concentrations. These sensors are usually sensitive, compact, low cost, and easily integrated into field-deployable units [1–4].

Stripping voltammetry for trace metal ions usually involves preconcentration of metal ions at an electrode surface, followed by quantification of the accumulated species by voltammetric methods. Preconcentration of metal species at mercury drop or mercury film electrodes have been available for decades. However, mercury drop electrodes have the disadvantage of being mechanically unstable during various steps of the assay procedure, thus they are less desirable than solid-state sensors in routine field applications [5,6]. In addition, mercury-based electrodes have issues related to the use and disposal of toxic mercury. On the other hand, in adsorptive stripping voltammetry (AdSV), preconcentration at an electrode modified with functional ligands uses the specific binding properties of the ligand (towards the target metal ions) to accumulate the metal ions via ion exchange or chelation onto the electrode without applying any potential. In addition to being solid-sate and mercury-free, this technique has several advantages: (1) it can preconcentrate metal ions that cannot be reductively accumulated, (2) electrolytes are not required in the preconcentration solution, thus reduces the risk of introduction of contaminants or competing ligands, and (3) with the appropriate ligand, the overall selectivity of the analysis for the targeted metal ions may increase.

Electrodes for AdSV for trace metal ions can be fashioned by adsorption of monolayers of host molecules [7] (e.g., functionalized self-assembled monolayers (SAMs) and

* Corresponding author. Tel.: +1-509-376-0529; fax: +1-509-376-5106.
E-mail address: yuehe.lin@pnl.gov (Y. Lin).

0003-2670/$ – see front matter © 2003 Published by Elsevier B.V.
doi:10.1016/j.aca.2003.10.001

polymeric films) on the electrode surfaces, or by embedding suitable functional ligands in a conductive porous matrix [8–16]. The number of functional groups on SAM thin films may be limited and the stability and durability of the SAM films may be poor. Although, the polymeric films have superior stability and durability over SAM thin films, the detection may be affected by shrinking and swelling of the polymeric films caused by the changes in solution pH or electrolyte concentration, leading to slow and reduced electrode responses [17,22].

Carbon paste electrodes modified with functional ligands have been more widely used to preconcentrate and quantify trace metal ions [8–16]. However, the ligands in these sensors are in loose association or physical contact with the electrode. Thus, to avoid degradation of the sensor over time as a result of depletion of ligand-bearing material, the modifiers must be insoluble in the solvents employed [8]. Alternatively, the ligands may be first covalently bonded to high surface area substrates (such as porous silica) before being embedded into the carbon graphite matrix, which allows chemical functionality to be retained despite diffusion or abrasive wear. Polysiloxane-immobilized amine ligands [18] and aminopropyl-grafted silica gel [19] have been used successfully by Walcarius et al. as electrode modifiers in order to study the uptake of copper(II) from an aqueous solution. In the preconcentration stage, the diffusion of the target analytes to the binding sites located inside of amorphous materials (i.e., silica gel) having a tortuous structure can be slow. Because such diffusion is normally the rate-determining step in the voltammetric analyses that rely on porous materials as electrode modifiers [20], having easy accessibility to the binding sites is an important feature of the electrode modifiers. With that in mind, well-ordered, hexagonal porous silicas (MCM-41) have been recently exploited as a substrate for immobilization of simple functional groups like amine and thiol [20]. However, such study is still limited to material aspects of functionalized amorphous silicas versus functionalized MCM-41 as electrode modifiers by using mercury as a representative metal ion and not the metrological aspects of adsorptive stripping voltammetry. This work reports the application of the MCM-41 modified with a self-assemble monolayer functionality as electrode modifier for simultaneous detection of toxic metal ions.

For a number of years, PNNL has been a leader in the development of a new class of nanoengineered sorbents, the self-assembled monolayer on mesoporous supports (SAMMS) [21–25]. These nanoporous hybrid materials are highly efficient sorbents and their interfacial chemistry can be fine-tuned to selectively sequester any specific target species. One successful material is the acetamide phosphonic acid self-assembled monolayer on mesoporous silica (Ac-Phos SAMMS) [24,25]. Fig. 1a shows the schematic of SAMMS with acetamide phosphonic acids as terminal monolayers (Fig. 1b). The mesoporous silica (MCM-41) had a surface area of 989 m^2/g and a nominal pore size of 5.0 nm. The high surface area of MCM-41 and the monolayer assembly technique afforded a high functional group density on the Ac-Phos SAMMS (i.e., 2.0 mmol acetamide phosphonic acid per gram of Ac-Phos SAMMS). In addition to the suitable pore structures and high number of binding sites, Ac-Phos SAMMS has been demonstrated to be highly selective for cadmium, copper, and lead in aqueous solutions without significant interference from other common cations like Na^+, which were present at much higher concentrations [25]. For example, in the presence of 5 mg/l (each) of Cd^{2+}, Co^{2+}, Cr^{3+}, Cu^{2+}, Mn^{2+}, Pb^{2+}, Zn^{2+}, and Ni^{2+} and 2,300 mg/l of Na^+ (at pH 5.5 and the solution per solid ratio of 200) the mass-weight distribution coefficients (K_d) of cadmium, copper and lead are in the order of 10^4. This selectivity is a result of the molecular recognition properties of acetamide phosphonic acid ligands, which prefer heavy metal ions over alkaline and alkaline earth metals.

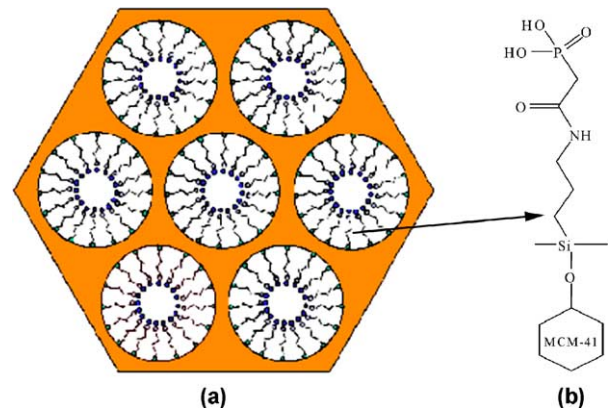

Fig. 1. Schematics of (a) self-assembled monolayer on mesoporous silicas (SAMMS) with (b) acetamide phosphonic acid as terminal monolayers.

This work investigated the use of a carbon paste electrode modified with Ac-Phos SAMMS for simultaneous detection of cadmium(II), copper(II), and lead(II) after preconcentration at an open circuit. Factors affecting the preconcentration process, including preconcentration time, metal ion concentrations, and the pH of the solution, were investigated. Then the optimal operating parameters and the electrode application/regeneration are reported.

2. Experimental

2.1. Apparatus

Square wave voltammetry (SWV) experiments were performed on an electrochemical detector, model CHI660A (CH Instruments Inc.), equipped with a three electrode system: a self-made carbon paste electrode modified with Ac-Phos SAMMS as the working electrode, a platinum wire as the auxiliary electrode, and a KCl saturated Ag/AgCl electrode as the reference electrode. All measurements were made at room temperature and under an atmospheric environment. Square wave voltammetry was operated at a

Table 1
Operating parameters during each step of the voltammetric detection experiments

Conditions	Preconcentration	Electrolysis	Stripping	Regeneration
Metal ion/electrolyte	0.5–200 ppb Cd, Cu, Pb	0.2 M HNO_3	0.2 M HNO_3	0.2 M HNO_3
Solution volume	15 ml	15 ml	15 ml	15 ml
Immersion time	2–30 min	1 min	–	0–5 min
Stirring speed	400 rpm	0	0	400 rpm
Applied potential	Open circuit	−1.0 V	−1.0 to 0.4 V	0.4 V

frequency of 100 Hz with a pulse amplitude of 50 mV and a potential step height of 5 mV.

2.2. Chemicals

Single-component lead (Pb^{2+}) solution and multi-component $Cu^{2+}/Pb^{2+}/Cd^{2+}$ solution were prepared daily by diluting atomic absorption standard solutions from Aldrich (comprised of 1000 mg/l each metal ion in a 1% HNO_3 solution) with ultrapure Millipore water (18 MΩ cm). The pH of the solution was normally 5. For the pH study, the metal ion solutions were diluted in 0.05 M sodium acetate (CH_3COONa) buffer solution instead of the ultrapure water. Before adding metal ion solution, the pH of the acetate solution was adjusted to a nominal value of 2, 5, or 7 with 1.0 M HNO_3 solution.

2.3. Working electrode

From our previous study [26], the most sensitive and reliable SAMMS modified carbon paste electrode has been found to consist of 20% SAMMS and 80% carbon paste. The electrode was prepared by thoroughly mixing a 0.05 g quantity of Ac-Phos SAMMS with a 0.15 g quantity of CPO carbon paste (Bioanalytical Systems Inc.). The preparation and characterization of Ac-Phos SAMMS are described elsewhere [24,25]. A 0.05 g quantity of mineral oil (Aldrich) was added to the carbon paste/Ac-Phos SAMMS mixture and mixed until obtaining a uniformly wetted paste. Unmodified carbon paste, prepared in the same fashion, but without adding Ac-Phos SAMMS, was packed into an 8 cm long cylindrical PTFE tube (inside cross-section area of 0.08 cm^2) with a copper piston providing an inner electrical contact. Then the Ac-Phos SAMMS modified carbon paste was packed into the end of the same tube. The electrode surface was smoothed on a weighing paper. When necessary, a new electrode surface was obtained by removing about 2–3 mm (from the surface) of electrode material, adding freshly-made Ac-Phos SAMMS/carbon paste mixture, and polishing it. All freshly-made electrodes were activated by performing three to five cycles of preconcentration/electrolysis/stripping/regeneration.

2.4. Voltammetric detection procedure

The voltammetric detection procedure consisted of preconcentration (accumulation), cathodic electrolysis (deposition), stripping (detection), and regeneration steps (if necessary). Table 1 summarizes operating conditions for the experiments. During preconcentration step, the electrode was immersed (at 2 cm from the solution surface) in a 20 ml cell (2 cm inside diameter) containing 15 ml of metal ion solution at open circuit for a specified period of time (i.e., normally 2 min, but varied from 1 to 30 min in the preconcentration time study). During preconcentration, the solution was stirred at over 300 rpm using a magnetic stirring bar. The electrode was then removed, rinsed with DI water, and transferred to another 20 ml cell containing 15 ml of 0.2 M HNO_3 as the supporting electrolyte solution. A negative potential (−1.0 V) was applied to the electrode immediately after immersing it in the acid solution for 60 s. The stripping voltammetry was performed in the same cell by a sweeping square wave potential toward positive direction (i.e., from −1.0 to 0.4 V). Both cathodic electrolysis and stripping steps were done under quiescent conditions. Then square wave potential was swept toward positive values one more time to ensure that no metal was still left on the electrode surface. If the electrode surface is clean, no peak will be detected in the second sweep. When metal ion peaks were detected, a regeneration of the electrode was performed by applying a positive potential (0.4 V) to the electrode while it was immersed in 0.2 M HNO_3 under stirred conditions. No de-aeration of solutions is required in any step. Each measurement was performed in duplicate, and the average values were reported.

3. Results and discussion

Because SAMMS is an electronic insulator, desorption of previously accumulated metal ions from the surface of SAMMS to the electrode/solution interface must occur, usually by immersing the electrode in an acidic solution, for the voltammetric detection to be accomplished. Concurrent to the desorption process, a thorough electrolysis is performed by applying a negative potential to reduce the desorbed metal ions (M^{2+}) to metal elements (M(0)), followed by the quantification of metal ions via square wave anodic stripping voltammetry, which oxidizes the previously reduced M(0) to M^{2+}. A 60 s electrolysis period at −1.0 V in 0.2 M HNO_3 was found to be best for complete desorption of metal ions from the surface of SAMMS and deposition of metal ions onto the electrode/solution interface [26].

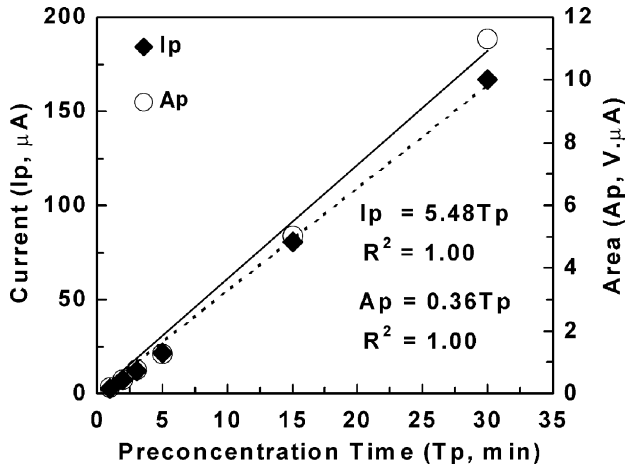

Fig. 2. The effect of preconcentration time on the voltammetric responses (currents, I_p and areas, A_p) of 50 ppb Pb^{2+} solution.

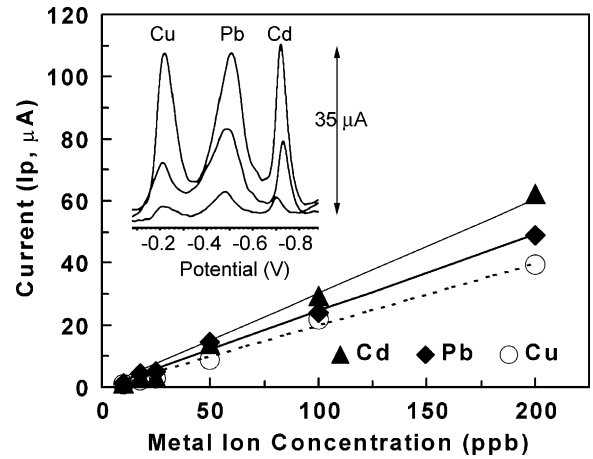

Fig. 3. The voltammetric responses of Cu^{2+}, Pb^{2+}, and Cd^{2+} measured after a 2 min preconcentration period in multi-component $Cu^{2+}/Pb^{2+}/Cd^{2+}$ solutions with concentrations ranging from 10 to 200 ppb of each metal ion. Inset shows representative voltammograms in the ascending order of 25, 50, and 100 ppb $Cu^{2+}/Pb^{2+}/Cd^{2+}$ solutions.

3.1. Factors affecting the preconcentration process

Factors affecting the preconcentration of metal ions onto the electrode surface, which in turn affect the voltammetric responses in the detection step, include preconcentration time, metal ion concentration, and pH of the preconcentration solution.

3.1.1. Preconcentration time

Fig. 2 shows the effect of preconcentration time on the voltammetric response studied using 50 ppb Pb^{2+} solution as a representative metal ion. Peak currents and areas increased proportionally with time from 0 to 30 min and in parallel to each other. The same experiment was also performed on an unmodified carbon paste electrode and did not yield any voltammetric responses (currents) for lead, indicating that the conductive matrix (carbon graphite) was inert with respect to lead adsorption. For rapid analysis of lead, a 2 min preconcentration period at the modified electrode was found to be sufficient for this lead concentration range (i.e., 50 ppb Pb^{2+}). The short preconcentration period is attributed to the rigid, open-parallel mesopores of the silica that allow easy access to hydrated metal ions. For the analysis of Pb^{2+} at a much lower concentration range (i.e., 0.5 ppb Pb^{2+}), a longer period may be required in order to sufficiently accumulate the metal ion to a detectable level. Changing the metal ion concentrations would change the response versus preconcentration time profile. Nevertheless, the large linear response range (from 0 to 30 min) demonstrated that the SAMMS-modified electrode having high functional group density would not likely to be saturated easily by metal ions even up to 30 min of preconcentration period and at 50 ppb Pb^{2+}.

3.1.2. Metal ion concentrations

Fig. 3 shows the voltammetric responses of Cu^{2+}, Pb^{2+}, and Cd^{2+} measured after a 2 min preconcentration period in a multi-component $Cu^{2+}/Pb^{2+}/Cd^{2+}$ solution with concentration ranging from 10 to 200 ppb of each metal ion. The representative voltammograms were (in the ascending order) of 25 ppb (each) $Cu^{2+}/Pb^{2+}/Cd^{2+}$, 50 ppb (each) $Cu^{2+}/Pb^{2+}/Cd^{2+}$, and 100 ppb (each) $Cu^{2+}/Pb^{2+}/Cd^{2+}$ solutions. The Cu, Pb, and Cd peaks appeared at −0.2, −0.5, and −0.75 V, respectively.

The response of each metal ion was linear to its concentration in both single-component and multi-component solutions. In Fig. 3, the slopes (in μA/ppb) for Cu^{2+}, Pb^{2+}, and Cd^{2+} calibration curves were 0.200 ± 0.006 ($R^2 = 0.99$), 0.246 ± 0.006 ($R^2 = 0.99$), and 0.303 ± 0.011 ($R^2 = 0.99$), respectively. Below 200 ppb, the peak overlapping between Cu and Pb, or between Pb and Cd was insignificant. Above 200 ppb, metal voltammetric peaks started to interfere with each other. Therefore, for real sample analysis, a dilution of the samples before analysis is recommended if samples contain high concentration of multiple heavy metal ions.

We have found that at any given concentration below 200 ppb the voltammetric response of copper obtained from the multi-component $Cu^{2+}/Pb^{2+}/Cd^{2+}$ solution (slope = 0.200 ± 0.006, $R^2 = 0.99$) was not significantly different from that obtained from the single component Cu^{2+} solution (0.182 ± 0.002, $R^2 = 1.00$). Therefore, one can infer that the electrochemical responses for copper ions were not affected by the presence of lead and cadmium in the concentration range studied. Although the three metal ions exhibit comparable affinity for the binding sites on the Ac-Phos SAMMS, based on the K_d values (8800 for Cu, 9000 for Cd, and 12,000 for Pb [25]), the response intensity loss due to the competitive adsorption for the binding sites was not observed. This may be because the total adsorption capacity of the three metal ions was well below the total number of binding sites (2.0 mmol phosphonic acid/g Ac-Phos SAMMS). Such high surface functional group density is desirable for a successful simultaneous detection of metal ions based on an AdSV technique because it minimizes the competition

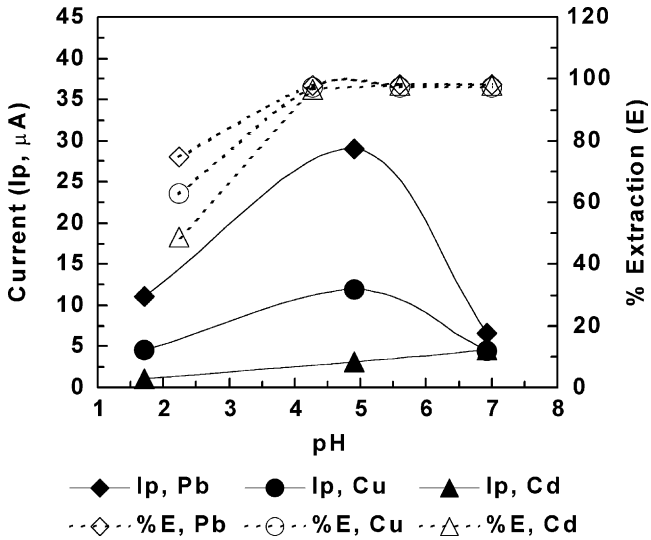

Fig. 4. Primary *Y*-axis: the peak currents recorded at the 20% Ac-Phos SAMMS modified electrode preconcentrated for a 2 min period with 50 ppb $Cu^{2+}/Pb^{2+}/Cd^{2+}$ in 0.05 M CH_3COONa solutions of pH 1.7–6.9; secondary *Y*-axis: the adsorption isotherm (percent extraction) obtained after equilibration of 0.05 g of Ac-Phos SAMMS with a 10 ml of a 5 mg/l multi-component heavy metal ion solution.

for the binding sites among metal ions in the concentration range of interest.

3.1.3. pH of the preconcentration solutions

Fig. 4 shows the adsorption isotherm, presented as the percent (by mass) of extraction, obtained after equilibration of 0.05 g of Ac-Phos SAMMS with a 10 ml aliquot of a 5 mg/l (each) multi-component heavy metal ion solution at various pH values [25]. Fig. 4 also shows the peak currents recorded using the 20% Ac-Phos SAMMS modified electrode that was preconcentrated for a 2 min period with 50 ppb $Cu^{2+}/Pb^{2+}/Cd^{2+}$ in 0.05 M CH_3COONa solutions of pH 1.7–6.9. The adsorption of Cd^{2+}, Cu^{2+}, and Pb^{2+} was low at pH 2 and increased rapidly to reach a maximum value (100% extraction) above pH 4.5. The pH of the preconcentration solution was found to exert a significant but predictable effect on the preconcentration process [9]. The evolution of the peak currents of metal ions, with the exception of Cd^{2+}, behaved in the same fashion as the adsorption isotherms in the pH range of 2–6. Above pH 6, while the adsorption isotherms still remained at maximum, the peak currents were negligible due to the formation of metal hydroxide complexes that may be sparingly soluble. These hydroxide complexes may precipitate either on the wall of the electrolytic cell or on the electrode surface, thereby causing a significant decrease in the quantity of solution phase metal ions that may reach the electrode surface [18].

3.2. Detection limits

Detection limits at a specified period of time (i.e., 2 or 20 min) were estimated based on a signal-to-noise ratio of 3 from the stripping voltammograms. The detection limits improved significantly as the preconcentration time was increased. The detection limits for Cd^{2+}, Cu^{2+}, and Pb^{2+} were 10 ppb after a 2 min preconcentration period and improved greatly to 0.5 ppb after a 20 min preconcentration period.

3.3. Reproducibility

The SAMMS-modified electrode (with 20% SAMMS) has good reproducibility for the metal ion detections both at a single and various electrode surfaces. For example, for a single electrode surface the %R.S.D. for the detections of 50 ppb Pb^{2+} after 2 min of preconcentration (number of samples = 7) was 5%. For five electrode surfaces after surface renewal and activation (by performing 3–5 cycles of preconcentration/electrolysis/stripping/regeneration), the %R.S.D. of the current responses for 50 ppb Pb^{2+} after 2 min of preconcentration was 12%. Although the stripping step is performed in an acidic medium, the reproducible data can be obtained because the pH re-equilibration occurs fast enough, thanks to the rigid and open parallel pore structure and the right pore sizes of the SAMMS material as well as the hydrophilicity of the functional groups.

3.4. Electrode regeneration

The extent of electrode regeneration depended on the size of the peak response, which was related to the amount of accumulated species from the previous run. When stripping in 0.2 M HNO_3 solution and the peak current was smaller than 20 μA, the regeneration of the electrode was not required (no metal ion peak was detected after the re-sweep). For a peak size larger than 20 μA, regeneration was normally accomplished within 2 min for Cd and Pb, whereas it could take up to 5 min for Cu.

4. Conclusions

The self-assembled monolayer chemistry enables ready installation of a wide variety of functional interfaces on mesoporous MCM-41 silica, leading to excellent specificity and selectivity for any desired analyte when the materials are used as modifiers in electrochemical sensors. The high functional density of the monolayers on Ac-Phos SAMMS, resulting from the combined effects of an extremely large surface area of MCM-41 and the self-assemble chemistry used in the installation of the functional groups, enables high sensitivity for the sensors as well as minimizes the competition among metal ions, allowing them to be detected simultaneously without sacrificing the response intensity. The Ac-Phos SAMMS modified carbon paste electrode provides a new tool for simultaneous detection of cadmium, copper, and lead at ppb levels. The new electrode has advantages of being mercury-free and solid-state. The voltammetric detection procedure consisted of preconcentration, cathodic

electrolysis, and stripping steps. The pH of the preconcentration solution strongly affected the voltammetric responses of metal ions; the best operating pH was between 4.5 and 6. The electrolysis step was performed at −1.0 V in an acidic solution for 60 s. The stripping step was also performed in highly acidic solution, thus the electrode regeneration is often not needed. Based on the encouraging results reported in this paper, the Ac-Phos SAMMS modified electrode will be incorporated into a flow system to test the simulated and real waste samples. The results will be reported in due course.

Acknowledgements

This work was supported by the SERDP Program, US Department of Defense and the EMSP Program, US Department of Energy (DOE). Pacific Northwest National Laboratory (PNNL) is operated by Battelle Memorial Institute for the US DOE. The research described in this paper was performed in part at the Environmental Molecular Sciences Laboratory (EMSL), a national scientific user facility sponsored by the DOE's Office of Biological and Environmental Research and located at PNNL. The authors thank Christian D. Johnson for reviewing the manuscript and Prof. Joseph Wang at New Mexico State University for helpful discussion.

References

[1] J. Wang, Y. Lin, L. Chen, Analyst 118 (1993) 277.
[2] J. Wang, Analytical Electrochemistry, VCH, New York, 1994.
[3] Y. Lin, R. Zhao, K.D. Thrall, C.A. Timchalk, W.D. Bennett, D.W. Matson, Proc. SPIE 3877 (1999) 248.
[4] Y. Lin, C.A. Timchalk, D.W. Matson, H. Wu, K.D. Thrall, Biomed. Microdevices 3 (2001) 331.
[5] J. Wang, J. Wang, B. Tian, M. Jiang, Anal. Chem. 69 (1997) 1657.
[6] J. Wang, J. Lu, D.D. Larson, K. Olsen, Electroanalysis 7 (1995) 247.
[7] I. Turyan, M. Atiya, D. Mandler, Electroanalysis 13 (2001) 653.
[8] S.V. Prabhu, R.P. Baldwin, L. Kryger, Anal. Chem. 59 (1987) 1074.
[9] R.P. Baldwin, J.K. Christensen, L. Kryger, Anal. Chem. 58 (1986) 1790.
[10] Z. Navratilova, Electroanalysis 3 (1991) 799.
[11] I.G. Svegl, M. Kolar, B. Ogorevc, B. Pihlar, Fresenius J. Anal. Chem. 361 (1998) 358.
[12] V.S. Ijeri, A.K. Srivastava, Anal. Sci. 17 (2001) 605.
[13] M.F. Mousavi, A. Rahmani, S.M. Golabi, M. Shamsipur, H. Sharghi, Talanta 55 (2001) 305.
[14] T.H. Degefa, B.S. Chandravanshi, H. Alemu, Electroanalysis 11 (1999) 1305.
[15] T. Molina-Holgado, J.M. Pinilla-Macías, L. Hernández-Hernández, Anal. Chim. Acta 209 (1995) 117.
[16] B. Ogorevc, X.H. Cai, I. Grabec, Anal. Chim. Acta 305 (1995) 176.
[17] H. Ju, Y. Gong, H. Zhu, Anal. Sci. 17 (2001) 59.
[18] A. Walcarius, N. Lüthi, J.-L. Blin, B.-L. Su, L. Lamberts, Electrochim. Acta 44 (1999) 4601.
[19] M. Etienne, J. Bessiere, A. Walcarius, Sens. Actuators B: Chem. 76 (2001) 531.
[20] A. Walcarius, M. Etienne, S. Sayen, B. Lebeau, Electroanalysis 15 (2003) 414.
[21] X.D. Feng, G.E. Fryxell, L.Q. Wang, A.Y. Kim, J. Liu, K. Kemner, Science 276 (1997) 923.
[22] X.B. Chen, X.D. Feng, J. Liu, G.E. Fryxell, M. Gong, Sep. Sci. Technol. 34 (1999) 1121.
[23] Y. Lin, G.E. Fryxell, H. Wu, M. Engelhard, Environ. Sci. Technol. 35 (2001) 3962.
[24] J.C. Birnbaum, B. Busche, Y. Lin, W.J. Shaw, G.E. Fryxell, Chem. Commun. 13 (2002) 1374.
[25] W. Yantasee, Y. Lin, G.E. Fryxell, B.J. Busche, J.C. Birnbaum, Sep. Sci. Technol. 38 (2003) 3809.
[26] W. Yantasee, Y. Lin, T. Zemanian, G.E. Fryxell, Analyst 128 (2003) 467.