Voltammetric detection of lead(ii) and mercury(ii) using a carbon paste electrode modified with thiol self-assembled monolayer on mesoporous silica (SAMMS)

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The anodic stripping voltammetry at a carbon paste electrode modified with thiol terminated self-assembled monolayer on mesoporous silica (SH-SAMMS) provides a new sensor for simultaneous detection of lead (Pb²⁺) and mercury (Hg²⁺) in aqueous solutions. The overall analysis involved a two-step procedure: an accumulation step at open circuit, followed by medium exchange to a pure electrolyte solution for the stripping analysis. Factors affecting the performance of the SH-SAMMS modified electrodes were investigated, including electrode activation and regeneration, electrode composition, preconcentration time, electrolysis time, and composition of electrolysis and stripping media. The most sensitive and reliable electrode contained 20% SH-SAMMS and 80% carbon paste. The optimal operating conditions were a sequence with a 2 min preconcentration period, then a 60 s electrolysis period of the preconcentrated species in 0.2 M nitric acid, followed by square wave anodic stripping voltammetry from −1.0 V to 0.6 V in 0.2 M nitric acid. The areas of the peak responses were linear with respect to metal ion concentrations in the ranges of 10–1500 ppb Pb²⁺ and 20–1600 ppb Hg²⁺. The detection limits for Pb²⁺ and Hg²⁺ were 0.5 ppb Pb²⁺ and 3 ppb Hg²⁺ after a 20 min preconcentration period.

Introduction

Accurate quantification of metal ions in groundwater and waste water currently relies upon collection of water samples for subsequent laboratory analysis by means of standard spectroscopic techniques, such as atomic absorption spectrometry (AAS) and inductively coupled plasma-mass spectrometry (ICP-MS). On-site metal ion monitoring using sensors may provide a significant saving in time and operating costs. Desirable characteristics of the metal ion sensors include specificity for targeted metal ions, enhanced measurement frequency and precision, robustness, inexpensive to fabricate, and infrequent regeneration of sensor material. Electrochemical detection is sensitive, compact, and low cost which appears to be a promising technique that meets these needs.1–6

Adsorptive stripping voltammetry (AdSV) is an extremely sensitive electrochemical technique for measuring trace metals. Its remarkable sensitivity is attributed to the combination of a selective preconcentration step with advanced measurement procedures that generate an extremely favorable signal-to-background ratio. Electrodes for adsorptive stripping voltammetry of trace metal ions can be fashioned by immobilizing functional ligands on the electrode surfaces using self-assembled monolayer (SAM) thin films7,8 or thin-polymeric films,9,10–11 or by embedding suitable functional ligands in an electrically conductive porous matrix.12–20 Using ligand modified electrodes allows the preconcentration of metal ions (via ion exchange or coordination/chelation) under open circuit potential. Thus if pH of the solution is not a concern (no buffer is needed), the preconcentration step can be performed in aqueous medium without adding any electrolyte to make the solution conductive. This prevents the introduction of trace heavy metal ions or potentially competing ligands with the reagents. This technique also allows the preconcentration of metal ions that cannot be feasibly accumulated (e.g., those requiring an excessive negative reduction potential).

One major limitation for chemically modified electrodes (CMEs) based on polymeric films is slow diffusion across the film. CMEs based on SAM thin films can effectively eliminate this limitation. This approach has shown to provide a reproducible method for the sensitive and selective determination of trace cadmium2 and chromium(vi).5 The potential drawback of CMEs modified with SAM thin films is that the total number of binding sites in SAM thin films is limited, which may lead to narrow linear range of the calibration curves.

Chemically modified carbon paste electrodes are often used in AdSV because they have low background currents, have a large potential domain, are low cost, and are easy to prepare and regenerate.6 Carbon paste electrodes modified with functional ligands have been employed to detect heavy metal ions, including nickel on dimethylglyoxime,12 mercury on diphénylcarbazide13 and vermiculite,14 lead on crown ethers,15 anthaquinone,16 N-p-chlorophenylcinnamohydroxamic acid,17 and diphenylthiocarbazone,18 and copper on phenanthroline19 and vermiculite.20 The drawback of these organic ligand modified electrodes is that the ligands in these sensors are in loose association or physical contact with the electrode, thus the sensor may easily degrade over time from depletion of ligand-bearing material, especially in some solvents in which these ligands have a high degree of solubility. If the ligands are first immobilized via covalent bonding onto substrates (i.e., high surface area silica supports) before being embedded in the carbon graphite matrix, the chemical functionality of the sensor is retained despite diffusion, abrasive wear, or degree of solubility of the ligands.

The use of carbon paste electrodes modified with functional groups grafted on mesoporous silica supports for the detection of metal ions is relatively rare. Several unmodified silica materials were incorporated into carbon paste electrodes for copper(n)21–23 and mercury(n)24,25 detection by exploiting the silanol groups inherent in the silica materials. The optimized detection procedure involves preconcentration (accumulation) of targeted metal ions on the electrode surface under an open circuit, then cathodic electrolysis of the preconcentrated species, followed by a detection step using square wave anodic stripping voltammetry. By using unmodified silica materials,
specificity for the targeted metal ions was limited to the silanol groups of the silica materials. In addition, ammoniacal medium was required as preconcentration medium so that the silanol groups can be ionized and accumulate positively charged species such as Cu(NH₃)₂⁺. Polysiloxane-immobilized amine ligands and aminopropyl-grafted silica gel were later used as electrode modifiers in order to study the uptake of copper(II) from aqueous solution.

Two factors believed to affect voltammetric detection responses of copper ions are the number of immobilized functional groups and the structure of the organically modified silicates, the latter of which governs the accessibility to the binding sites and the diffusivity of the copper ions. Despite the fact that amine-grafted MCM-41 silica and aminopropyliimmobilized silica gel show very promising results as electrode modifiers, the studies have been performed on copper ions mainly because amine is known to be highly selective for copper ions. Using this class of materials as the electrode modifiers for other toxic heavy metal ions, especially lead and mercury, would be very desirable.

Recently we have developed a new class of nanoengineered sorbents, the self-assembled monolayer on mesoporous supports (SAMMS). These nanoporous hybrid materials (in powder form) are highly efficient sorbents. Their surface area can be up to 1000 m² g⁻¹ and their interfacial chemistry can be fine-tuned to selectively sequester a specific target species. The thiol (SH)-SAMMS material has been demonstrated to be highly selective for lead and mercury in aqueous solutions without significant interference from other common cations and anions. The SH-SAMMS has also shown high metal ion loading capacity (e.g., 0.64 g Hg g⁻¹ SH-SAMMS) due to the high density of the functional groups, and rapid metal ion uptake rates due to the open pore structure and fast interfacial reaction.

The work discussed in this paper investigated the feasibility of using carbon paste electrode modified with SH-SAMMS for simultaneous detection of lead(II) and mercury(II). The effort was focused on determining optimal operating parameters that affect both the preconcentration and detection steps (i.e., electrode compositions, electrolysis and preconcentration time, and choices/compositions of electrolysis and stripping media).

**Experimental**

**Apparatus**

Square wave voltammetry (SWV) experiments were performed on an electrochemical detector, model CHI660A (CH Instruments, Inc.), equipped with a three electrode system: a homemade carbon paste electrode that was modified with SH-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 frequency of 100 Hz with a pulse amplitude of 50 mV and a potential step height of 5 mV.

**Working electrode**

The modified carbon paste electrode was prepared by thoroughly mixing 0.05 g of SH-SAMMS with 0.15 g of the CPO carbon paste (Bioanalytical Systems, Inc.). The preparation and characterization of SH-SAMMS with 82% thiol coverage are described elsewhere. A 0.05 g aliquot of mineral oil (Aldrich Co.) was added to the carbon paste mixture and mixed until obtaining a uniformly wetted paste. The final composition (by weight) was 20% SH-SAMMS, 60% CPO carbon paste, and 20% mineral oil. The composition was varied in the electrode composition study. Unmodified carbon paste, prepared in the same fashion but without adding SH-SAMMS, was packed into a 5 cm long PTFE cylindrical tube (geometric area 0.08 cm²) with a copper piston providing an inner electrical contact. Chemically 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 surface was obtained by removing about 2–3 mm (from the surface) of electrode material, adding freshly-made material, and polishing it.

**Voltammetric detection procedure**

SAMMS modified carbon paste electrodes contain two components: a nonconductive component (e.g., SAMMS) for adsorption of target metal ions and a conductive component (e.g., carbon graphite) for electrochemical detection. The procedure for measuring metal ion concentrations consisted of preconcentration (e.g., metal ions adsorption on nanopore surfaces inside the SAMMS particles), desorption and cathodic electrolysis (e.g., metal ions release from the nanopore surfaces, diffuse out of the nanopores, and deposit on the surface of graphite particles), detection, and regeneration (if necessary). Table 1 summarizes operating conditions for voltammetric detection experiments. During preconcentration, the electrode was immersed (at 2 cm from the solution surface) in a 20 mL cell (id 2 cm) containing 15 mL of metal ion solution at an open circuit for a specified period of time. Lead (Pb²⁺) solution and Pb²⁺/Hg²⁺ mixture solution were prepared daily by diluting atomic absorption (AA) standard solutions from Aldrich Co. (comprised of 1000 mg L⁻¹ of each metal ion in a 1% HNO₃ solution) with ultrapure Millipore water (18 MΩ cm). The pH of the diluted metal ion solution was between 5 and 6, thus no addition of buffer solution was required. During preconcentration, the solution was efficiently stirred (above 300 rpm). The electrode was removed at the end of the preconcentration step, rinsed with DI water, and transferred to another 20 mL cell containing 15 mL of supporting electrolyte solution (i.e., HNO₃, KNO₃). A negative potential was applied to the electrode immediately after immersing it into the electrolyte solution, thereby reducing the desorbed metal ion into elemental metal (cathodic electrolysis). The electrolysis step was performed for 60 s, except in the electrolysis time study. Stripping voltammetry was subsequently performed by sweeping a square wave potential towards the positive direction (i.e., from −1.0 V to 0.4 V for Pb, from −1.0 V to 0.6 V for Pb/Hg). Quiescent conditions (no stirring) were required in both cathodic electrolysis and stripping steps. The sweeping of a square wave

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Preconcentration</th>
<th>Electrolysis</th>
<th>Stripping</th>
<th>Regeneration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solution/electrolyte</td>
<td>0.5–1500 pph Pb²⁺, 3–1600 pph Hg²⁺</td>
<td>0.2 M HNO₃</td>
<td>0.2 M HNO₃</td>
<td>0.2 M HNO₃</td>
</tr>
<tr>
<td>Immersion time</td>
<td>2–20 min</td>
<td>0–2 min</td>
<td>—</td>
<td>1–2 min</td>
</tr>
<tr>
<td>Stirring speed</td>
<td>400 rpm</td>
<td>0</td>
<td>0</td>
<td>400 rpm</td>
</tr>
<tr>
<td>Applied potential: Pb</td>
<td>Open circuit</td>
<td>−1.0 V</td>
<td>−1 V–0.4 V</td>
<td>0.4 V</td>
</tr>
<tr>
<td>Applied potential: Pb/Hg</td>
<td>Open circuit</td>
<td>−1.0 V</td>
<td>1 V–0.6 V</td>
<td>0.6 V</td>
</tr>
</tbody>
</table>

**Table 1** Typical operating parameters during each step of the voltammetric detection experiments

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potential toward positive values was performed one more time to ensure that no metal ion was accumulated on the electrode surface. If the surface was clean, no peak would be detected in the second sweep. If a peak is detected, regeneration of the electrode is required for the subsequent run by applying a positive potential (0.4 V for Pb and 0.6 V for Hg/Pb) to the electrode, while the electrode was immersed in 0.2 M HNO₃ under stirred conditions. Unless specified otherwise, each measurement was performed in triplicate and the average value was reported. The relative standard deviations (% RSD) were normally less than 5%. No de-aeration of the samples or solutions was required in any step.

**Results and discussion**

The evaluation of a SH-SAMMS modified carbon paste electrode as a voltammetric sensor for metal ions involves optimizing the experimental parameters that affect both the preconcentration and detection steps. Lead (Pb²⁺) was used as a representative analyte in finding the optimal parameters, which would then be used in subsequent experiments to obtain calibration curves and detection limits for simultaneous detection of Pb²⁺ and Hg²⁺.

**Factors affecting the detection process**

**Electrolysis and stripping media.** Because SH-SAMMS is an electronic insulator, desorption of Pb²⁺ previously accumulated on SH-SAMMS to the electrode/solution interface must occur for the voltammetric detection to be possible. Then the desorbed Pb²⁺ may be detected directly by reduction from lead ion to elemental lead (Pb²⁺ → Pb(0)). However, it is more sensitive and quantitative if a thorough electrolysis by applying a negative potential to deposit Pb(0) on the electrode surface, followed by anodic stripping voltammetry to oxidize the previously reduced Pb(0) to Pb²⁺, is performed.

Different electrolysis and stripping media were investigated with an electrode composed of (by weight) 11% SH-SAMMS, 66% CPO carbon paste, and 23% oil. The experiments were performed at conditions as follows: 100 ppb Pb²⁺ preconcentration solution, 2 min preconcentration time, and 60 s electrolysis time. The results are summarized in Table 2. Decreased adsorption or increased desorption of Pb²⁺ from SH-SAMMS occurs at low pH. Therefore, electrolysis and stripping in neutral solution such as 0.1 M KNO₃ was ineffective for detection of lead, leading to no voltammetric response (zero current). When the stripping was performed in acid solutions (0.1 M or 0.2 M HNO₃) after the electrolysis was performed in 0.1 M KNO₃ solution, the voltammetric response (current) increased. However, the most effective lead detection was accomplished by performing both electrolysis and stripping in acid solution. Increasing the concentration of nitric acid solution as the electrolysis and stripping media from 0.05 M to 0.2 M did not significantly improve the sensitivity or reproducibility of lead detection but did decrease the need for regeneration of the electrode for the subsequent run and thus reduced the total analysis time. Therefore, 0.2 M HNO₃ is recommended as electrolysis and stripping media.

**Electrolysis time.** A complete desorption and electrolysis is required for an accurate quantification of lead ions. Fig. 1 shows the effect of electrolysis time on the voltammetric response for Pb²⁺ using an electrode composed of (by weight) 10% SH-SAMMS, 60% CPO carbon paste, and 30% oil. The experiments were performed under conditions as follows: 100 ppb Pb²⁺ preconcentration solution, 2 min preconcentration time, and 0.2 M HNO₃ as the electrolysis and stripping media. The peak current increased significantly as the electrolysis time was increased from 0 to 60 s and remained constant from 60 to 120 s. However, the reproducibility of the data was poor at the 120 s electrolysis period. This is probably due to the generation of H₂ bubbles on electrode surface that affected the stability of the signals. Therefore, a 60 s electrolysis period was chosen for lead deposition. A maximum voltammetric response obtained after an electrolysis period of only 1 min suggested a rapid desorption and diffusion rate of lead ions from inside the nanopores of SH-SAMMS to the electrode/solution interface.

**Factors affecting preconcentration process**

**Preconcentration time.** The effect of preconcentration time on the voltammetric response for Pb²⁺ using an electrode, composed of (by weight) 10% SH-SAMMS, 60% CPO carbon paste, and 30% oil, is shown in Fig. 2. The experiments were performed under conditions as follows: 100 ppb Pb²⁺ preconcentration solution, 60 s electrolysis time, and 0.2 M HNO₃.

**Table 2.** The effect of electrolysis and stripping media on lead detection

<table>
<thead>
<tr>
<th>Electrolysis medium</th>
<th>Stripping medium</th>
<th>Current/μA</th>
<th>RSD (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 M KNO₃</td>
<td>0.1 M KNO₃</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0.1 M KNO₃</td>
<td>0.1 M HNO₃</td>
<td>1.07</td>
<td>1.3</td>
</tr>
<tr>
<td>0.1 M KNO₃</td>
<td>0.2 M HNO₃</td>
<td>2.32</td>
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</tr>
<tr>
<td>0.05 M HNO₃</td>
<td>0.05 M HNO₃</td>
<td>4.15</td>
<td>1.7</td>
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<tr>
<td>0.1 M HNO₃</td>
<td>0.1 M HNO₃</td>
<td>3.62</td>
<td>2.9</td>
</tr>
<tr>
<td>0.2 M HNO₃</td>
<td>0.2 M HNO₃</td>
<td>4.33</td>
<td>1.3</td>
</tr>
</tbody>
</table>

**Fig. 1** Dependance of the 10% SH-SAMMS electrode response on the electrolysis time after 2 min preconcentration in 100 ppb Pb²⁺ solution.

**Fig. 2** Dependence of the 10% SH-SAMMS electrode response on the preconcentration period in 100 ppb Pb²⁺ solution.
as electrolysis and stripping media. Both peak currents and areas increased significantly and in parallel to each other as the preconcentration time was increased from 1 to 20 min with a more gradual increase from 20 to 30 min. For rapid detection of lead, a 2 min preconcentration period was found to be sufficient at this concentration range (100 ppb Pb²⁺). For the detection of Pb²⁺ at a much lower concentration (i.e., 1 ppb Pb²⁺), a 20 min preconcentration period may be required to obtain higher lead adsorption and hence larger peak size.

**Electrode compositions.** Four compositions of the SH-SAMMS modified electrode were studied and the results are summarized in Table 3. The experiments were performed under conditions as follows: 100 ppb Pb²⁺ preconcentration solution, 2 min preconcentration time, 60 s electrolysis time, and 0.2 M HNO₃ as electrolysis and stripping media. The same experiment was also performed on an unmodified carbon paste electrode. The powdered SH-SAMMS, when used as the modifier in a carbon paste electrode, clearly enhanced the sensitivity of the electrode for lead detection. The experiments performed on the unmodified carbon paste electrode (electrode #1) did not yield any voltammetric responses (currents) for lead, indicating that the conductive matrix (carbon graphite) was inert with respect to lead adsorption, similar to the results found by Walcarius and Bessière.²⁴

When the weight percent of SAMMS was kept relatively constant at 10% and the weight percent of oil was increased from 23% to 30%, the voltammetric responses decreased. As the fraction of oil increased, the electrode surface had increasing hydrophobicity and hence a decrease in the surface reaction between the metal ions and the functional ligands.²⁷ When the oil content was kept relatively constant at nominally 20 wt.%, increasing the weight percent of SH-SAMMS from 11% to 30% increased the voltammetric responses due to the increase in number of the binding sites. However, the reliability of the 30% SH-SAMMS electrode was poor after only 10 consecutive runs, whereas the reliability of the 20% SH-SAMMS electrode was still good even after 80 consecutive runs. When the composition of the electrode matrix included too high a SH-SAMMS loading and too low an oil loading, the electrode had poor reproducibility because the electrode material was not compact enough.²⁷ Therefore, the optimum electrode composition was 20% SH-SAMMS, 60% CPO carbon paste, and 20% mineral oil (electrode #4).

**Calibration and detection limits**

The calibration curve represents the voltammetric response (current and area) versus the metal ion concentration in the preconcentration solution. The experiments were performed on the optimal electrode and conditions found in previous sections (electrode #4: 20% SH-SAMMS, 60% CPO carbon paste, and 20% oil; conditions: 60 s electrolysis time, and 0.2 M HNO₃ as the electrolysis and stripping media). Fig. 3 shows representative voltammograms: (a) measured after 2 min preconcentration in a 30 ppb Pb²⁻/160 ppb Hg²⁺ solution and (b) measured after 20 min preconcentration in a 1.5 ppb Pb²⁻/3 ppb Hg²⁺ solution. Fig. 3 also shows that Pb²⁻ and Hg²⁺ peaks appear at −0.5 V and 0.4 V, respectively. The differential potential (ΔE) of 0.9 V indicates that the Pb²⁻ and Hg²⁺ peaks are not likely to interfere with each other, and hence could be detected simultaneously.

Fig. 4 shows the calibration curves as (a) currents and (b) areas of the Pb and Hg peak responses, measured after 2 min preconcentration time in a bi-component Pb²⁻/Hg²⁺ solution. For both metal ions, the peak area (Fig. 4b) appeared to be more useful as the detection response because it was linear with respect to metal ion concentrations for broader ranges than the peak current (Fig. 4a). When varying the concentration ratios of

### Table 3

<table>
<thead>
<tr>
<th>Electrode</th>
<th>SH-SAMMS (%)</th>
<th>CPO Carbon paste (%)</th>
<th>Oil (%)</th>
<th>Current/μA</th>
<th>RSD (%)</th>
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</thead>
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<tr>
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</tr>
<tr>
<td>4</td>
<td>20</td>
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<td>20</td>
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</tr>
<tr>
<td>5</td>
<td>30</td>
<td>52</td>
<td>18</td>
<td>12.90</td>
<td>1.6</td>
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</table>

![Fig. 3](image-url)  
Fig. 3 The voltammetric responses of Pb²⁺ and Hg²⁺ (a) measured after 2 min preconcentration in 30 ppb Pb²⁻/160 ppb Hg²⁺ solution and (b) measured after 20 min preconcentration in 1.5 ppb Pb²⁻/3 ppb Hg²⁺ solution.

![Fig. 4](image-url)  
Fig. 4 The Pb²⁻ and Hg²⁺ calibration curves as (a) currents and (b) area of the peak response after 2 min preconcentration in Pb/Hg solutions with varying concentrations.
Hg$^{2+}$ and Pb$^{2+}$ in the preconcentration solution from 0.5 to 2.0, the peak responses obtained for the two metal ions were still on the calibration curves. Therefore, the peak response for Hg$^{2+}$ was independent of the concentration of Pb$^{2+}$ in the solution and vice versa. Two factors may have contributed to this behavior: (1) the concentrations of both metal ions in solution were well below saturation point, thus metal ions did not need to compete for the binding sites, and (2) the pore size of the SH-SAMMS was large enough that the diffusion of the two metal ions was not limited by their hydrated sizes. This is a major advantage of SAMMS modified carbon paste electrodes compared with SAM thin film electrodes and organic ligand modified carbon paste electrodes.

Detection limits were evaluated at the same conditions as in the calibration curve measurements. The detection limit for Pb$^{2+}$ was 10 ppb after a 2 min preconcentration period and improved significantly to 0.5 ppb after a 20 min preconcentration period. Similarly, the detection limit for Hg$^{2+}$ was 20 ppb after a 2 min preconcentration period and improved to 3 ppb after a 20 min preconcentration period.

Electrode activation and regeneration

A virgin electrode surface was found to be less efficient (i.e., low peak response and low reproducibility) for preconcentration than surfaces that had previously been exposed to metal ions. For example, the voltammetric responses of 100 ppb Pb$^{2+}$ at the electrode #3 stabilized after 3–4 cycles of preconcentration/electrolysis/stripping. To avoid a time-dependent sensitivity in subsequent runs, all freshly made electrodes were activated by going through five cycles of preconcentration/electrolysis/stripping.

The extent of electrode regeneration depended on the concentration of the stripping acid and the size of the peak responses, which in turn were proportional to the amount of metal ion accumulated on the surface. When stripping in 0.2 M HNO$_3$ solution and the peak current was smaller than 5 µA, regeneration of the electrode was not required (no metal ion peak detected after the re-sweep), which differed from the results when stripping in 0.05 M or 0.1 M HNO$_3$. A higher acid concentration was better for desorption of lead and preventing the desorbed species from being re-accumulated on the surface than the lower acid concentration. For example, the re-sweep after the detection of 100 ppb Pb$^{2+}$ at electrode #3 (approximate current of 4 µA) yielded a residual peak current of 1.0 µA, 0.2 µA, and 0.0 µA when 0.05 M HNO$_3$, 0.1 M HNO$_3$, and 0.2 M HNO$_3$ were used as the electrolysis/stripping media, respectively. The larger the peak response was, the longer period was required for regeneration. However, regeneration in 0.2 M HNO$_3$ solution was normally accomplished within 1–2 min for a peak current size of 5–20 µA.

Interferences

An ionic species may be considered as an interference to the voltammetric detection of mercury(II) and lead(II) if: (1) it can out-compete Hg and Pb for the binding sites on SH-SAMMS during the preconcentration step, or (2) its peak response can overlap Hg or Pb peak in the detection step. The first factor may be indicated by the selectivity of the SH-SAMMS material for that ionic species, compared with those for Hg and Pb. From batch competitive adsorption experiments previously performed at PNNL, we have learned that the SH-SAMMS sorbent has exceptional affinity for binding Hg and Pb. For example, in the presence of Ag, Cr, Zn, Ba, and Na, the SH-SAMMS sorbent has demonstrated the mass-weighted distribution coefficients ($K_D$) of Hg and Pb on the order of magnitude of 10$^{10}$ at neutral pH. The high $K_D$ values are a result of thiol being a “soft” ligand, which preferably binds with “soft” Lewis acids like Hg and Pb.$^{31}$ The background ions, such as sodium, barium, and zinc, although present at high concentrations (i.e., 350 times higher concentrations than Hg and Pb) did not bind to the SH-SAMMS. Other “soft” Lewis acids like Cd, Cu, Ag, and Au may also bind to the SH-SAMMS, but not as effectively as Hg and Pb. The $K_D$ values of Cu and Cd, for instance, are about twenty-five times lower than those of Hg. In addition, the redox potential of these metal ions (Cd, Cu, Ag, and Au) are different from Hg and Pb, thus their peak responses will not overlap with those of Hg and Pb. The presences of other anions (i.e., CN$^-$, CO$_3^{2-}$, SO$_4^{2-}$, PO$_4^{3-}$) also did not significantly interfere with the adsorption of lead and mercury ions onto the SH-SAMMS, and are thus presumed to not be likely to interfere with the detection of lead and mercury.

Conclusions

The SH-SAMMS modified carbon paste electrode coupled with an anodic stripping voltammetry technique can be used to detect lead(II) and mercury(II) simultaneously. The SH-SAMMS modified carbon paste electrode has many advantages over the existing chemically modified electrodes (CMEs), which normally use commercially-available ligands as the modifiers. The high surface area of the mesoporous silica and the covalent binding between the thiol (-SH) groups in SH-SAMMS and metal ions in solution make SAMMS a better sorbent than existing commercial ligands.$^{29}$ The SH-SAMMS has been shown to be dramatically faster and more selective for adsorption of Hg, with the selectivity a factor of 1000 higher than that of Duoliter™ GT-73, an organic ion exchange resin commonly used for Hg removal. The selectivity of SH-SAMMS to the target metal ions (Hg and Pb) is excellent. SAMMS will not accumulate common metal ions such as sodium and calcium, which are often present in waste waters at much higher concentrations than the target ions. The high loading capacity and high selectivity of SH-SAMMS are desirable for metal ion detection based on the AdSV technique because they minimize the competition for the binding sites of the non-target species, thereby reducing the interferences and preserving the signal intensity of the target metal ions. Besides, since SAMMS particles are not conductive the high surface of the material does not contribute to the charging current of the SAMMS modified carbon paste electrode. This leads to the low background current of the electrode. The binding between SH-SAMMS and metal ions is reversible, therefore the SH-SAMMS based electrodes can be easily regenerated without damaging the ligand monolayer by desorption of the preconcentrated species in an acidic solution. By choosing an appropriate acid solution as a stripping medium, the electrodes usually are ready for reuse after the stripping voltammetric measurement. The special advantage of using SAMMS over other organic ligands is that de-aeration of the sample, electrolysis medium, and stripping medium is not required, making the SAMMS-modified electrodes suitable for integration into portable sensor devices for on-site metal detection. In addition, self-assembled monolayer chemistry readily allows installation of a wide variety of chemical monolayers that can be tailored to specific metal ion detection needs when used as electrode modifiers. Other sensors that are based on different functionalized mesoporous materials are currently being investigated at PNNL.

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