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Electrochemistry with Mesoporous Silica: Selective Mercury(II) Binding

Alain Walcarius* and Jacques Bessière

Laboratoire de Chimie Physique pour
l'Environnement, Unité Mixte de Recherche UMR
7564, CNRS—Université H. Poincaré Nancy I, 405,
rue de Vandoeuvre, F-54600 Villers-les-Nancy, France

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The ever-growing family of ordered mesoporous solids, first reported in 1992,[1] continues to stimulate interest in various fields of chemistry, having wide potential application in catalysis, separations, adsorption, coatings, or microelectronics.[2,3] Their implication in electrochemistry is desirable with respect to, for example, the development of new sensors or supported electrocatalysts, but is strongly limited by their insulating properties. Here we report the incorporation of pure silica MCM-41 in a conductive composite matrix, and we evaluate the interest of the resulting electrode for exploiting the combination of the adsorption properties of the mesoporous material with a selected electron-transfer reaction. This is exemplified by the electrochemical monitoring of the highly selective mercury(II) binding on the silica surface. The choice of mercury is supported by the still actual contamination of the environment by this element,[4] which has led to remarkable efforts toward finding selective adsorbents for wastewater treatment,[3d,5] and/or developing analytical methods for this metal.[6] No regeneration of the electrode surface was required allowing multiple successive analyses. In addition, this inherently simple technique appears to be promising for the rapid screening, in nondestructive conditions, of the binding properties of novel materials such as mesoporous organic−inorganic hybrids.

The modified electrode was made of a homogeneous dispersion of MCM-41 particles, typically 10 wt %, within a graphite composite (i.e., graphite paste, a common matrix in electrochemistry).[7] The former was immersed during a selected period of time into a solution containing Hg(II) species at pH 5.5, and then transferred to acid medium where square wave voltammetry was performed. Voltammograms (Figure 1) show a well-defined anodic peak at 0.25 V, resulting from the oxidation of preelectrolyzed metallic mercury (2 min deposition time at −0.2 V). This figure demonstrates the capacity of pure silica MCM-41 for the uptake of Hg(OH)$_2$ (the main form of mercury at pH 5.5) which is

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* To whom correspondence should be addressed: Fax: (+33) 3 83 27 54 44. E-mail: walcariu@lcpe.cnrs-nancy.fr.

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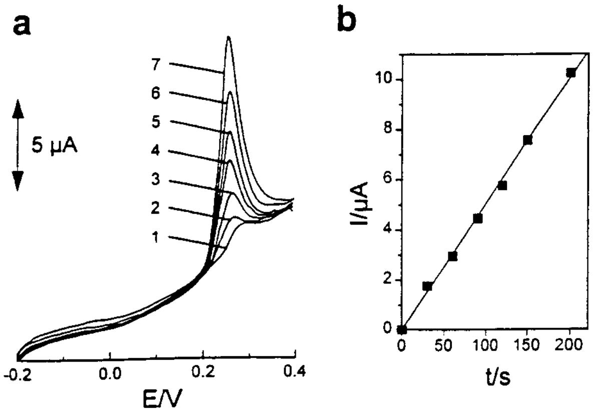

Figure 1. Accumulation of mercury(II) at a pure silica MCM-41-modified graphite paste electrode. (a) Anodic stripping square wave voltammograms recorded in 0.2 M HNO_3 after accumulation during selected periods of time at open circuit from a 1.0×10^{-5} M mercury solution of 1×10^{-2} M acetate buffer (pH 5.5), and an electrolysis performed during 2 min at a potential of −0.2 V, relative to Ag/AgCl reference electrode. Accumulation times: (1) without accumulation, (2) 30 s, (3) 60 s, (4) 90 s, (5) 120 s, (6) 150 s, and (7) 210 s. (b) Anodic peak currents of mercury as a function of preconcentration time.

known to be a fully soluble metal hydroxide at concentration lower than 2×10^{-4} M.[8] The same experiment performed on unmodified carbon paste did not reveal any signal for mercury, pointing out the inertness of the conductive matrix with respect to mercury adsorption. Accumulation is governed by the ease of transport of the analyte to binding sites, so that efficiency was high when using materials displaying high specific surface area and regular channels of tailor-made monodispersed dimensions. This advantage also belongs to the detection step for which sensitivity is controlled by the desorption rate and diffusion of Hg^{2+} species out of the mesoporous silica to reach the conducting substrate. Compared to amorphous silica gel, the regular tridimensional structure imparts to the MCM-41 an easier (and probably faster) route to the binding sites. As an illustration, an electrode modified with a MCM-41 displaying a pore size of 2.9 nm gave an amperometric response of the same order of magnitude as that recorded when using amorphous silica gel with an average pore size of 6.0 nm. In addition, no chemical modification of MCM-41 (for example by thiol groups[3]) to obtain specific binding sites was required for the material to exhibit a preconcentration behavior toward mercury species, making very simple its possible use for mercury removal, and promising for the further development of selective amperometric sensors.

Contrary to most electrochemical devices based on chemically modified electrodes,[9] no regeneration procedure for the MCM-41-modified electrode was required because the detection step solely ensured complete desorption of the previously accumulated mercury species which cannot be adsorbed again on the electrode

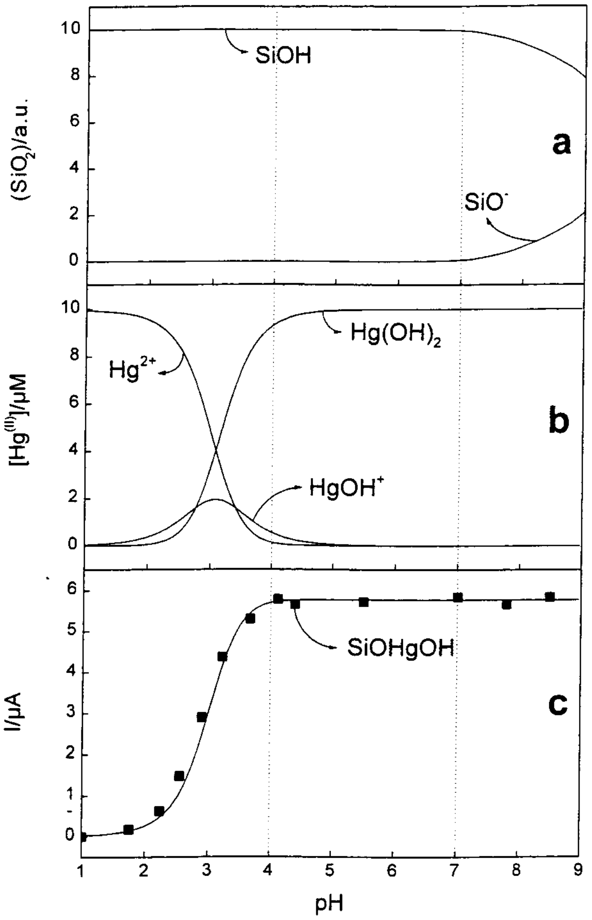

Figure 2. (a) Evolution of the mesoporous silica surface as a function of pH; (b) speciation with pH for mercury at a total concentration of 1.0×10^{-5} M; and (c) adsorption isotherm obtained for 1.0×10^{-5} M mercury on MCM-41. Data were obtained at a MCM-41-modified graphite paste electrode after a 5 min accumulation period; other conditions as in Figure 1. Dotted lines at pH 4 and 7 define the pH range where selective mercury adsorption occurs.

modifier in strong acid medium (pH < 2). More than 100 successive "adsorption−voltammetric detection" measurements were performed from a 1.0×10^{-5} M mercury solution without any deterioration of the voltammetric signal. For the purpose of multiple successive analyses under various experimental conditions, optimization was carried out by varying several parameters (electrode composition, pH, time of accumulation, potential and time of deposition, and stripping potential waveform), and a linear dependence of peak currents was observed in the range of 1×10^{-6} M to 1×10^{-4} M mercury, with a relative standard deviation of 3% (n = 6), using the same electrode surface.

The MCM-41-modified electrode displays very high selectivity for hydroxylated mercury(II) species. For example, the accumulation of 1.0×10^{-5} M $Hg(OH)_2$ at pH 5.5 (and further detection in acid medium) was not affected by the presence of 1 M Na^+ + 1 M K^+ + 0.5 M Ca^{2+} + 0.5 M Mg^{2+} (Hg^{II} recovery: 98 ± 2%). A similar experiment performed in the presence of 5×10^{-3} M Cu^{II}, Ni^{II}, Co^{II}, Zn^{II}, Se^{IV} gave a recovery of 101 ± 2%, while 1×10^{-3} M Cd^{II} and 1×10^{-3} M Pb^{II} led to Hg^{II} recoveries of 100 ± 2% and 96 ± 2%, respectively. The high selectivity can be rationalized by considering the intrinsic adsorption mechanism and the fact that the

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accessibility to the electrode surface was restricted to only the soluble species. In contrast, the evolution of the MCM-41 surface (Figure 2A) and mercury speciation (Figure 2B) with pH should be considered. At pH lower than 7, the internal surface of MCM-41 is made of nonionized hydroxyl groups (i.e., silanol). At pH higher than 4 and in the absence of complexing ligands in the medium, mercury(II) is entirely under the form of $Hg(OH)_2$ and soluble at concentrations up to 2×10^{-4} M.[8] Consequently, for pH values ranging from 4 to 7, soluble $Hg(OH)_2$ can be adsorbed on the MCM-41 material by reacting with silanol groups via a condensation process (eq 1), as is common for the fixation of metal hydroxides on surface hydroxyl groups of minerals.[10] When existing, $HgOH^+$ can also react with silanol groups (eq 2).

$$(\equiv SiOH) + Hg(OH)_2 \rightleftharpoons (\equiv SiO{-}Hg{-}OH) + H_2O \quad (1)$$

$$(\equiv SiOH) + HgOH^+ \rightleftharpoons (\equiv SiO{-}Hg^+) + H_2O \quad (2)$$

Figure 2c shows the ability of MCM-41 to adsorb mercury(II) species containing at least one hydroxyl group and also demonstrates the usefulness of electrochemistry at modified electrodes for the monitoring of the adsorption process. Selectivity is thus achieved in the pH range between 4 and 7 because the silica surface is mainly neutral in this pH range, preventing any accumulation by ion exchange, and because metal hydroxides other than those of mercury(II) are not soluble enough to reach MCM-41 particles located at the electrode surface. Therefore, metal species that are not hydroxylated (even those highly concentrated and soluble) are not able to bind to the MCM-41 surface in that pH range; they can only interact with silanolate groups which are formed in significant amounts at pH higher than 7. Note that mercury adsorption was still operative at pH higher than 7 (up to pH 10), at the same level as in the pH range 4−7, but it became less selective with respect to the presence of metal cations in the medium ($>5 \times 10^{-3}$ M) when the pH was raised.

The results obtained by electrochemistry were confirmed by performing simultaneous experiments using conventional batch analyses (by inductively coupled plasma−atomic emission spectrometry) of both solid and solution phases after equilibration. After normalization of the maximum voltammetric currents to the maximum adsorption capacity of MCM-41 for mercury(II), excellent agreement between the results obtained from both methods has been found, despite the fact that the heterogeneous nature of the modified graphite paste (i.e., the presence of a binder) could spoil the adsorption behavior in a way that the results could not be compared with those of studies with the pure adsorptive material.

In conclusion, we have highlighted here the use of a MCM-41-modified graphite paste electrode by characterizing the selective binding of mercury(II) on a pure silica MCM-41 material. In addition, we have proposed a practical and experimentally simple method for the rapid evaluation of the ability of silica-based materials, to accumulate mercury(II) species. This methodology could be extended to the ever-growing family of organically modified mesoporous solids,[3,11] and contribute to a wider use of silica-modified electrodes in electroanalytical chemistry.[12]

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