Vattenrening och återvinning av tungmetaller med elektrokemiska legeringar

(Water purification and recycling of toxic heavy metals using electrochemical alloys)

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1. Overview of the project

The aim of this project was to develop a novel technique to recover toxic heavy metals from contaminated solutions. The technique is based on electrochemical alloy formation, where toxic heavy metal atoms or ions are incorporated in a noble metal placed on the cathode in an electrochemical cell. In this project, focus has been on recovery of mercury. Platinum was used to recover mercury from aqueous solutions via electrochemical formation of $PtHg_4$. The overall process is schematized in Figure 1, and comprises two steps: uptake of mercury from solution (alloy formation), and regeneration of the electrode for further re-use (decomposition of the alloy to regenerate platinum, and recover mercury). The technology has potential applications in decontamination of, e.g. industrial and natural waters containing toxic metals. The method is a reagent-free alternative to chemical processing, which requires the use and/or addition of chemical compounds.

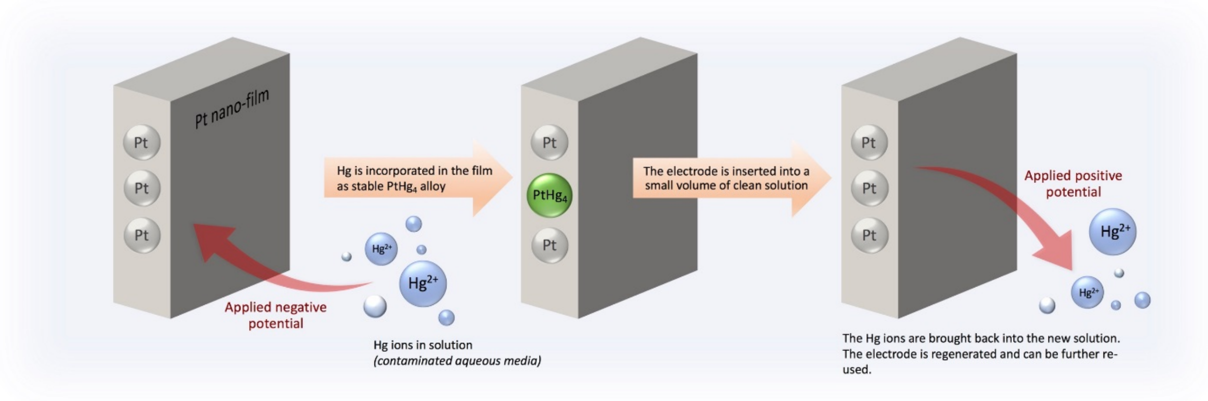

Figure 1 – Schematic representation of the proposed process.

2. Background

Emissions of toxic metals have been increasing linearly since the industrial revolution, and releases of mercury, arsenic, cadmium and lead are a major concern (1-3). Constant efforts have, and are being carried out to minimize these emissions. Such efforts rely on, e.g. cleaner and/or alternative processing, trapping the harmful substances to prevent their release in the environment, chemical conversion to more stable and/or less toxic species, etc. Despite these, heavy metal pollution is still a global issue, specifically releases of mercury to waters.

Anthropogenic sources of mercury include gold mining, burning of fossil fuels, metal production, cement production, waste incineration, contaminated sites, chloralkali industries, and dental amalgam production/use (4, 5). The estimates of mercury emissions have large uncertainties, bur are in the range of 1010 – 4070 tonnes/year. Anthropogenic sources account for 30% of the total annual emissions to air, the rest being attributed to re-emission of mercury from oceans and lakes (60%), and natural sources (10%).

Contamination of water is an important issue that needs addressing, given its vital role, and the fact that it plays a major part in the cycling of mercury in the environment. Mercury in aquatic streams raises additional concerns due to its mobility, volatility, and potential for bioaccumulation (6). Current solutions to reduce mercury levels in aqueous feeds include precipitation, flocculation, absorption (e.g.

on activated charcoal), ion exchange, and solvent extraction (7). One of the major downsides is the addition of chemicals to facilitate decontamination, e.g. addition of sulphides to precipitate soluble mercury as stable mercury sulphide. Some applications are also limited by metal concentration and feed volume.

The technology investigated and developed in this project has potential to be an environmentally-friendly alternative to chemical processing, due to several advantages:

- capability to process large volumes of contaminated solution;
- no addition of chemicals is needed;
- low current is needed;
- regeneration of the electrodes for further re-use is possible;
- it is possible to recover mercury in different form: ions in solution or solid compounds (by further treatment of the former).

3. Proposed work and experimental procedure

Several research questions have been raised in the project application:

- How thick alloy films can be formed using this method?
- How efficient is the process at very low Hg concentrations, different pH, and presence of other compounds?
- What is the best way of regenerating the electrodes and extracting the Hg?

Thin platinum films (100 nm) were used to study the process, and to estimate the potential of the technology. Thin films offer large surface area, thus good contact between the working electrode and the contaminated solution. Fused silica (15 mm x 30 mm x 0.5 mm) was used as substrate. A 3 nm layer of titanium (binder), followed by a 100 nm layer of platinum were deposited on the substrate using physical vapour deposition. A flat design, with a 2.25 cm^2 platinum area immersed in solution, was chosen (Figure 2). This was sufficient to get an understanding of the process at bench scale.

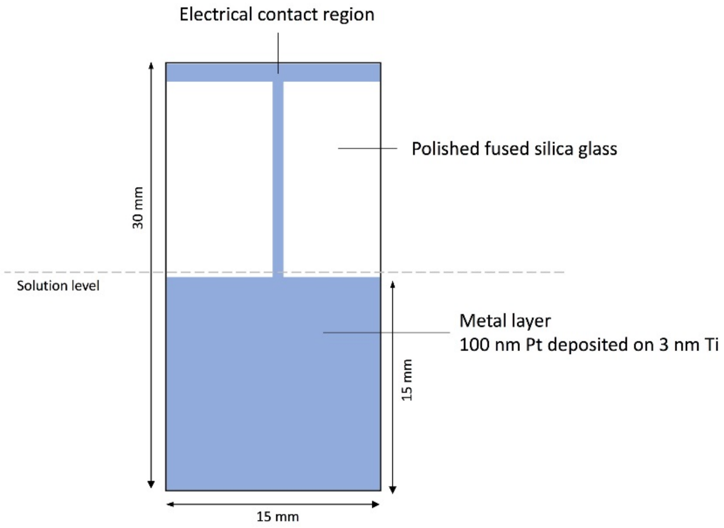

Figure 2 – Schematic representation of the Pt nano-film electrodes used.

The experimental work comprised of:

- Electrochemical investigations (cyclic voltammetry, chronoamperometry, and chronopotantiometry). These were done to determine the parameters for the process (the potential and the current), and to understand how they affect the formation and the stability of the alloy;
- Analysis of the mercury concentration in solution during and after electrochemical treatment. This was done using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS);
- Studying the changes occurring in the platinum film. The electrodes before and after electrochemical treatment were analysed using Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDS) and X-Ray Diffraction (XRD).

The experimental setup used is schematized in Figure 3.

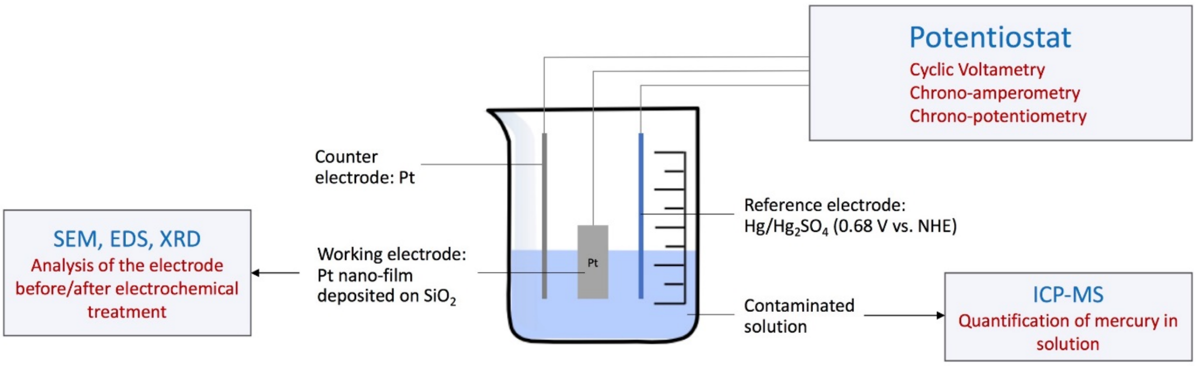

Figure 3 – Experimental setup used to study the decontamination process

4. Main results and discussions

4.1. Alloy formation on platinum nano-films

Early pre-tests showed that it is possible to decrease the mercury concentration in solution by forming mercury-platinum alloys on platinum electrodes, when an electrical potential is applied. In the absence of an electrical potential, alloy formation was not noticed. Clean platinum nano-film electrodes and electrodes loaded with mercury (25% of the $PtHg_4$ stoichiometric saturation limit) were immersed into 1 M nitric acid containing 10 mg/L mercury. No noticeable decrease of the mercury concentration, nor any increase of platinum concentration in solution was noticed during >48 h. This confirmed the stability of platinum and platinum-mercury alloy.

The present investigations showed that it is possible to decrease the mercury content by at least 95% of the initial amount, when applying a potential of 0.18 V vs. RHE (-0.5 V vs. REF) (Figure 4).

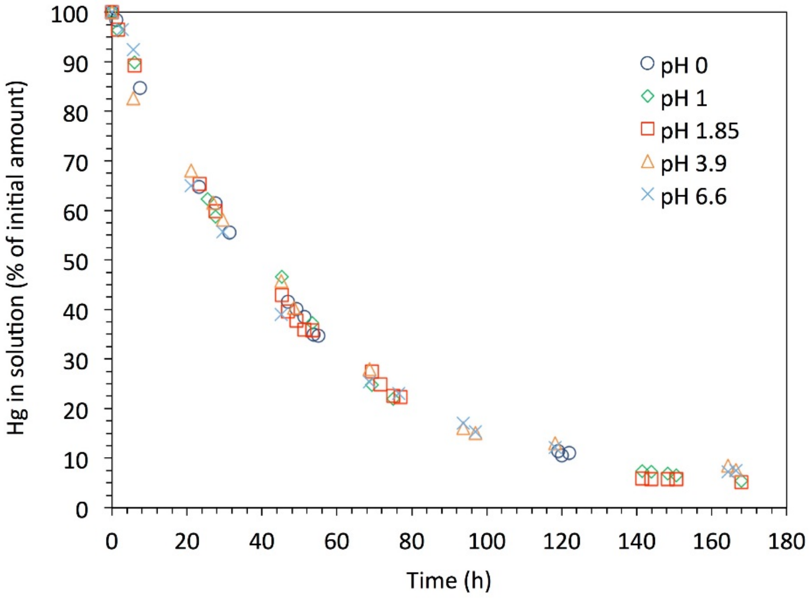

Figure 4 – Decrease in mercury concentration from 50 mL nitric acid solution, initially containing 10 mg/L mercury. [NO_3^-] = 1 M. WE: 100 nm Pt nano-film (2.25 cm^2); CE: Pt wire; REF: Hg/Hg_2SO_4. E=0.18 V vs. RHE.

To get additional information about the process, the electrodes before and after electrochemical treatment were analysed using SEM, EDS and XRD. It was concluded that the major specie formed during the process was $PtHg_4$ (Figure 5).

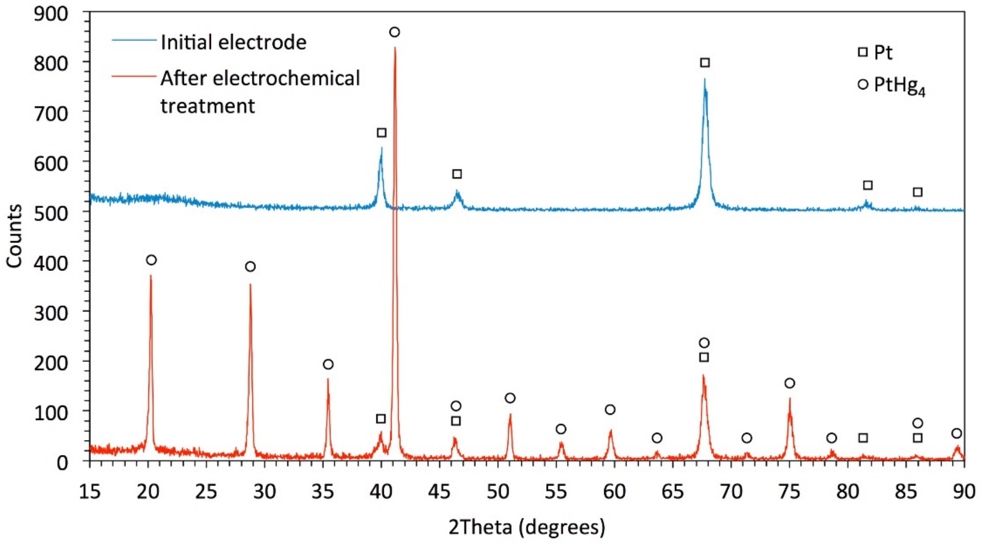

Figure 5 – XRD pattern of the Pt nano-film before and after electrochemical treatment.

The alloy is formed in two steps. First, the mercury ions in solutions are reduced to elemental mercury, according to Equation 1. Afterwards, elemental mercury reacts with platinum, forming the alloy, which penetrates the platinum nano-film (Equation 2).

$Hg^{2+} + 2\ e^{-} \leftrightarrow Hg^{0}$ (1)

$Pt + 4\ Hg \leftrightarrow PtHg_4$ (2)

Additional reduced mercury atoms will require penetration into the metallic film to form the alloy. It was reported that mercury is more abundant in the first layers after deposition (8). This penetration is a rather slow process, especially after several layers of alloy have formed. The reduction of available active platinum atoms on the surface slows down the absorption of more mercury, affecting the kinetics. These observations seem to correlate with those made by Wang et al. (9) and Ojea-Jiménez (10), who also reported slow inward metal inter-diffusion of mercury, albeit on gold particles.

However, by using electrodes with larger surface area, decontamination is expected to be faster. In this study, the active platinum surface was relatively small (2.25 cm^2), but sufficient to get an understanding of the process at laboratory scale. For industrial processing, the electrodes will have significantly larger active surface area, e.g. packed bed design, porous construction, mesh with embedded nanoparticles, etc.

4.2. The influence of pH on the decontamination process

The pH is an important parameter in the decontamination of aqueous streams. To study how this affects alloy formation, mercury solutions with pH values in the range 0 – 6.6 were subjected to electrochemical treatment. The pH was controlled by addition of nitric acid, and the ionic strength was kept constant by addition of sodium nitrate. Approximately 50 mL of contaminated solution (10 mg/L initial mercury) was used in each experiment. The results are presented in Figure 4. It was concluded that the pH did not play a significant role in the decontamination process. This is a clear advantage for decontamination of (almost) neutral solutions, e.g. natural waters, as acidification is not needed to facilitate alloy formation. The fact that the process is capable of handling very acidic streams is also a significant plus, e.g. the processing of industrial wastes with very low pH, as it bypasses a neutralization step (further consumption of chemicals and possible generation of secondary effluents).

4.3. The influence of mercury concentration in solution

Mercury concentration also plays an important role in decontamination. A challenge for some existing processes is the effective decontamination of large volumes containing very low mercury content, e.g. µg/L amounts. Processes which are efficient in a wide range of concentrations are desired, e.g. effective decontamination efficiencies are obtained at low and at high concentrations of mercury.

The experimental data showed good decontamination efficiencies in a wide range of concentrations (Figure 6).

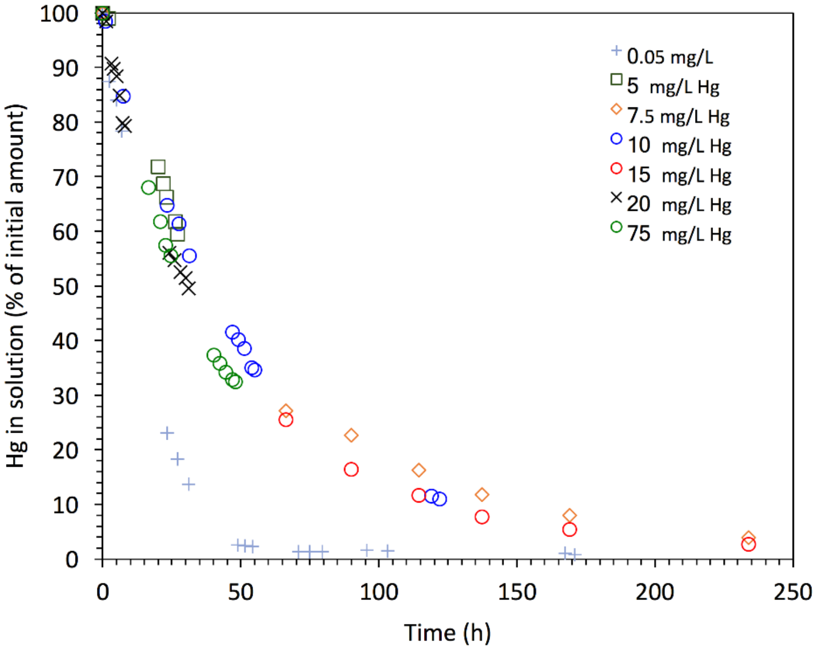

Figure 6 – The influence of mercury concentration in solution on the efficiency of the decontamination process. Electrolytes: 50 mL solution nitric acid 1 M with 0.05-75 mg/L mercury. WE: 100 nm Pt nano-film (2.25 cm^2); CE: Pt wire; REF: Hg/Hg$_2$SO$_4$. E=0.18 V vs. RHE.

About 35 – 40 h were needed to reduce the mercury content by 50% in solutions containing 5 – 75 mg/L mercury. For more diluted solutions, e.g. 0.05 mg/L (50 µg/L), the process was faster. In this case, over 75% of the mercury was absorbed in 24 h. This different behaviour at low concentrations relates to the slower penetration of reduced mercury atoms after several layers of alloy are formed (as explained in section 4.1).

Possible treatment of low concentrated streams is a clear advantage. The fact that the concentration of mercury in solution can be decreased to such low values (<0.4 µg/L here, after starting with 0.05 mg/L mercury) can be applied to purify water to drinking standards. The mercury limit in drinking water is around 2 µg/L (11).

4.4. Saturation capacity

The theoretical saturation capacity of the working electrode can be calculated based on Equation 2, if the thickness and the surface area of the platinum film is known. To completely decontaminate a solution with 10 mg/L mercury, about 25% of the saturation capacity of our working electrode will be required. The results of a test with a solution containing mercury well above the saturation limit of the working electrode (75 mg/L) is presented in Figure 7.

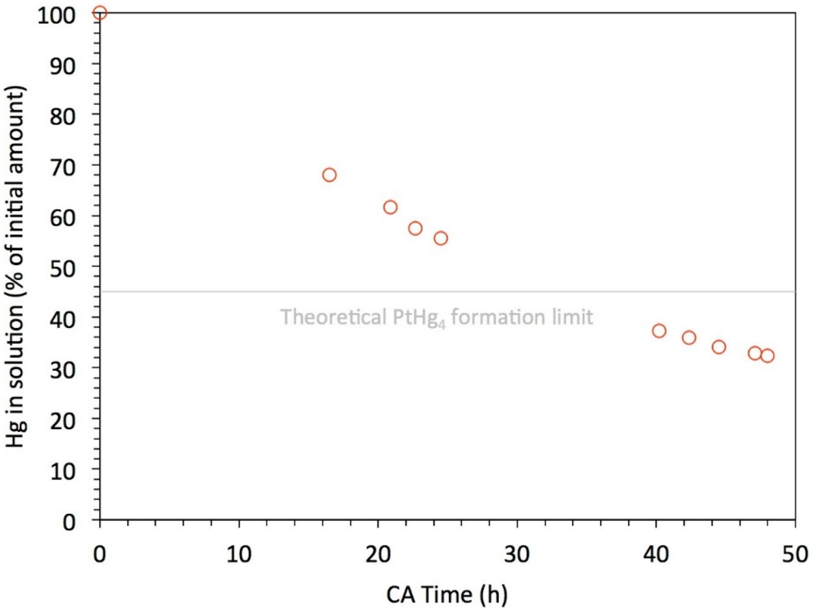

Figure 7 - Decrease of mercury concentration in 50 mL solution 1M HNO_3 containing 75 mg/L mercury. WE: 100 nm Pt nano-film (2.25 cm2); CE: Pt wire; REF: Hg/Hg_2SO_4. E=-0.5 V vs. REF.

Although the saturation limit was reached after about 20 – 25 hours, the mercury levels in solution continued to drop somewhat. This is most likely due to the reduction of mercury ions (Equation 1), and their deposition as elemental mercury on the platinum-mercury alloy layer formed. This was confirmed by ICP-MS and EDS analysis, which showed a surplus of mercury on the electrode (more mercury than the weight percentages expected for $PtHg_4$). Loading of the electrode close to saturation comes with disadvantages regarding the stability of the layer formed. This becomes unstable, and cracks, as shown in Figure 8. It is recommended to carry out decontamination with electrodes that contain sufficient platinum to avoid saturation. This will also make regeneration easier.

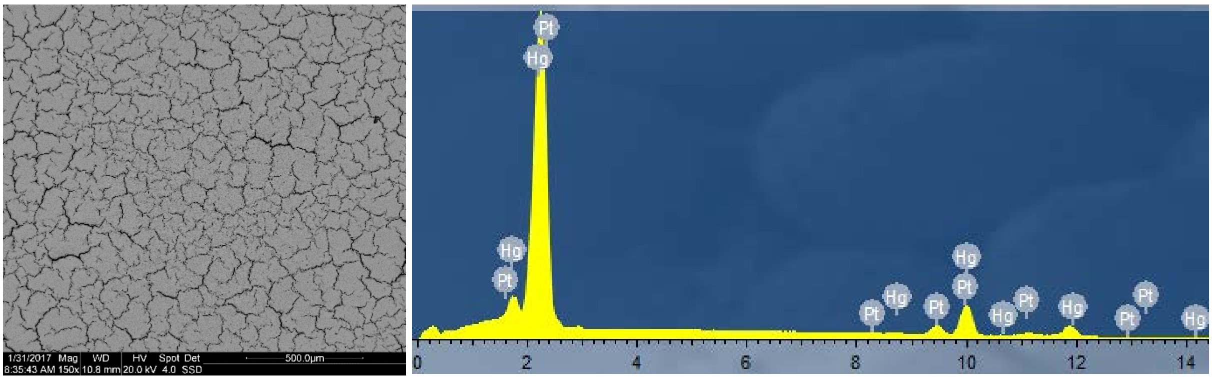

Figure 8 – SEM image of a saturated electrode (left) and the corresponding EDS spectrum (right), showing the presence of mercury and platinum. EDS data: 82 %wt. mercury and 18 %wt. platinum. Mercury and platinum amounts in $PtHg_4$: 80.4 %wt. and 19.6 %wt., respectively.

4.5. Electrode regeneration

It was observed that, during alloy formation, the current was in the range of about -40 µA (Figure 9).

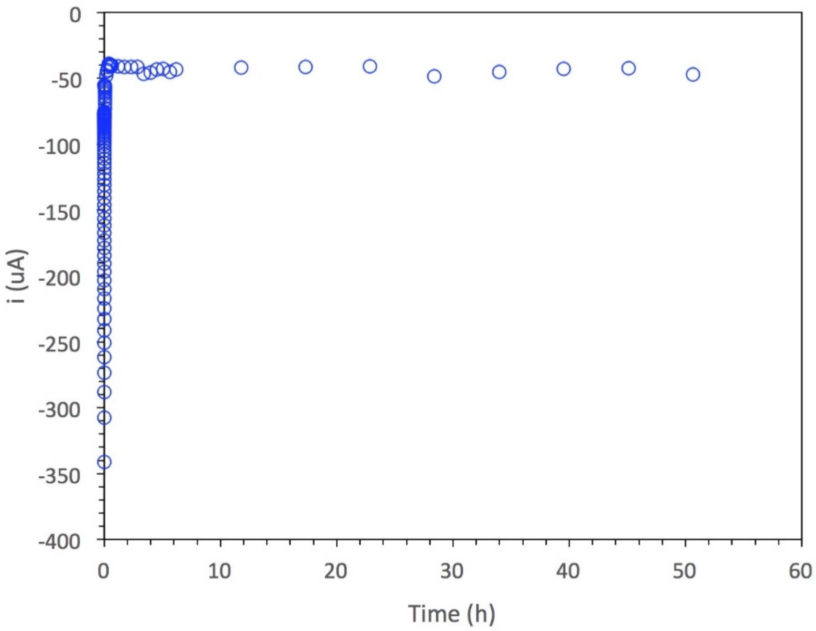

Figure 9 – Chrono-amperometry data obtained during electrochemical treatment of 50 mL solution 1 M HNO_3 *solution containing 10 mg/L mercury. WE: 100 nm Pt nano-film (2.25* cm^2*); CE: Pt wire; REF:* Hg/Hg_2SO_4*. E=-0.5V vs. REF (0.18 vs. RHE).*

To regenerate the electrodes after loading of mercury, a reverse current can be applied to the system, as schematized in Figure 1. In this case, the mercury absorbed can be brought back into a significantly smaller volume of clean solution, which can be very easily processed or contained. An alternative is to heat the electrodes to convert the alloy into elemental mercury (volatile at higher temperatures), and metallic platinum.

When applying a 40 µA current to an electrode containing $PtHg_4$, the concentration of mercury in solution increased due to decomposition of the alloy (Figure 10). This step is significantly faster when compared to the alloy formation step. More than 95% of the mercury in the electrode was brought back into 1 M HNO_3 solution in little over one day.

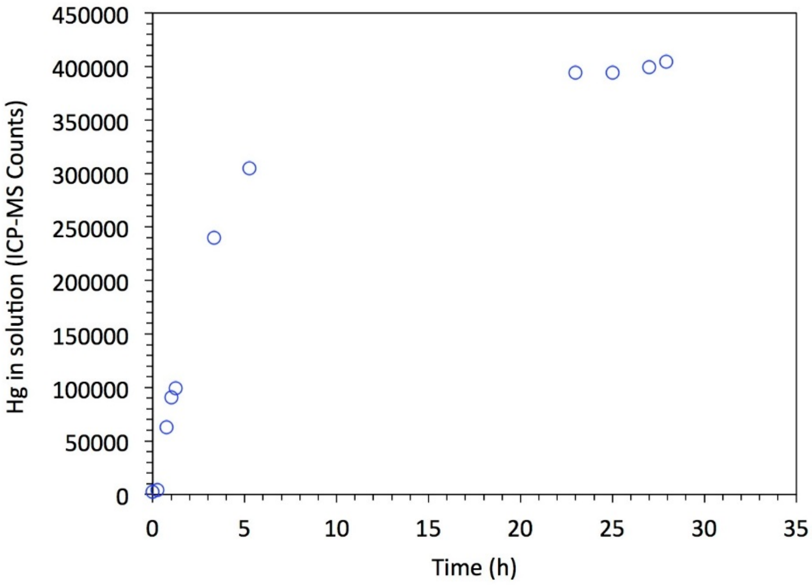

Figure 10 – The increasing of mercury concentration in solution during the regeneration of an electrode previously used for decontamination (containing platinum and $PtHg_4$ alloy). More than 95% of the mercury in the electrode was brought back in solution during the investigated time. CE: Pt wire; REF: Hg/Hg_2SO_4. Applied current: 40 µA.

Investigations using SEM, EDS and XRD revealed that the major phase in the electrode after the regeneration step becomes, again, pure metallic platinum (Figure 11).

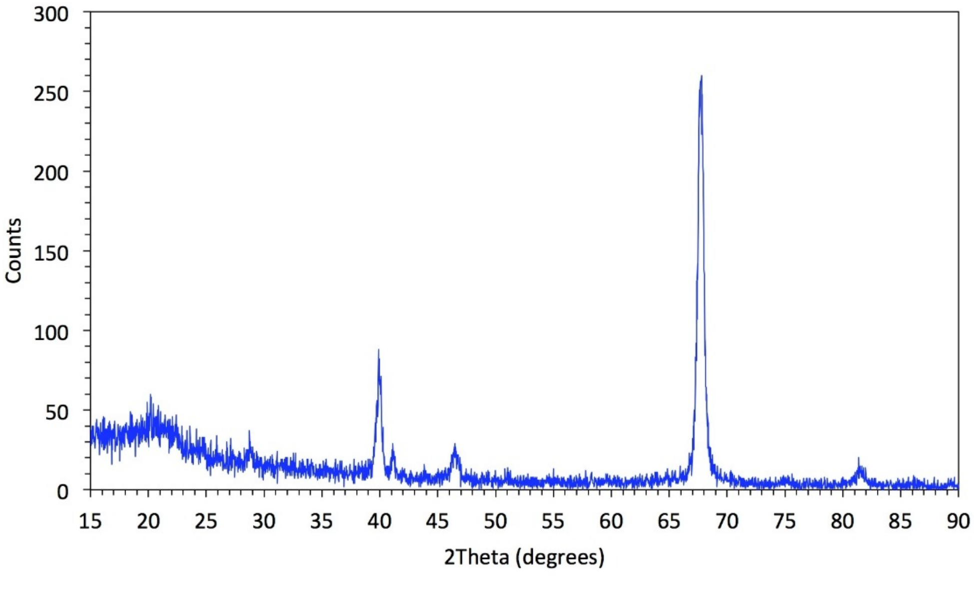

Figure 11 – XRD pattern of the stripped electrode, revealing the presence of platinum as major constituent (also see Figure 3).

4.6. The influence of other metal ions in solution.

The electrochemical behaviour of other cations in solution was studied using a 1 M nitric acid electrolyte containing 10 mg/L of each mercury, calcium, magnesium, manganese, sodium, nickel, cadmium, copper, lead and zinc, and 20 mg/L iron. During 7 days of experiment, the mercury content in solution decreased significantly (>90% efficiency), forming $PtHg_4$ on the working electrode in a very similar manor as the previous experiments with only mercury in the solution. No significant change in the concentrations of calcium, magnesium, sodium, nickel, cadmium, zinc, and iron was noticed. The copper concentration in solution decreased by about 40 %. SEM/EDS revealed the presence of copper on the working electrode (*Figure 12*). Manganese and lead concentrations in solution also decreased with about 10% and 70%, respectively. SEM/EDS showed that these metals became incorporated in a surface layer on the platinum wire counter electrode (the anode), which changed colour from silver to black.

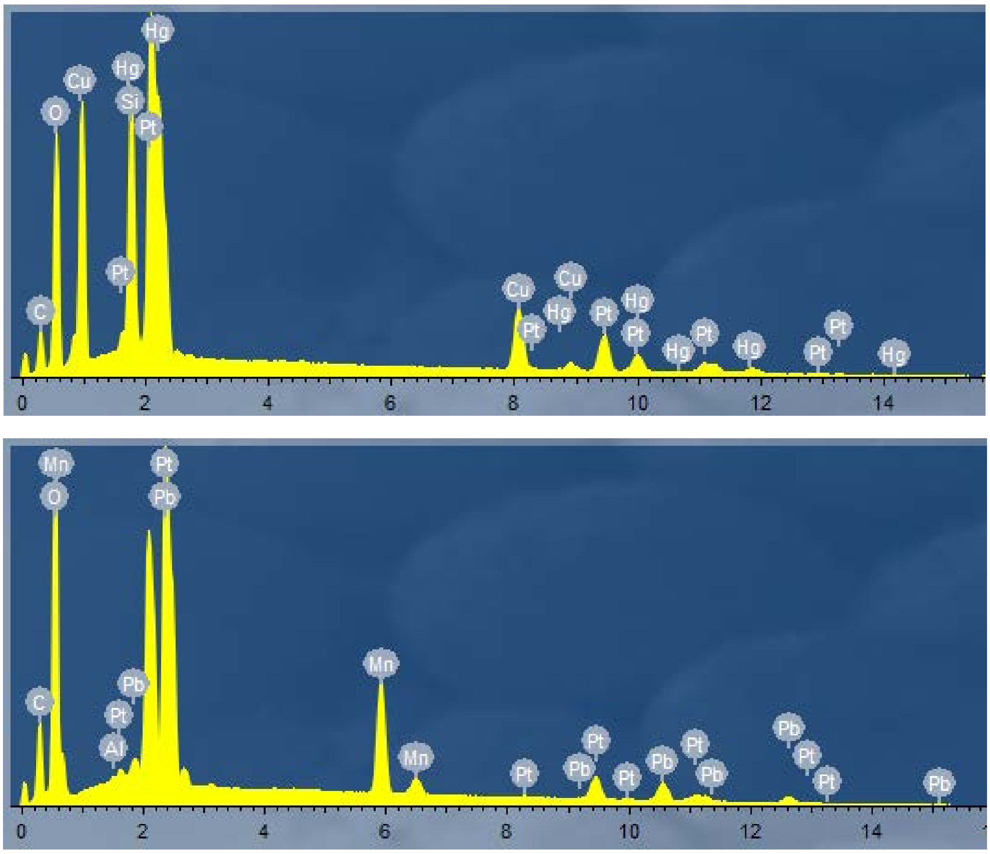

Figure 12 – EDS spectrum of the working (top) and counter (bottom) platinum electrodes after electrochemical treatment of a solution containing 10 mg/L of each mercury, calcium, magnesium, manganese, sodium, nickel, cadmium, copper, lead and zinc, and 20 mg/L iron.

5. Conclusions and future perspectives

The investigations carried out in this project showed that electrochemical alloy formation is a promising method for decontamination of solutions containing toxic heavy metals. Mercury can be electrochemically reduced and incorporated into platinum films as stable $PtHg_4$ alloy. The process works in wide pH and concentration ranges, and can achieve >95 % decontamination efficiencies. It was possible to decontaminate solutions below the limits allowed for mercury in drinking water. Regeneration of used electrodes, and recovery of absorbed mercury is possible, with low current consumption. The efficiency and kinetics can be improved by choosing an electrode with increased surface area, e.g. porous or packed bed design. Large scale systems can be used to decontaminate various streams, from contaminated industrial solutions to natural waters. Due to the very low power consumption, it would be straight forward to design portable systems powered by, e.g. solar cells and/or batteries.

6. Project outcomes

A patent application describing this technology will be filed in the end of October 2017. The application is currently undergoing a final revision prior to submission. Due to patenting, publication of the data was postponed. A manuscript summarizing the relevant findings will be submitted to a high impact journal after the patent is filed. In addition, Chalmers Ventures together with Chalmers School of Entrepreneurship has formed a project around the technique and two master students will work on utilization and commercialisation.

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