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Electrochemical removal of mercury from contaminated aqueous solutions

Master's Thesis in Nanotechnology

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Department of Physics
Chalmers University of Technology
Gothenburg, Sweden 2019

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Abstract

Because mercury is one of the most toxic heavy metals known, there are multiple techniques for the removal of mercury from aqueous solutions. A new technique introduced uses electrochemical alloy formation to reduce mercury concentrations. By controlling the potential applied, this method has been proven to reduce mercury in aqueous solutions from different initial concentrations. The main conclusion is that the method can reduce the amount of mercury in solution to under 6 μg/L, which is the World Health Organisation's guideline value for drinking water.

Keywords: electrochemistry, alloy, mercury.

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Emma Feldt, Gothenburg, June 2019

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Introduction

Heavy metals pollution is a big problem in the global environment today. They cause health problems for humans and other living organisms in the world. One of the most toxic heavy metals is mercury (Hg). All over the world, mercury is an existing problem. Mercury exists everywhere, in the crust of the earth, in the atmosphere, in the waters, and soil.[1] Since industrialization, the amount of mercury that has been released has increased so we today can see the consequences of these emissions. The problems with mercury pollution for humans is its presence in water and food. Mercury tends to bioaccumulate and be passed down in the food chain.[2, 3] On a more regional plane, Sweden also has mercury problems. The majority of lakes in Sweden are contaminated with mercury, which is a threat to the health of both humans and wildlife. Due to mercury's high toxicity, the water in many lakes is unsafe to drink, and freshwater fish are toxic and unsafe to eat.[3] Therefore, it is necessary to find a solution to work towards mercury-free lakes in Sweden. The main contributors to the contamination are abolished as well as operational industrial sites in Sweden, and airborne mercury from emissions in other countries. From these sources, mercury and other heavy metals can leak out into natural waters, bringing it to lakes and groundwater. Natural water can contain different kinds of mercury solutes: metallic mercury (also termed dissolved gaseous mercury, DGM), mercury ions (Hg^+ or Hg^{2+}) and organic mercury (mercury bound in small organic molecules or ions, e.g. dimethylmercury, $(CH_3)_2Hg$ and methylmercury, $[CH_3Hg]^+$).
Recently, a new method for cleaning of mercury from contaminated waters via electrochemical alloy formation on thin platinum films has been shown promising results. This method is promising both due to the efficiency of removing the mercury from the water but also because the platinum electrode can be regenerated and reused.[4] Although platinum is rare and expensive, the films used in this method will be thin enough that not much platinum is required even when scaling up the process. Past studies of this method have focused on high concentrations of mercury. Presented is a study into the possibility of removing low concentrations of mercury, concentrations down to that of natural, safe water.

1.1 Aim of the project

This project aims to investigate if there is a low limit for the concentration of mercury in the removal process and to understand if the method can be applied to natural water.
Limitations: The experiments have been done in 50 ml batches. The solutions and water have all been mixed from a standard mercury solution of 1000 ppm Hg, and the water used is taken from the tap. This project will only focus on the removal of mercury, no other heavy metals in solution. Also, the working electrode in the electrochemical processes will be platinum-based.

2

Background and theory

2.1 Mercury

Mercury is a heavy metal that is liquid at standard conditions for temperature and pressure. In the environment mercury can be found in different states, as elemental mercury (Hg^0), inorganic mercury (mercury ions, Hg^{1+} and Hg^{2+}), organic mercury (like methylmercury (CH_3Hg^+)) and mercury bound to particulate matter (Hg^P).[1, 5, 2] The amount of mercury in the Earth's crust is approximately 0.08 parts per million (ppm = mg/L).[6] Metallic mercury is rare to find in water and the ground; it is likely to be inorganic or organic bound to other compounds.[6] In the atmosphere, elemental mercury travels long distances before oxidizing. The oxidized form will then be deposited in the environment.[1] Mercury is known to be one of the most toxic heavy metals that exist.[7] The toxicity is due to mercury's abilities to bioaccumulate and biomagnify in animals and its volatility. Persistent exposure to large amounts of mercury will damage the human brain, heart, kidneys, lungs, and immune system. Exposure during pregnancies could harm the development of the nervous system of the fetus.[2, 3] One reason for the toxicity of mercury ions is because they can bind to exposed sulfhydryl (-SH) groups which are present in enzyme proteins. Another is that living tissue has a high affinity for methylmercury.[6] In 2011 the World Health Organization (WHO) set guideline value for drinking-water as 6 μg/L for inorganic mercury, this is the form found in drinking water. The tolerable daily intake is set to 2 μg/kg body weight of inorganic mercury.[8] Methylmercury is bioaccumulated through all levels of the food chain. Methylation in the environment can be carried out by archaea, bacteria, and fungi. Human activity has primarily affected the level of Hg in the environment. The mercury cycle in the environment is, to an extent impacted by the activity of microorganisms.[9]

2.1.1 Sources of mercury

Industrial processes, agriculture, mining, and coal combustion all emit volatile mercury into the atmosphere. These are some of the anthropogenic sources that have increased the emissions of mercury since industrialization. In the case of mercury-organic compounds used in agriculture and industrial applications, most have been removed and banned to prevent further environmental pollution.[9] There are natural processes that release and re-emit mercury into the atmosphere including volcanoes, soil erosion, water bodies (both fresh and salt-water), wildfires, and geothermal sources.[10] The emission from these natural sources is estimated to be 500 tons per year in total.[1] Other sources of emission (coal combustion, smelting, and waste incineration) are human-related and exceed the amount from natural emissions.[11] The estimated values for anthropogenic emissions to the atmosphere range from 2200 to 4000 tons per year.[1]

2.1.2 Mercury in air

Emissions of mercury come in three forms: elemental mercury in the gas phase, gaseous divalent inorganic compounds, and mercury in particle-phase. Elemental mercury is capable of being transported long distances in air, while the mercury ions will be removed within a few hundreds of kilometers from the source due to the water-solubility properties. Particle-bound mercury is presumably to be deposited after a reasonable distance. From the air (atmosphere), the mercury is removed through both wet and dry processes.[10] The levels of mercury in air range from 2 to 10 ng/m^3.[12]

2.1.3 Mercury in lakes

The amount of mercury in freshwater can vary, typically from 0.01 to 10 parts per billion (ppb = μg/L).[6] The process of methylation of inorganic mercury occurs both in freshwater and seawater. The amount of mercury in lakes depends on the lakes location and surrounding activity, though there are naturally occurring mercury levels less than 0.5 ppb.[12]

2.1.4 Mercury in the sea

A variety of mercury forms can be found in the sea: Hg^0, Hg^{2+}, organic mercury, and particulate mercury. The concentration of mercury in seawater differs depending on the ocean. Selin states the Mediterranean sea has 0.5 ng/L mercury and the North Atlantic sea has 0.48 ng/L, which is the highest concentrations, while the Pacific Ocean has 0.24 ng/L, which is the lowest concentration, the average is 0.3 ng/L.[1]

2.1.5 Mercury in the ground

In soil, mercury exists mostly as organic mercury, in compounds such as methylmercury or ethylmercury. A small amount exists as inorganic mercury, sometimes as mercury vapor absorbed to soil matter.[6] The most common mineral of mercury is Cinnabar (HgS), and it is found in large-scale deposits in the environment.[9] The mobility of the different mercury species in soil influences toxicity and bioaccumulation. The organic mercury species are more mobile than the inorganic mercury species, which contributes to higher toxicity and increased bioaccumulation. Natural processes easily transport soluble inorganic mercury species, such as mercuric chloride ($HgCl_2$). Soluble inorganic mercury and organic mercury species are the major contributors to potential mercury toxicity in soils. Elemental mercury and mercury-metal amalgams are less toxic because of their lower mobility compared with the others mentioned.[13]

2.2 Techniques for mercury removal

Today there are multiple techniques to remove mercury from the environment, such as ion exchange, flotation, coagulation and flocculation, membrane filtration, and adsorption. Some advantages and disadvantages for some of the removal techniques are shown in table.2.1 What also has been done to combine multiple techniques such as the ion exchange membrane bioreactor.[14]

Table 2.1: Advantages and disadvantages of some of the available methods for mercury removal.

Method	Advantages	Disadvantages	
Ion exchange	High treatment capability High removal efficiency Fast kinetics	Selective to many cations, not only mercury Efficiency affected by other cations	[15] [16]
Flotation	Integrated physio-chemical process	High initial cost Requires chemicals pH dependent	[17]
Coagulation /flocculation	Simple process	Large sludge production	[17] [18]
Chemical precipitation	Effective at sufficiently high levels of Hg	Require addition of chemicals and isolation of the formed precipitate Not suited for very low concentrations and large volumes	[17]
Membrane filtration	High removal efficiency	Expensive High sludge production Limited flow rates	[18] [19]
Adsorption (activated carbon)	Simple technology	Regeneration of adsorption material needed frequently Expensive	[18] [19]

2.3 Electrochemistry

Electrochemistry is a field of chemistry and surface science that focuses on the relations between electricity and chemical reactions. In an electrochemical system, interest lies with the process of transferring charge across an interface between an electrolyte and an electrode. These chemical phases can be between an electrical conductor, an electrode, and an ionic conductor, the electrolyte. An electrochemical cell is a physical structure, called an electrode compartment, with two electronic conductors and an electrolyte. Two different kinds of electrochemical cells can be implemented, a galvanic cell or an electrolytic cell. In the galvanic cell, a spontaneous reaction will occur, which will produce electricity. In an electrolytic cell, the reaction is nonspontaneous

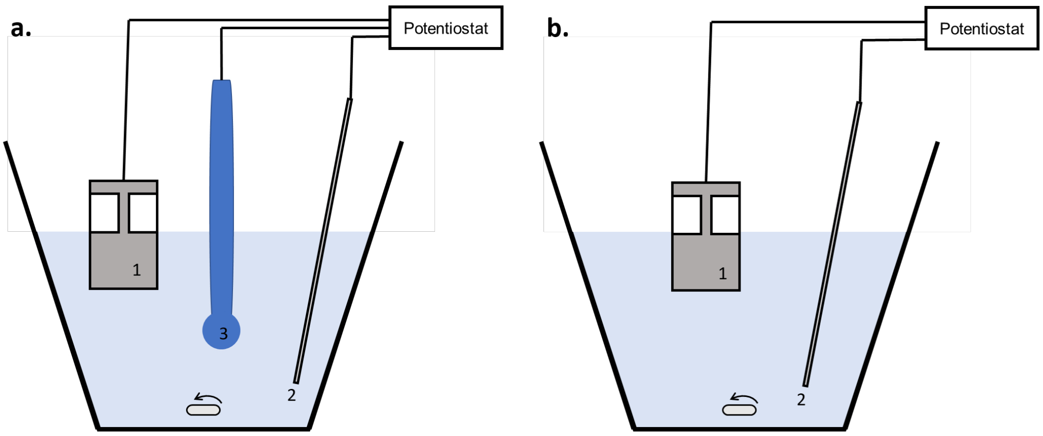

Figure 2.1: Sketch of the electrochemical cell set up. **a.** Three electrodes set up with a working electrode (1), a counter electrode (2) and a reference electrode (3). **b.** Two electrodes set up with a working electrode (1) and a counter electrode (2).

and has to be driven by an external source of direct current. Reactions occur at the anode and cathode electrodes. The anode is where the oxidation reaction occurs while the cathode is where the reduction reaction occurs. When the reaction takes place, electrons from the reaction are released and travel through the external circuit from the anode and then return to the cell at the cathode. Electrons move to areas of higher potential energy from areas of lower potential energy, and the cathode has a higher potential than the anode.[20, 21] An electrochemical cell can have different set-ups; for example, two or three-electrode set up as can be seen in figure 3.2. The set up with three electrodes is the most common set up used to study electrochemical reactions. Here the current is passed between the working electrode and the counter electrode, while the potential of the working electrode is monitored versus the reference electrode.[22] For the two-electrode set-up, which is more used in practical applications, the current is passed between the working and the counter electrode and the potential of the working electrode is monitored versus the counter electrode.

2.4 Alloy formation

An alloy is a mixture of at least two elements, where at least one of these elements is a metal, there will be metallic bonding in the alloy. The purpose of alloys is to obtain desired properties, for example, strength, hardness, or resistance to corrosion to the metal.[23]

2.5 Electrochemical alloy formation between Hg and Pt

The alloy in this research are of platinum and mercury, $PtHg_4$. The alloy forms at the working electrode, which consist of a 100 nm thick layer of platinum on glass. Mercury ions in the electrolyte are reduced to mercury atoms at the platinum surface when a current is flown through the electrochemical cell, and the alloy is formed.

2.6 Analysis methods

Analysis methods used in this research include Inductively coupled plasma mass spectroscopy (ICP-MS), Cold vapor atomic fluorescence spectroscopy (CV-AFS), Energy-disperse X-ray spectroscopy (EDX) and X-ray photoelectron spectroscopy (XPS).

ICP-MS: Inductively coupled plasma mass spectroscopy is a useful analytical technique for the detection of elements and isotopic analysis. The instrument takes advantage of the high-temperature ionization source to convert the atoms of the elements in the sample into ions. These ions are then transferred, separated, and detected by the mass spectrometer. The machine consists of a sample inlet with a pump, a nebulizer, and a spray chamber, then the ICP, where the sample is introduced to argon plasma, through an interface into a vacuum, guided past ion lenses and into mass spectroscopy region with a quadrupole mass filter. ICP-MS is a very sensitive technique with a low detection limit, and it can also handle a continuous flow of sample.[24]

CV-AFS: Cold vapor atomic fluorescence spectroscopy is a type of AFS method that is used for the determination of mercury. In this AFS does not use any vaporization step because the sample is a volatile heavy metal, already a vapor at room temperature, instead chemical reagents are used to convert mercury dissolved in aqueous solution to elemental mercury. In the machine, a flow of argon transports the mercury to a quartz cell, where it is converted into gaseous atoms, then further transported into the AFS, where detection includes a wavelength selector, a photo-detector, a signal processor and a readout unit. The CV-AFS is a sensitive and straightforward technique. With a detection limit as low as 0.1 parts per trillion (ppt = ng/L) for industrial instrumentation.[25]

EDX: Energy-dispersive X-ray can be used in both scanning electron microscope (SEM) and transmission electron microscopy (TEM). This technique is used for chemical analysis of individual particles and the characterization of a sample. SEM-EDX is usually used for analyzes metals. The method includes an electron beam hitting the sample which will transfer part of its energy to the atoms of the sample, from this, different signals will be generated, for example, scattering of electrodes and X-rays. An X-ray detector detects the signal which, is then analyzed.[25]

XPS: X-ray photoelectron spectroscopy (XPS) is also an analytical technique used for chemical characterization and surface analysis. The technique measures the energy distribution of photon-excited electrons from atoms in the surface of the sample. The spectrum that recorded is used for analysis; the peaks in the spectrum determines which elements are present.[25]

3

Methods

3.1 Electrode fabrication

A round fused silica wafer (101.6 mm in diameter and 0.5 mm thick, Mark Optics Inc.) was diced into rectangular pieces 30×15 mm with a dicing machine (Loadpoint Microace 3+). The pieces were washed in an ultrasonic cleaner in acetone, isopropyl alcohol and lastly distilled (DI) water. The pieces were then masked with Kapton tape to cover the areas that should not have platinum deposited. The electron beam evaporator (Lesker PVD 225) was used to deposit first a 3-nanometer thick layer of titanium (Ti), for adhesion, and then a 100 nm layer of Platinum (Pt). The electrode in this stage can be seen in figure 3.1a. A copper wire was connected at the top of the electrode with the help of copper tape to hold the wire in place and to maintain conduction. Hot glue was used to ensure that no copper would leak out into the solution. This electrode design was chosen as it offers a well-known area where the alloy is being formed and ensures that no other materials are in contact with the electrolyte. In figure 3.1b. the finished electrode is shown.

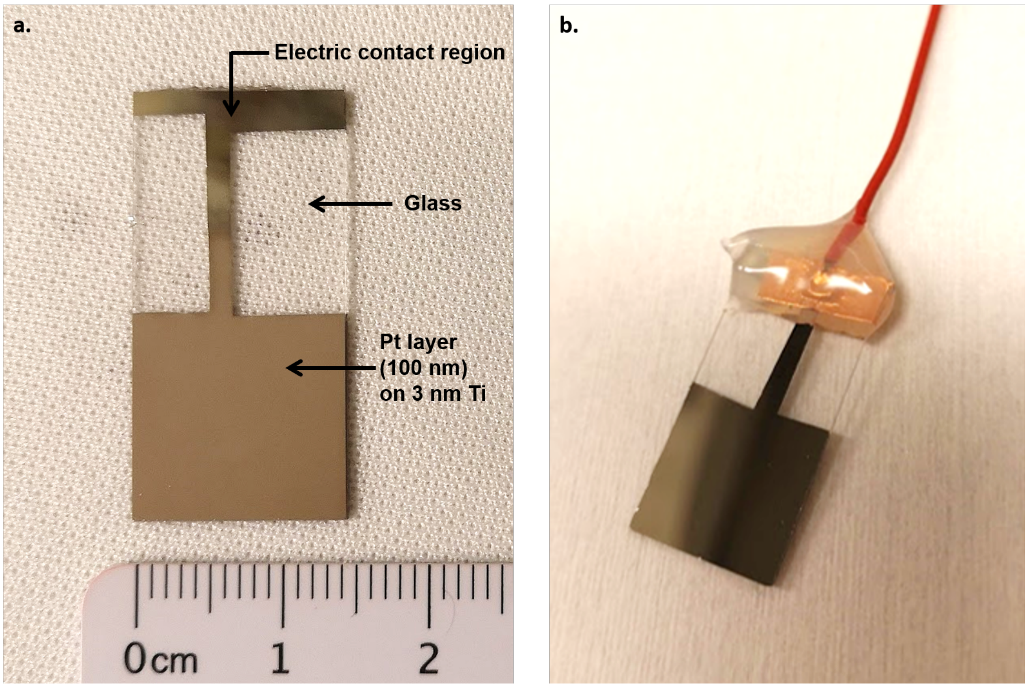

Figure 3.1: Working electrode. **a.** Design of the electrode, before the copper wire was attached. **b.** Completed electrode.

3.2 Experimental setup

Batch experiments were conducted in a glass cell with a 50 ml electrolyte, seen in figure 3.2a. The setup was operated in two or three-electrode configuration. For three-electrode measurements, a working electrode (a sample with a 100 nm Pt film), a counter electrode (Pt wire) and a reference electrode (Hg/Hg_2SO_4, SI Analytics) were inserted in the electrolyte. For two-electrode measurements, only the working and the counter electrode were present. In the measurements with a mercury concentration below 0.1 mg/L, the electrolyte was stirred to ensure that Hg ion diffusion in the solution was not limiting the processes. The working electrode was placed in the electrolyte in such a manner that all the 15×15 mm platinum area was covered, as can be seen in figure 3.2a. The controlled-potential chronoamperometry used during the experiments had different set potentials depending on the electrode configuration. The potential used for the three-electrode configuration was -0.5 V versus the reference electrode, which corresponds to 0,16 V versus RHE.[4] When two-electrode configuration was used, the potential was to -1.81 V versus the counter electrode. This value was achieved by measuring the potential between the working electrode and the counter during a three-electrode experiment. For the experiment in tap water, the fixed potential was -0.91 V versus the reference electrode, to correct for the difference in pH.

Continuous flow experiments were conducted in a commercial flow cell (Electro MP Cell), seen in figure 3.2b. The setup in the cell used a three-electrode configuration and one compartment channel, a working electrode (porous platinum film), a counter electrode (Titanium plate) and a reference electrode (Ag/AgCl, Leak-free reference electrode, ElectroCell). The electrolyte was poured through the reactor at different flow rates to measure the variation in uptake of mercury depending on the rate. The whole setup included a tank with the electrolyte on an elevated platform, the flow cell, a collection container, and tubes from the tank to the cell and from the cell to the container. Also, in these experiments, chronoamperometry was used with a fixed potential of -0.45 V versus the reference electrode.

3.3 Experiments

3.3.1 Concentration study

Experiments with nine varying concentrations of mercury dissolved in HNO_3 were carried out in batches of 50 ml solution. The concentrations ranged from 1 ppm mercury to 1 ppt mercury. Most of the concentrations were performed both with two and three-electrode setup. The electrolyte for the experiments was diluted from a stock solution with the mercury concentration of 1000 ppm with 1 M nitric acid (HNO_3), this acid had been mixed from ultra-pure HNO_3 and Milli-Q water. Samples were collected with an auto-pipette during the experiments in different volumes, and these were diluted with 1 M hydrochloric acid (HCl), to reach a concentration of mercury the ICP-MS could analyze. Experiments with the lowest concentration (100, 10 and 1 ppt) were

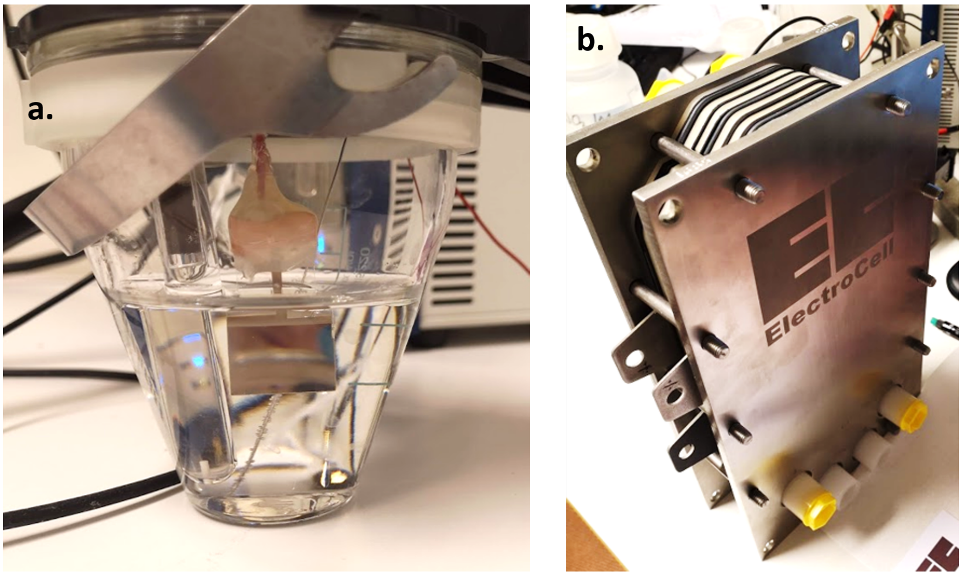

Figure 3.2: Experimental setups. **a.** Batch setup, 50 ml electrolyte, three-electrode configuration. **b.** The flow cell.

handled differently as CVAFS analysis was to be performed by IVL Svenska Miljöinstitutet AB. Bottles with the volume 50 ml were assigned for the samples that where to be measured, the bottles were kept in double zippy bags and contained pure water before use to reduce contamination of the bottles before adding the sample. The three electrolytes were prepared, 100 ml of each, by dilution of the mercury stock solution with 1 M HNO_3 to the desired concentration. As an initial sample, 50 ml of the electrolyte was collected in one of the bottles. The remaining 50 ml electrolyte was used for the experiment after a certain amount of hours the experiment was turned of, and the electrolyte was placed in another bottle labeled as "end sample." When all three experiments were done, the bottles were handed back to IVL for analyses.

3.3.2 Simulated natural water

Only one concentration of electrolyte was examined in both HNO_3 and tap water, 100 ppb (µg/L) mercury. The electrolyte was produced by dilution of the mercury stock solution with tap water to the desired concentration. Samples were handled in the same way as in the concentration study. The experimental setup was a three-electrode configuration because the tap water does not conduct electricity as well as HNO_3.

3.3.3 Flow cell measurements

Electrolyte with 100 ppb mercury in tap water was prepared in a 10-liter tank that was connected with tubes to the flow cell. The different flow rates were controlled by a clamp on the outflow tube, which could be adjusted with a difference in tightness. Samples were collected in triplicates for each flow rate by redirecting the outflow tube into centrifuge tubes and collecting an amount of the processed electrolyte. From the collected samples, a defined volume was diluted with 1 M HCl and then analyzed with the ICP-MS.

4

Results and discussion

The results will here be presented and discussed.

4.1 Three versus two electrodes

During the experiment with 10 ppb mercury and three-electrode setup, the concentration of mercury increased from the initial concentration. This can be seen in figure 4.1c, where the blue dots in the graph correspond to that experiment. The reason for this could be that mercury from the earlier more concentrated experiments contaminated the porous frit of the reference electrode and was released into the solution during this experiment, because of the low concentration (10 ppb), it made a significant impact on the results. Hence, the experimental set up was changed to two electrodes, to remove the uncertainty of reference electrode contamination.

A discovery was made when comparing the results between the three and two electrode experiments. The decrease in mercury content is faster when using a two-electrode setup, and this can be seen with all the different concentrations that were run with both three and two electrodes, shown in figure 4.1. The difference in uptake could be due to the lack of reference electrode for potential control, though this difference was surprising because the potentials are supposed to be the same. In the two-electrode system, reactions happen at both electrodes, which can affect the stability of the electrode potential.

4.2 Concentration study

The results of the concentration study are shown in figures 4.2, 4.3, 4.4 and table 4.1. Looking at the reduction of mercury in solution in the graphs in figure 4.2, especially in a, there is an obvious trend where the decrease in the percentage of mercury is faster for lower initial concentrations. Also, this trend can be seen in graph b, but is not as evident. After 20 hours of the experiments running all concentrations in figure 4.2b where down to below 10% of the initial concentration of mercury in the electrolyte left, 90% was taken up with the alloy formation process. Experiments with lower initial concentrations reduce faster because of the mechanism of alloy formation. The alloy forms in two steps. A surface layer of reduced mercury atoms forms then diffuses inside to be replaced by more mercury. The surface layer forms faster than the mercury atoms diffuse into the platinum to form the alloy.

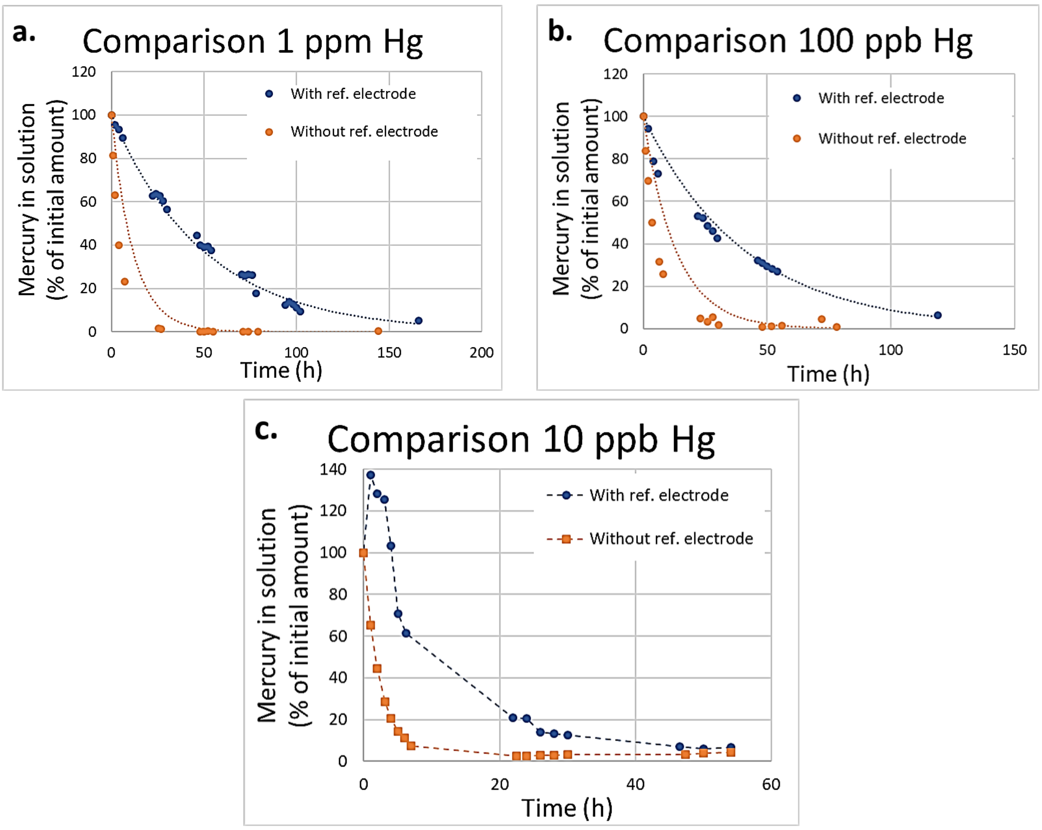

Figure 4.1: Graphs showing comparisons between using three-electrode and two-electrode setup. **a.** Comparison with initial electrolyte concentration of 1 ppm. **b.** Comparison with initial electrolyte concentration of 100 ppb. **c.** Comparison with initial electrolyte concentration of 10 ppb.

All the experiments mercury concentrations are reduced to below the line for where WHO has their limit for drinking water, shown in figure 4.3b at 6 µg/L Hg, which means that the electrochemical alloy formation method can be used to decontaminate drinking water in countries where it is needed. We can also see that even at the lowest initial concentrations, the mercury concentration is reduced even further. The lowest initial concentration from which an alloy can form is 100 ppt, as can be read from table 4.1. Here one of the aims of the project can be answered, if there is a lower limit to the methods uptake capability, from these results the lower limit is found between 100 ppt and 10 ppt, probably around 70 ppt. What also can be seen from the table 4.1 is that the prepared initial concentration of all three experiments is near to the desired concentration, which is a measure of the accuracy of the dilution of the mercury stock solution. But also that the end concentrations of the two experiments with the least initial mercury content have increased in mercury concentration, which can be an indication that the cleanliness of the equipment could have been better. There could have been mercury on the wall of the batch cell or stuck to the counter electrode, even though the equipment had been cleaned.

From the first solution samples (one or two hours after the beginning of the experiment) of each experiment, the deposition velocity was calculated. The depositing velocity versus the initial concentration of the experiment is shown in figure 4.4. The relationship between the experiments is linear, depending on the initial concentration.

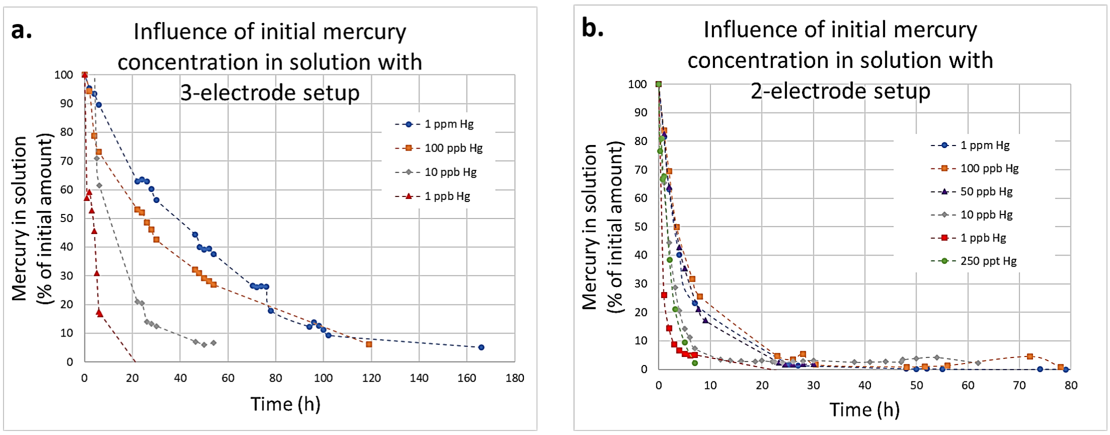

Figure 4.2: Graphs showing the decrease in mercury content in the electrolyte during batch experiments. All experiments with mercury dissolved in HNO_3. **a.** Experiments with three-electrode setup. Potential = -0.5 V versus the reference electrode. **b.** Experiment with two-electrode setup. Potential = -1.81 V versus the counter electrode.

The experiments with higher concentration have a faster depositing velocity, which can indicate that the diffusion of mercury to the electrode matters at the beginning of the experiment and that the deposition velocity is the speed of the reduction of mercury ions and the formation of the mercury layer on the surface of the platinum electrode. Additional calculations were done to evaluate the composition of the working electrode after the experiments were ended; the results from this can be seen in table 4.2. These results can then be compared with the results from the EDX analysis of some of the electrodes; the results from the EDX can be seen in table 4.3. The results show a logical decrease in mercury portion versus the initial concentration and uptake of mercury. Each spectrum was sampled from a small area of the working electrode surface. The 1 ppm sample has 6.3% mercury from EDX, which is comparable to the calculated value of 9.06%. EDX shows that the alloy formation is uneven because each spot contains a different amount of mercury.

In the SEM pictures in figure 4.5 can be seen that the surface of the electrode has spots on it, the spots could be clusters of mercury on the surface. Because this is the 1 ppm experiment, there should be alloy formed in the platinum layers, but still could have been a layer of mercury on the surface. It could be preferred for the alloy to form where alloy already is formed which could explain the spots.

Table 4.1: Results from analysis done by IVL using CVAFS. All experiments with mercury dissolved in HNO_3. Potential = -1.81 V vs. counter electrode.

Experiment:	100 ppt Hg	10 ppt Hg	1 ppt Hg
	Hgtot (ng/L)	Hgtot (ng/L)	Hgtot (ng/L)
Initial concentration:	90	18	4.6
End concentration:	74	72	124

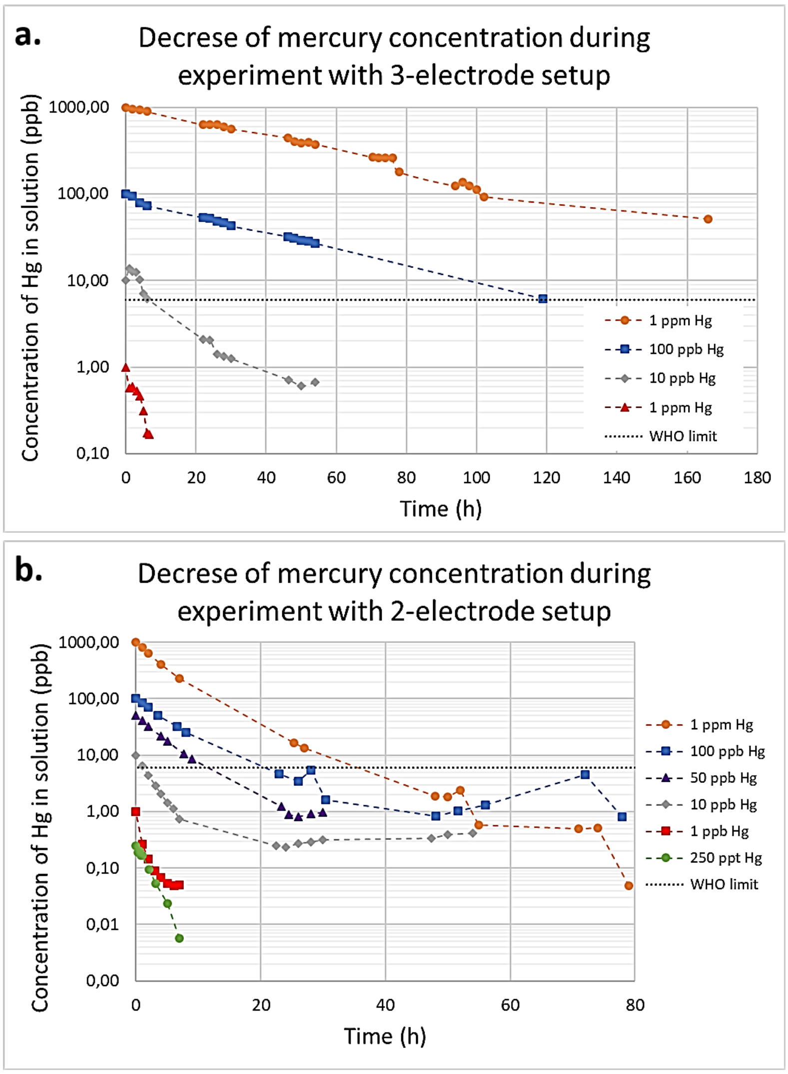

Figure 4.3: Graphs show the decrease in mercury concentration in the electrolyte during batch experiments. All experiments with mercury dissolved in HNO_3. **a.** Experiments with three-electrode setup. Potential = -0.5 V versus reference electrode. **b.** Experiment with two-electrode setup. Potential = -1.81 V versus counter electrode.

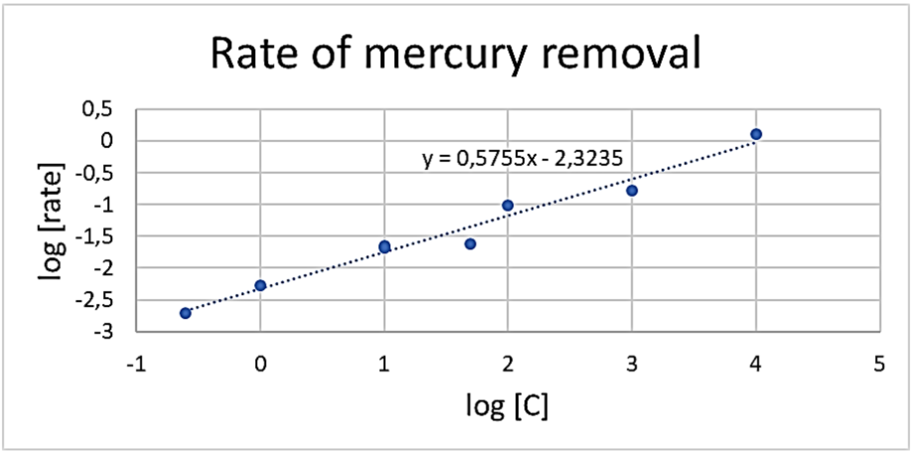

Figure 4.4: Calculated rate of mercury removal in the batch experiments verses the initial concentration.

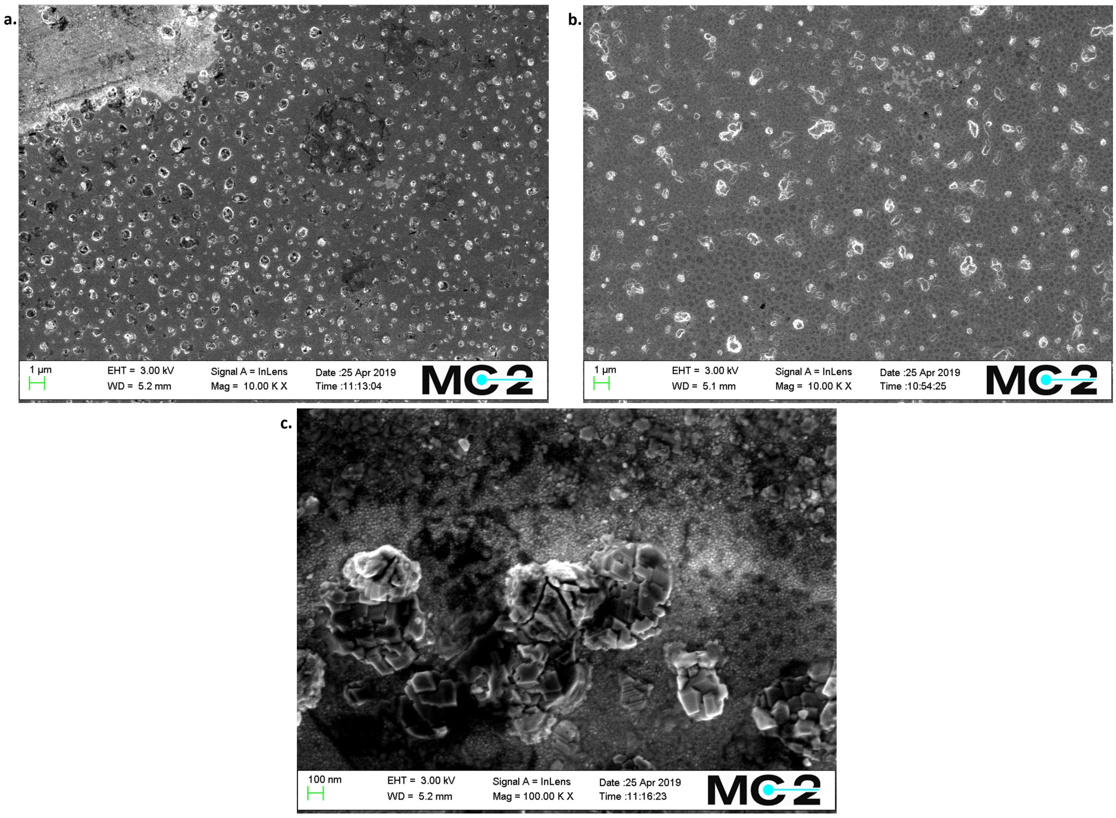

Figure 4.5: SEM pictures from the working electrode that preformed the 1 ppm Hg experiment with three-electrode setup. **a.** and **b.** are done with 3.0 kV and 10k magnification. **c.** are done with 3.0 kV and 100k magnification.

Table 4.2: Calculated electrode composition after experiment with initial electrolyte concentration stating the experiment. All experiments with mercury dissolved in HNO_3. Potential = -1.81 V vs. counter electrode.

Experiment:	1 ppm Hg	100 ppb Hg	50 ppb Hg	10 ppb Hg	1 ppb Hg	250 ppt Hg
Hg (%)	9.0594	0.9485	0.5251	0.0993	0.0112	0.0029
Pt (%)	90.9406	99.0515	99.4749	99.9007	99.9888	99.9971

Table 4.3: EDX measurements from a SEM-EDX.

Experiment:	1 ppm Hg			100 ppb Hg			50 ppb Hg	
	Pt (%)	Hg (%)		Pt (%)	Hg (%)		Pt (%)	Hg (%)
Spectrum 1	91,709	8,291						
Spectrum 2	92,804	7,196					98,817	1,183
Spectrum 3	96,214	3,786		98,152	1,848		98,908	1,092
Spectrum 4	93,561	6,439						
Spectrum 5	92,202	7,798						
Spectrum 6	95,583	4,417						
Average	**93,679**	**6,321**		**98,152**	**1,848**		**98,863**	**1,138**

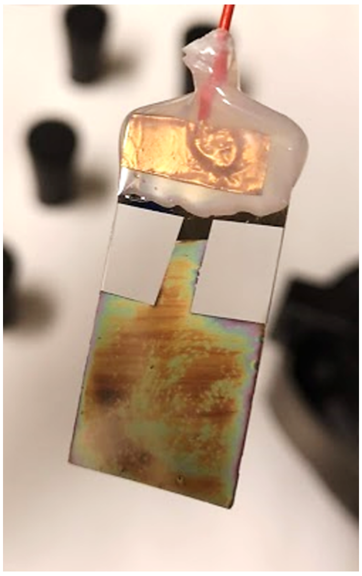

Figure 4.6: Working electrode that preformed the 100 ppb Hg in tap water with a three-electrode setup. Potential = -0.91 V versus reference electrode.

Table 4.4: XPS results from the electrode run in 100 ppb mercury in tap water, shown in figure 4.6.

Electrode	Ratio (%)								Pt:Hg (%)	
	C	O	Pt	Hg	Ca	Fe	Cr		Pt	Hg
Spot 1	48.9	24.2	13.4	3.3	2.6	2.7	4.9		80	20
Spot 2	43.5	22.4	15.2	3.6	4.5	3.6	7.1		80.7	19.3
Spot 3	45.1	21.8	14.7	3.7	3.9	3.2	7.5		79.9	20.1
Average	**45.8**	**22.8**	**14.4**	**3.5**	**3.2**	**3.2**	**6.5**		**80.2**	**19.8**

4.3 Simulated natural water

Figure 4.6 illustrates the appearance of the working electrode after an experiment in tap water, and the color could indicate that other atoms or compounds are on the surface of the electrode. This is evident also in the XPS results of this electrode, seen in table 4.4, water from the tap can contain low concentrations of calcium, chromium, and iron, which explains the amounts of these elements on the electrode. Carbon can come from impurities that emerged after the experiment and the oxygen from the air. In XPS only the outer most surface is analyzed and the area analyzed is just a small spot, in this case, which is the reason for the high amount of mercury on the electrode, and can thus not be compared with the calculated amounts of the electrode composition. What can be taken from this experiment is that even if other compounds were present in the electrolyte, this did not affect the alloy formation, the decrease in mercury was as fast as in the acid experiments as can be seen in figure 4.7.

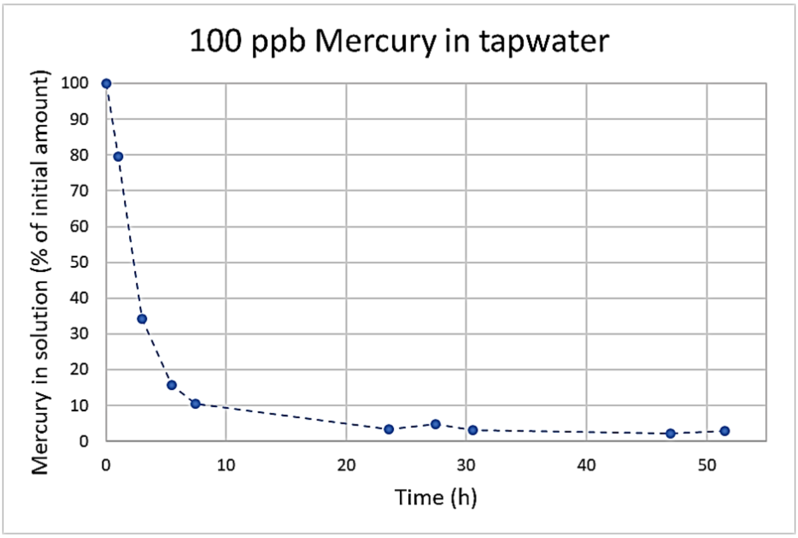

Figure 4.7: Graph showing the decrease in mercury content in the electrolyte during batch experiments. Electrolyte which consists of mercury dissolved in tap water. Potential = -0.91 V vs. reference electrode.

4.4 Flow cell measurements

The results of the experiment in the Electro MP Cell is shown in figure 4.8. As expected, lower flow rates of the electrolyte would take up more mercury from the solution than faster rates. Based on calculations, flow rates in the range of 58-30 ml/min would remove 90% of the mercury in solution, but as seen in the figure, much less than expected is removed. The reason for this is not known, a theory is that the flow in the cell was not optimal or that the electrode was not behaving as expected.

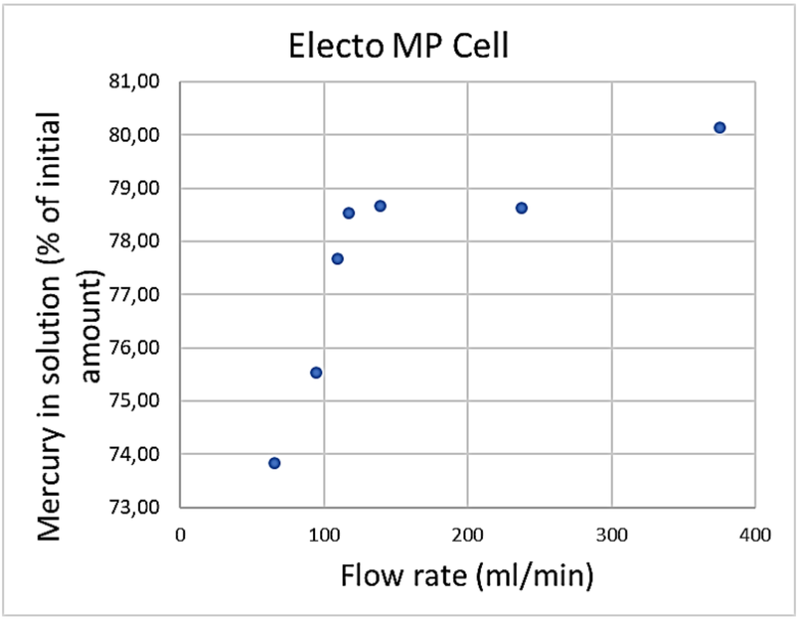

Figure 4.8: Amount of mercury still in solution after the experiment, versus the flow rate of the electrolyte.

5

Conclusion

This research aimed to identify if there is a lower limit for the removal process of Hg from water using electrochemical alloy formation, a limit was found at initial electrolyte concentration between 100 and 10 ppt mercury, results point to 70 ppt mercury to be a limiting concentration where no more mercury is being removed. Another aim was to determine if the method would work for natural water, tap water had to represent the natural water in this work, the results show that there is no difference in the outcome when working with natural water even if traces of other compounds were found on the electrode surface after experiments. The results from the flow cell are promising, mercury was removed, shows that the method can be scaled.

5.1 Outlook

In the future, further experiments can be done to see if this alloy formation method would work with other forms of mercury than inorganic mercury. Perhaps organic mercury can be removed, but the bond between the mercury and the organic part may have to be broken by force to be able to remove it. Further studies with the flow cell will have to be performed to find the range of flow rates to remove at least 90% of mercury. It would be helpful to develop a technique to recirculate the solution through the reactor or have more reactors in a series to get more out of the process.

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