Thesis for The Degree of Licentiate of Engineering

Decontamination of Mercury from Aqueous Systems via Electrochemical $PtHg_4$ Alloy Formation

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Cover: Electrochemical alloy formation between mercury ions (yellow) and platinum (grey), forming $PtHg_4$ (grey and blue). Image by Rasmus Svensson.

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Abstract

Mercury is worldwide a severe heavy metal pollutant and a serious threat to human health and ecosystems. Mercury can be released into the environment by various natural processes; however, mercury pollution has been significantly amplified by human activities such as mining, production of fertilizers, waste incineration and disposal. Once mercury enters aquatic ecosystems, it bioaccumulates and biomagnifies, and mercury can travel vast distances in water, resulting in widespread contamination and devastation. It is thus crucial for the well-being of humans and ecosystems to address the mercury contamination of water. It is important not only to reduce the mercury pollution at its source, but also reduce the present contamination of water. Current technologies used to mitigate the situation are far from optimal and the development of more efficient and effective removal methods are needed. A novel method based on electrochemical alloy formation between mercury ions in solution and a platinum surface has been shown to offer various advantages over previous techniques. The method can be used to decontaminate both waste and natural waters, as well as highly corrosive acids generated from mining industries.

In this thesis, the fundamental principles of electrochemical $PtHg_4$ alloy formation for mercury removal are studied. The reaction mechanisms and energetics are examined, and its potential for future large-scale applications in industries is explored. It is shown that mercury can be efficiently removed from industrial concentrated sulfuric acid derived from zinc smelting. Comparison between laboratory-scale and a medium-scale demonstrator show excellent scalability of the removal method. Additionally, mercury is efficiently removed from diluted acids with initial mercury concentrations as low as 0.25 µg/L, making the method applicable for both environmental and industrial settings. This thesis establishes an important foundation for further research and optimization of electrochemical alloy formation as a mercury removal method. With continued development and advancements, the method has the potential to contribute significantly to the mitigation of global mercury pollution for the protection of human health and ecosystems.

Keywords

Mercury Removal; Electrochemistry; Platinum; Mercury; Alloy Formation

List of Publications

This thesis is based on the following publications:

Paper I

Roth, V., Järlebark, J., Ahrnens, A., Nyberg, J., Salminen, J., Vollmer, T. R., and Wickman, B.
"Mercury Removal from Concentrated Sulfuric Acid by Electrochemical Alloy Formation on Platinum"
ACS ES&T Engineering **3**, 823 (2023).

Paper II

Feldt, E., Järlebark, J., **Roth, V.**, Svensson, R., Gustafsson, P. K., Molander, N., Tunsu, C., and Wickman, B.
"Temperature and concentration dependence of the electrochemical $PtHg_4$ alloy formation for mercury decontamination"
Separation and Purification Technology **319**, 124033 (2023).

Paper III

Roth, V., Valter-Lithander, M., Järlebark, J., Bilesan M. R., and Wickman, B.
"On the Mechanism of Electrochemical Alloy Formation Between Mercury and Platinum for Mercury Removal from Aqueous Systems"
In Manuscript

Author Contributions

Paper I

I contributed to the design of the experimental process and preparation of the working electrodes. I performed ICP-MS analyses, prepared the first draft of the manuscript, and was involved in the finalization of the manuscript.

Paper II

I handled the finalization of the manuscript, which included the final version of the figures and presentation of the data.

Paper III

I contributed to the design of the experiments and was responsible for the preparation of the working electrodes. I conducted EQCM measurements and ICP-MS analyses, and prepared the first draft of the manuscript.

Contents

Chapter 1

Introduction

Environmental pollution is one of the most urgent and rapidly escalating issues facing the modern world. Across the globe, toxic chemicals are incessantly released into the environment, leading to detrimental impacts on soil, air and most critically, water. Water is essential to all forms of life, and the implications of its pollution are far-reaching and devastating. Contaminated water impacts entire ecosystems, and becomes in many cases a vector for disease and death [1–3].

Mercury, which is a highly toxic heavy metal, has been identified as one of the current top six most toxic threats in the world. According to the Green Cross, mercury is surpassed only by lead and radionuclides in terms of the number of people affected, the severity of exposure, and the geographical extent of its contamination [4]. In addition, the World Health Organization (WHO) has listed mercury among the top ten chemicals of major public health concern [5]. The significant impact of mercury is further highlighted by the fact that the element is the sole focus of a global environmental treaty, the Minamata Convention on Mercury, which emphasizes the severity of its pollution and the urgency of global recognition [6].

Mercury is found naturally in the environment and is emitted into the atmosphere through natural processes such as rock weathering, geothermal activity and volcanic eruptions [7]. However, mercury emissions from anthropogenic sources exceed the natural ones by more than one order of a magnitude, with over 2500 tonnes being emitted annually through activities such as mining, fertilizer production, waste incineration and disposal. Through human activities alone it is estimated that a total of 1,540,000 tonnes of mercury was released between the years 1850 – 2010, with 470,000 tonnes directly emitted into the atmosphere and 1,070,000 tonnes released into land and water systems [8]. Once mercury is emitted into the atmosphere, it can travel vast distances before being deposited onto land and water bodies. Within these environments, mercury can either be sequestered within the soils or sediments, or be re-emitted back into the atmosphere. Mercury's unique cycling ability, allowing it to continuously be re-emitted from land and water surfaces, means

that mercury released decades ago is still circulating in today's environment [9]. Mercury can persist in the environment for millennia, remaining mobile and posing a toxic threat until its ultimately bound in deep ocean sediments or subsurface soils [10]. Water plays a key role in the mobility and distribution of mercury, contributing to approximately 60% of its environmental cycling [8]. When mercury enters water bodies, it can bioaccumlates in aquatic organisms and subsequently biomagnify up the food chain, posing a significant threat not only to humans but also to all aquatic and terrestrial wildlife [11]. Therefore, addressing the issue of mercury pollution in water is of paramount importance for both global environmental sustainability and public health. There is an urgent need to develop effective strategies to manage and mitigate the impact of mercury.

Current established methods for mercury removal from aqueous solutions, although functional, are far from optimal. The main methods include techniques such as adsorption, filtration, ion exchange, and precipitation, which, depending on the specific context and application, have their own advantages and disadvantages [12, 13]. Common limitations include low selectivity for mercury, high capital cost and energy consumption, technical complexity and the generation of secondary waste. Moreover, the effectiveness of these methods can be greatly influenced by the pH of the solution, and to date, no method has proven effective for mercury removal from concentrated acids [13, 14].

Recently, a promising new method for mercury removal from aqueous solutions has been presented, based on electrochemical alloy formation between mercury ions in solution and a platinum surface [15]. This technique holds the potential to overcome the limitations of existing removal techniques and provide a more effective and efficient approach to mercury removal [15, 16]. With further research and optimization, this removal method could play a significantly role in mitigating the environmental and health impacts associated with mercury contamination in water systems.

1.1 Scope of the Thesis

This thesis presents research and findings aiming to further enhance our understanding of electrochemical alloy formation as a method for mercury removal from aqueous systems. Through electrochemical experiments and detailed analysis, the reaction mechanisms and energetics of the electrochemical process are studied. Furthermore, the potential of this method for large-scale mercury removal is explored. Chapter 2 provides a background on mercury pollution, detailing its sources, impacts, and various removal methods. Chapter 3 presents the fundamentals of electrochemistry and the structure of an electrochemical cell, along with the underlying thermodynamics and kinetics of the electrochemical processes. Chapter 4 outlines the experimental methods and analytical techniques used in this study, while Chapter 5 discusses and expands upon some of the results from **Paper I** through **III**. Lastly, Chapter 6 concludes the thesis and gives suggestions for future research directions.

Chapter 2

Mercury

This chapter provides an overview of mercury pollution, examining its natural and anthropogenic sources, as well as its impact on both human health and ecosystems. In addition, it presents the current methods used for mercury removal from aqueous systems.

2.1 Sources

Mercury (Hg) is a naturally occurring element and is widely distributed in the earth's crust, oceans and atmosphere [17]. Despite its natural occurrence, human activities have significantly increased its abundance, leading to elevated levels of mercury pollution in the environment [18]. In recent decades, efforts have been made to reduce mercury emissions. Yet, the persistence of mercury in the environment remains a significant issue, as the mercury released years ago is still actively circulating in our environment. The issue of mercury emissions are of particular concern due to its high toxicity and the rapid pace at which it spreads and accumulates in natural water bodies [19].

Sources of mercury pollution can be broadly classified into two main categories [8]: natural and anthropogenic, which can be further subdivided into primary and secondary sources. Primary natural sources, such as volcanoes, rock weathering and geothermal activities, are estimated to release approximately 80 – 600 tonnes of mercury annually. In stark contrast, primary anthropogenic sources, originating from human activities, emit around 1900 – 2900 tonnes of mercury into the environment annually. It is further estimated that a total of 1,540,000 tonnes of mercury has been released by human activities prior to 2010, with 70% of these emissions occurring after 1850 [8]. This notable increase in mercury emissions can be linked to the industrial revolution and its rapid expansion of industrial processes such as mining, burning of fossil fuels, and waste incineration [20]. Today, the main activities increasing the total pool of mercury in the environment are processes such as burning of fossil fuels (49%), artisanal and small-scale gold mining (ASGM) (14%), mining of non-ferrous metals (11%), cement production (8%) and waste disposal (6%) [7,

21].

Once mercury is released into the environment, it can travel vast distances via air and water currents [11]. Mercury emitted in one region of the world can reach remote areas, such as the Arctic [22, 23]. After deposition, mercury cycles through a variety of environmental surfaces such as soil, vegetation and water bodies, which continuously re-emit mercury back into the atmosphere. This re-emission of mercury is often categorized as a secondary emission source and can originate from both primary anthropogenic and natural sources [10, 24]. Essentially, primary emissions increase the overall mercury pool in the environment, while secondary emissions redistribute it within ecosystems, resulting in widespread pollution of both terrestrial and aquatic environments. Mercury can persist in the environment for thousand of years, remaining mobile and cycle between re-emission and deposition, until its eventually bound in its final forms in deep ocean sediments or subsurface soils [25]. Estimates show that secondary emissions can be up to three times greater in magnitude than those from primary anthropogenic sources, with water playing a key role, contributing to more than 60% to the environmental cycling of mercury [18, 26]. Collectively, it is estimated that approximately 8400 tonnes of mercury is released annually into the atmosphere from all sources, with 8000 tonnes deposited on land and water bodies. As a results, approximately 950,000 tonnes of mercury is accumulated in soils and 310,000 tonnes in oceans [27]. A more detailed breakdown of different mercury sources is depicted in Fig. 2.1.

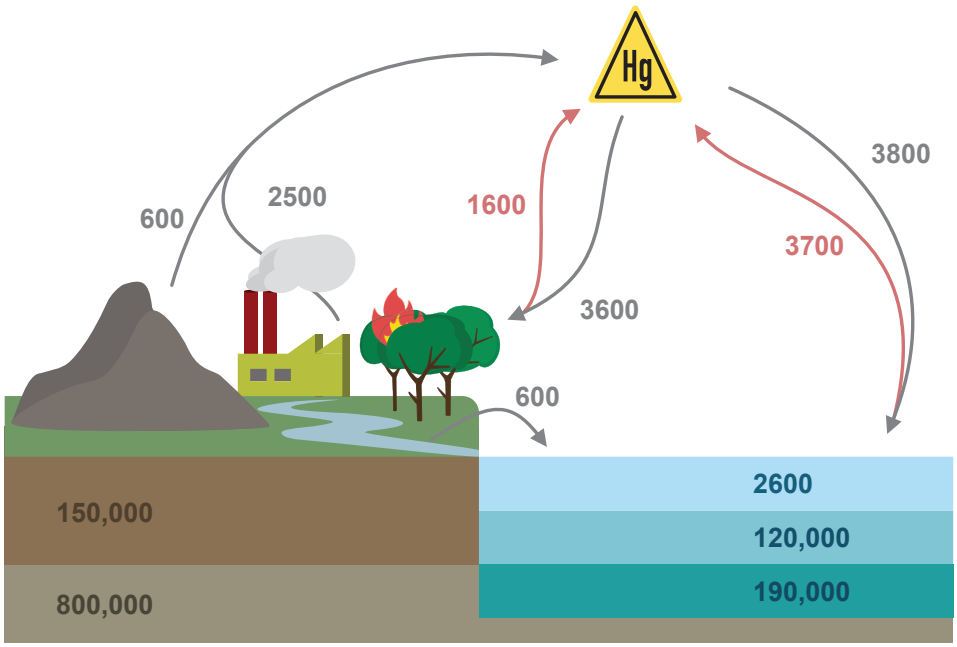

Figure 2.1: The annual cycle of estimated mercury emissions (in tonnes, for the year 2015), deposition, and re-emission (red arrows) in the environment. In addition, the total mercury estimated to be accumulated in various reservoirs is shown, including organic and mineral soils, as well as surface ocean, intermediate water, and deep waters. The data is obtained from Ref. 27.

2.2 Environmental Impact

Mercury is an element with physical and chemical properties that contribute to its complex and extensive effects on all forms of life and their ecosystems. Its high toxicity, mobility, and ability to bioaccumulate and biomagnify through the food chain make it a particularly concerning environmental pollutant [28]. In particular, aquatic ecosystems demonstrate extreme vulnerability to the impacts of mercury pollution. Mercury, once it enters bodies of water, can travel up the food chain, becoming progressively concentrated in fish, birds and mammals [18]. As a result, even relatively low levels of mercury in water can evolve into a more menacing threat, e.g., the concentration of mercury in tissues of top predators such as whales and seals, can exceed million times the levels in their surrounding waters [10]. The species affected can develop behavioral changes, reproductive issues, and in severe cases their populations may decline or even be driven towards extinction [29, 30].

The adverse effects of mercury pollution not only impact wildlife but also extend to the human population, see Fig. 2.2. Humans are primarily exposed to mercury through the consumption of contaminated fish and seafood, as well as occupational exposure in industries [31]. Short term exposure to high levels of mercury, mainly through inhalation in occupational settings, can result in mercury poisoning. Initial symptoms are often flu-like and can include soar throat, coughing, chest pain, nausea, headaches and vision problems. In severe cases, mercury poisoning can lead to respiratory and kidney failures, and may even prove fatal. Long term effects of mercury exposure typically stem from chronic exposure to lower levels of mercury largely through consumption of contaminated food, and can cause neurological and cardiovascular damage, potentially leading to life threatening conditions [10, 31, 32]. The most alarming aspect of long term mercury exposure may be its impact on developing children and fetuses. Their nervous system is particularly vulnerable to mercury toxicity, potentially resulting in cognitive impairments and learning disabilities [33–35].

In response to the extensive toxic effects of mercury, various global policies and initiatives have been set to raise public awareness and mitigate mercury pollution on a global scale. In 2015, the environmental organization Pure Earth together with Green Cross defined mercury as one of world's most toxic threats, alongside lead, radionuclides, chromium, pesticides and cadmium [36]. It was reported that approximately 20 million people worldwide are at risk from mercury exposure, with an estimated 1.5 million years of healthy life (Disability Adjusted Life Years, DALYs) lost due to its effects. Furthermore, the World Health Organization (WHO) has recognized mercury as one of the top ten chemicals of public health concern, listed along with chemicals such as arsenic, lead asbestos and hazardous pesticides [5]. As a results, both WHO and the European Union (EU) have implemented regulations for mercury concentration in drinking water, where only water with mercury concentration below 6 µg/L and 1 µg/L, respectively, is considered safe for consumption [5, 37]. In 2017, the Minatamata Convention on mercury came into force, which strives to reduce the harmful effects of mercury. This global treaty involves coordinated efforts

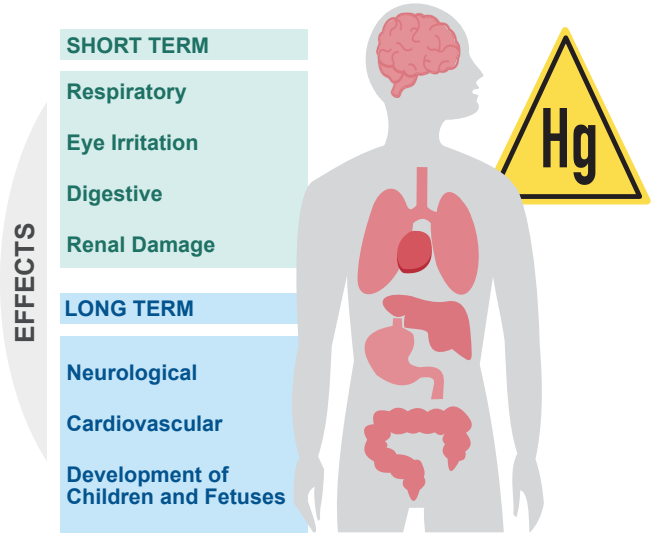

Figure 2.2: Short term and long term health effects of human exposure to mercury. The data is obtained from Ref. 10 and Ref. 31.

to minimize the supply and trade of mercury, reducing its use, and manage emissions [6].

2.3 Removal Methods

Various strategies have been employed to mitigate mercury pollution, such as mercury capture technologies, phasing out the use of unnecessary mercury-containing products and robust waste management systems. Despite these efforts, mercury continues to be a pervasive environmental issue [38].

Existing methods for mercury decontamination of aqueous systems are far from ideal and often prove ineffective under certain conditions, particularly in highly acidic and corrosive solutions [12, 13]. Traditional removal methods include adsorption, coagulation and flocculation, flotation, ion exchange resins, membrane filtration and chemical precipitation. Each of these techniques have their own set of advantages and limitations, as detailed in Table 2.1. Notably, the main limitations include high energy demands and operational costs, low selectivity, and a strong dependency on pH levels [39, 40]. Currently, no commercial method has the ability to operate in concentrated acids, e.g., for effective sulfide precipitation a pH range of 7 – 9 is required, and the optimum pH for adsorption methods is typically between 4 – 5 [41]. Furthermore, most materials used for ion-exchange, membrane separation, and adsorption methods, degrade when used to treat concentrated acids [13]. There is thus an urgent need for the development and implementation of new and improved solutions for mercury removal from various aqueous systems. Electrochemical alloy formation, though still in the early stages of development, presents a promising alternative to established methods [15]. A comparison of its primary advantages and drawbacks, relative to the other methods, is provided in Table

2.1. The fundamental principles, advantages, and limitations of the method are discussed in more detail in the following chapters of this thesis.

Adsorption is a widely used technique for mercury capture, particularly effective in treating vapor and wastewater streams However, the mercury removal capacity can greatly vary among different types of adsorbent. While activated carbon is the most commonly used adsorbent, cost-effective alternatives such as agricultural waste-based adsorbents and biosorbents, including microbes, algae, and non-living biomass, have been proposed. The efficiency of this removal technique is influenced by factors such as pH, temperature, and the saturation level of the adsorbent. Furthermore, the method shows limited selectivity for mercury, as other pollutants can also be adsorbed. The regeneration of the adsorbent material, although not always possible, can be expensive and may result in the degradation of the material [40, 42].

Coagulation and flocculation, commonly employed to treat wastewater, involve the addition of a coagulant to react with mercury ions, creating larger insoluble particles. Despite the methods simplicity and cost-effectiveness, the resulting particles need to be removed via additional methods, such as precipitation or filtration [38, 40].

Flotation is another technique used to extract pollutants from water, with ion flotation being particularly effective for the removal of heavy metal ions, such as mercury. The process involves adding an amphiphilic surfactant to the water, where the surfactant with the mercury ion will attach to air bubbles. The method's selectivity and efficiency can be high, although both these factors are pH dependent. In addition, the costs of installation and maintenance can be high [38, 43].

Ion exchange treatment, a process in which mercury ions are swapped with other non-toxic cations within an ion exchange resin, provides a quick and efficient approach to mercury removal. This method is particularly valuable for treating larger volumes of solutions containing low concentrations of mercury ions. However, the efficiency of this process is heavily influenced by factors such as pH, temperature, and contact time, and due to rapid resin saturation the technique is less applicable for higher concentrations of mercury [40, 44].

Membrane filtration includes a variety of technologies that utilize different types of membranes for wastewater treatment. One such technology is ultrafiltration, where low pressure is applied to force water through a membrane, separating molecules and colloidal particles larger than the membrane's pore size. In this process, ligands are introduced to the water to form larger chelates with mercury. However, due to the substantial cost associated with these ligands, their recovery and reuse are crucial to make this technique economically feasible. Other membrane filtration techniques are also reported to have rapid clogging of the membranes and removal efficiencies affected by pH [38].

Precipitation is the most frequently used method for industrial wastewater treatment. The process involves the addition of a chemical, typically a sulfide salt, to water, leading to the formation of insoluble precipitates like mercury sulfide. The effectiveness of this process is heavily dependent on pH, as well as not being selective for mercury, as it may cause other metals to precipitate as well [13, 38].

Table 2.1: Methods for removing mercury from aqueous solutions, along with their main advantages and limitations [13–15].

Method	**Advantages**	**Limitations**
Adsorption	Simple operation Low secondary waste High removal rate	High capital cost Low selectivity Secondary waste pH dependant
Coagulation/ Flocculation	Simple process Low capital cost High removal efficiency	Chemical consumption Secondary waste Ineffective at low/high conc. Secondary waste pH dependant
Flotation	High selectivity High removal efficiency	High capital cost High energy consumption pH dependant
Ion exchange	Simple operation Time efficient High removal efficiency	High capital cost Low selectivity Secondary waste pH dependant
Membrane filtration	Simple process Time efficient	High operation cost High energy consumption pH dependant Membrane clogging
Precipitation	Simple operation Cost efficient High removal rate	Low selectivity Ineffective at low conc. Secondary waste pH dependant
Electrochemical alloy formation	Simple operation low energy consumption High removal efficiency High selectivity Independent of pH	Early development stages

Chapter 3

Electrochemistry

In this chapter, the fundamentals of electrochemistry are presented, along with the structure of the electrochemical cell. The underlying thermodynamics and kinetics of electrochemical processes are also discussed.

3.1 Fundamentals of the Electrochemical Cell

Electrochemistry is a rapidly evolving branch of science that studies the relationship between electricity and chemical reactions. Electrochemistry has proven to be instrumental in many technological advancements, with applications in battery technology, fuel cells, electroplating, and corrosion processes [45]. Furthermore, electrochemistry presents new possibilities in environmental remediation, removing toxic heavy metals such as mercury from various aqueous systems [15, 16].

At the core of electrochemistry are oxidation-reduction (redox) reactions, in which electrons are transferred from one chemical species, the reducing agent, to another, the oxidizing agent. These reactions can be either spontaneous, generating electrical energy as in galvanic cells, or non-spontaneous, where electrical energy is used to drive a desired chemical reaction, as in electrolytic cells [45]. An electrochemical cell consists of two electrodes, the anode and the cathode, which are connected by an internal ionic pathway provided by an electrolyte and an external electric connection. Each electrode serves as the location of one of two half-reactions that occur at the interface between the electrode and the electrolyte. Electrons flow from the anode, where the oxidation occurs, to the cathode, where reduction takes place. For simplification, two electrodes within an electrochemical cell can be referred to as the working electrode (WE) and the counter electrode (CE). The WE is the site where the half reaction of interest takes place, and the CE serves as either the anode or cathode to counterbalance the reactions at the WE. A potential or current is applied between these two electrodes, and the resulting response is measured. However, to measure absolute potentials, a third electrode, a reference electrode (RE) can be introduced to the system. As no current passes through the RE, it

maintains a constant potential, and the potential is then measured relative to the RE. The current, meanwhile, is between the WE and the CE, as illustrated in Fig. 3.1 [45].

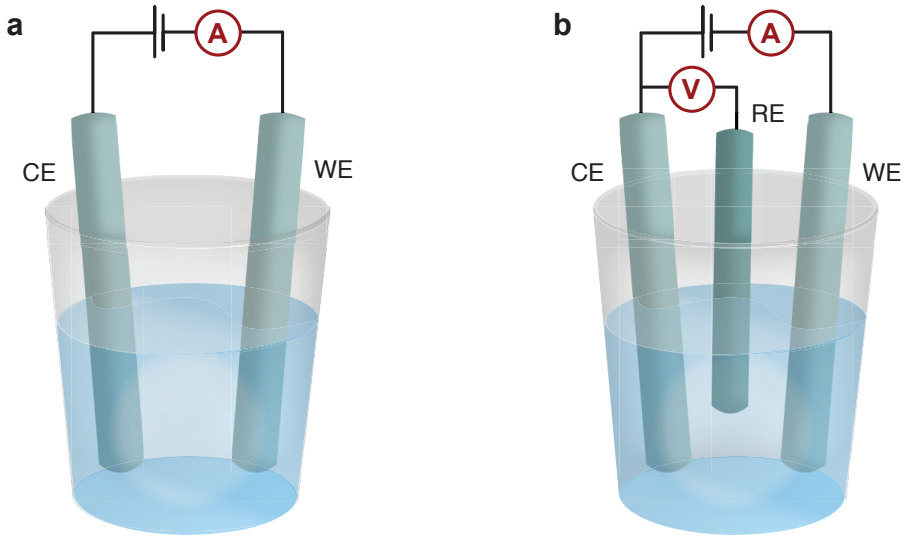

Figure 3.1: **(a)** A typical 2-electrode cell and **(b)** 3-electrode cell setup, including a working electrode (WE), counter (CE) and a reference electrode (RE).

3.2 Thermodynamics

A simple one step redox reaction, can be expressed with the following reaction, where an oxidizer O_x in a solution is reduced to R_{ed} by accepting n-electrons (e^-) [45]:

$$O_x + ne^- \rightleftharpoons R_{ed} \tag{3.1}$$

The reaction quotient (Q_r) represents the ratio of the activities (a) of the reduced species to the oxidised species. When these activities are near unity, the Q_r can be approximated by the ratio of their respective molar concentrations ([ ]):

$$Q_r = \frac{a_{red}}{a_{ox}} = \frac{[red]}{[ox]} \tag{3.2}$$

The Gibbs free energy (ΔG) can be defined as the maximum amount of work ($-W_{max}$) that can be extracted from a system, and can be written as a function of the cell potential (E_{cell}) and the total charge transferred (nF), where F is the Faraday's constant:

$$\Delta G = -W_{max} = -nFE_{cell} \tag{3.3}$$

The redox reaction is spontaneous if $\Delta G < 0$, and non-spontaneous if $\Delta G > 0$. ΔG can be further related to the Gibbs free energy under standard conditions (ΔG^0) and Q_r, where R is the gas constant and T the absolute temperature:

$$\Delta G = \Delta G^0 + RTlnQ_r \tag{3.4}$$

When Δ G = 0 and the redox reaction is at equilibrium, Eq. 3.3 and 3.4, can be rearranged to yield the Nernst equation for the reaction, wheere E^0_{cell} is the cell potential under standard conditions:

$$E_{cell} = E^0_{cell} - \left(\frac{RT}{nF}\right) lnQ_r \tag{3.5}$$

While the Nernst equation provides crucial information about equilibrium states, it does not provide information on how quickly a system reaches equilibrium, as reactions may not reach equilibrium due to kinetic limitations. Therefore, studying the reaction kinetics, particularly at the electrode surface, is crucial for a deeper understanding of electrochemical reactions [45].

3.3 Kinetics

The rate (r) of an electrochemical reaction can be defined as a function of the rate constant (k), the concentration of the reactant (C) and the reaction order (α) [45]:

$$r = kC^{\alpha} \tag{3.6}$$

The rate constant of a reaction can be greatly influenced by temperature, as described by the Arrhenius equation [45]:

$$k = Ae^{\frac{-E_A}{k_B T}} \tag{3.7}$$

In this equation, T represents the absolute temperature, A is the pre-exponential factor, k_B stands for the Boltzmann constant, and E_A is the apparent activation energy of the reaction. The apparent activation energy can be determined by measuring the reaction rate at various temperatures and at a constant concentration of the reactant.

Chapter 4

Methods

This chapter presents the electrochemical methods and analytical techniques that form the foundation for the studies detailed in **Papers I**, **II**, and **III**.

4.1 Electrochemical Alloy Formation

When elemental mercury (Hg^0) comes in contact with a noble metal such as platinum (Pt), a stable metallic alloy can form. This phenomenon has been extensively studied in the past [46–51]. However, its potential as a technique specifically for mercury removal from aqueous solutions has only recently been presented [15, 16].

To remove mercury, predominantly found in ionic form in contaminated waters, a sufficiently reductive potential is applied to a platinum electrode immersed in a mercury-ion containing solution, inducing the formation of an alloy in the thermodynamically favored phase, $PtHg_4$. The overall reaction of this formation can be written as follows:

$$Pt + 4Hg^{2+} + 8e^- \rightarrow PtHg_4 \tag{4.1}$$

The alloy formation is believed to be a multi step process, in which intermediates such as PtHg and $PtHg_2$ can form [15]. The process can be described in three main steps, as illustrated in Fig. 4.1: (i) Reduction of the mercury ions in solution on the platinum electrode surface. (ii) The insertion of elemental mercury into the Pt lattice to form the $PtHg_4$ alloy. (iii) Elemental mercury atom diffuses through the $PtHg_4$ to grow the alloy.

This new removal method has the potential to offer several significant advantages over other current available methods, as detailed in Section 2.3. It has previously been demonstrated that the method exhibits high selectivity for mercury and is efficient at both high and low initial concentrations of mercury, remaining unaffected by pH in the range of 0 – 6.6. In addition, the process consumes small amounts of energy and is reversible, allowing regeneration of the platinum

electrodes and ensuring safe recovery of mercury [15]. Once the electrodes are saturated with mercury, they can be transferred and regenerated by applying a positive potential in a small volume of solution specifically designed for regeneration. When the concentration of mercury in the regeneration solution reaches a high level, established removal methods such as precipitation can be utilized to recover mercury with high purity. In theory, other metals could serve as alternatives to platinum for the electrode material. Copper (Cu), being more abundant and cost-effective than platinum, could be an option; however, its instability in oxidizing acids and water without potential control, coupled with its inability to be regenerated for reuse, limit its applicability [16]. Gold (Au), another potential alternative, can form a stable amalgam with mercury, but its higher cost and lower mercury capacity in its most stable alloy compared to platinum (Au_3Hg vs. $PtHg_4$) render it a less efficient choice [52]. The usage of less noble metals such as zinc (Zn), aluminium (Al), and tin (Tn) is also an option, however their proneness to oxidation and degradation hinders efficient alloy formation, making them unsuitable in practice [53, 54].

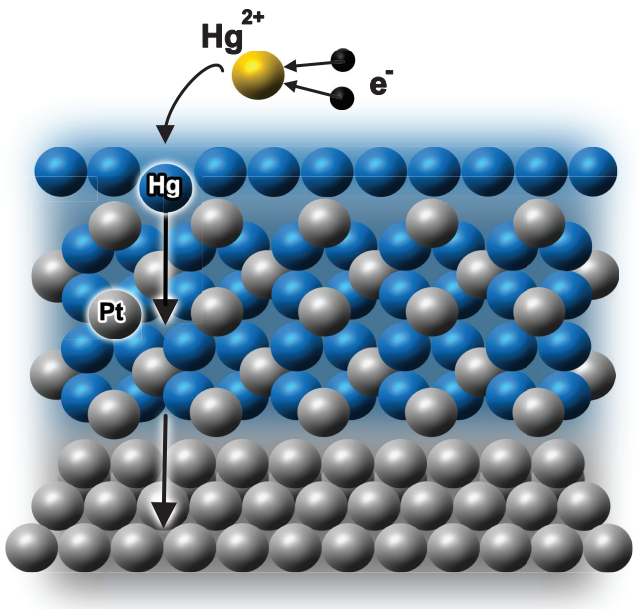

Figure 4.1: The alloy formation process, where a divalent mercury ion is reduced on the electrode surface and inserted into the alloy $PtHg_4$, followed by a diffusion through the alloy and a reaction with platinum at the alloy-platinum interface.

A more in-depth examination of the method is needed to further elucidate the exact reaction mechanisms of the alloy formation, to understand the precise thermodynamics and kinetics of the process, as well as the intricacies of the regeneration process. **Papers I**, **II**, and **III** delve into various aspects of the removal method, including the formation, growth, and dissolution of the alloy, offering crucial insights for the optimization of both the alloying and regeneration processes. Therefore, these investigations represent a vital step

towards establishing this technique as a viable solution for mercury removal from aqueous solutions.

4.2 Electrochemical Measurements

Electrochemical experiments, focusing on the alloy formation between a platinum electrode and mercury in solutions, are carried out to examine the mercury removal process. Various experimental techniques are used to examine different aspects of the method, from its fundamental principles to its more applied features.

4.2.1 Electrochemical Quartz Crystal Microbalance

Electrochemical quartz crystal microbalance (EQCM) is a technique that combines the principles of electrochemistry and piezoelectricity to investigate in real-time various electrochemical processes [55, 56]. In particular, EQCM can precisely measure mass changes in thin films on an electrode during processes such as electrodeposition and dissolution of metal films. By using EQCM, kinetic examination of processes that involve events at the monolayer level and thin films are able to be examined, which would otherwise remain undetected by conventional electrochemical methods [57].

The basis of EQCM operation lies in a quartz crystal sensor, coated on both sides with electrodes. When an alternating electric field is applied, the crystal oscillates at a specific resonant frequency (Δf_0). The frequency of oscillation is highly sensitive to the mass of the crystal; the frequency will shift if a mass is added or lost [55]. The Sauerbrey equation (4.2) can be used to relate the frequency shifts of the crystal to the mass change, where f_0 is the resonant frequency of the the sensor before any mass change, n is the overtone, A_s is the active surface area of the electrode, μ_q is the shear elastic modulus and ρ_q is the sensors density of the quartz [58].

$$\Delta f_n = -\frac{2 f_{0,n}^2 n}{A_s \sqrt{\rho_q \mu_q}} \Delta m \tag{4.2}$$

For the Sauerbrey equation to be valid, certain conditions need to be met and any deviations from these conditions can lead to inaccuracies in the calculated mass changes. The deposited or removed film must be considered rigid, contribute to less than 2% of the mass of the crystal sensor, and be uniformly distributed on its surface. A film is considered rigid if the frequencies shift of different overtones overlap, with minimal energy losses and dissipation changes (ΔD) close to zero. A high ΔD indicate that the surface is soft or viscous, and thus viscoelastic models should be used instead of the Sauerbrey equation. The ΔD can be written according to Eq. 4.3, where Q_s is the sum of all energy losses in the system per oscillation cycle. The Q_s factor can be further defined by f_0 over the resonance peak bandwidth BW [55].

$$\Delta D = \frac{1}{Q_s} = \frac{BW}{f_0} \tag{4.3}$$

In **Papers II** and **III**, EQCM is used to monitor in real time, both the alloy formation and the dissolution of the alloy. A typical EQCM setup used for electrochemical measurements can be seen in Fig. 4.2. The WE is a planar AT-cut quartz crystal sensor mounted in a dip holder, exposing only the top platinum electrode to the electrolyte solution.

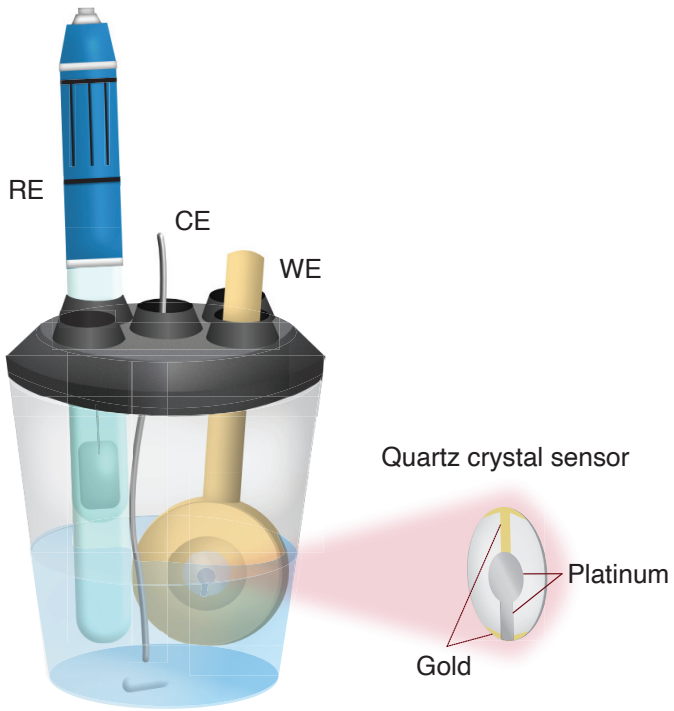

Figure 4.2: A typical 3-electrode setup for EQCM measurements. A quartz crystal sensor, mounted inside a dip holder, is used as the WE, with a platinum wire CE, and a glass RE.

4.2.2 Batch Experiments

Batch experiments are used to study the mercury removal process at laboratory scale or for scaled-up experiments more relevant for industrial applications. These experiments are distinct from in situ experiments, such as those conducted using EQCM, as they do not involve real-time measurements. During batch experiments, the concentration of mercury in the electrolyte solution, before, during and after electrochemical treatment, is directly measured using an analytical technique, namely Inductively coupled plasma mass spectrometry (ICP-MS).

Batch experimental setups can involve a 2-electrode or a 3-electrode configuration, and the selection of the WE is dependant on the study's objectives. When the focus is on understanding the fundamentals of an electrochemical process, such as reaction mechanisms, simple designs like thin silica glass plates

coated with platinum are often used at lab-scale (Fig. 4.3). In contrast, for studies that require a WE with a larger surface area or resilience under harsh conditions, steel or carbon foam-supported platinum WEs can be employed [59, 60]. Foam WEs can be particularly advantageous for large-scale batch experiments in concentrated acids, where fast and efficient mercury removal is the primary objective. A typical batch experimental setup, at lab-scale (50 mL) and a scaled-up version (20 L), is presented in Fig. 4.4.

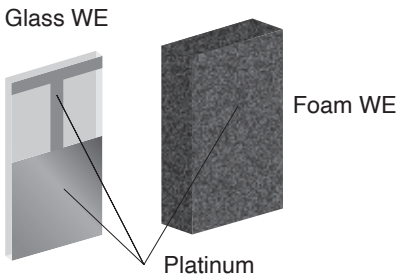

Figure 4.3: A silica glass WE, and a steel/carbon foam WE.

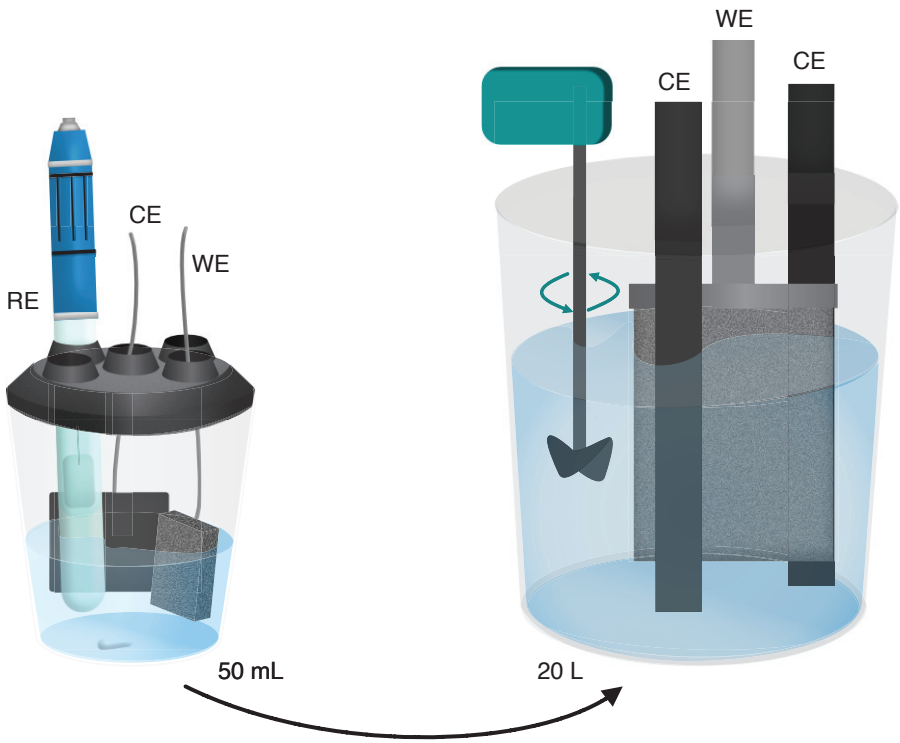

Figure 4.4: A typical 3-electrode setup for batch experiments at lab-scale (50 mL), consisting of a foam WE, diamond CE, and a glass RE. In addition, a scaled-up version (20 L) using a 2-electrode setup, with two foam WE and two diamond CE.

In **Papers II** and **III**, batch experiments at lab-scale are conducted using a glass WE to study the reaction mechanism of the removal method. Where in **Paper I**, batch experiments at lab-scale and a scaled-up version are used

to evaluate the removal efficiency and stability of different foam WEs, to investigate the removal method's potential for large-scale applications.

4.3 Analytical Techniques

4.3.1 Inductively Coupled Plasma Mass Spectrometry

Inductively coupled plasma mass spectrometry (ICP-MS) is a commonly used technique for measuring trace and ultra-trace levels of elements in a variety of matrices, including aqueous solutions. ICP-MS has diverse applications, prominently in fields such as environmental and pharmaceutical monitoring, clinical research, and toxicological studies Recently there has been a significant shift towards the use of ICP-MS in clinical laboratories, owing to the many advantages it can offer over other common techniques, such as atomic absorption (AAS) and atomic emission spectroscopy (AES). The main advantages of ICP-MS include multi-element detection, low detection limit and sample volume requirements. However, the initial cost of ICP-MS instrument can be high, as well as the operating costs themselves, as the instruments requires argon gas and other high purity gases. Nonetheless, the advantages of the ICP-MS often outweigh these expenses, particularly in settings where precise and accurate trace element analysis is essential [61].

The operation of an ICP-MS instrument can be described as follows: The sample, typically an acidic solution, is introduced into the system via a peristaltic pump and is nebulized into a fine aerosol. This aerosol is transported into a plasma torch, where the sample is atomized and subsequently ionized. The ions generated in the plasma are extracted and guided into a mass analyzer through a set of electrostatic lenses or ion optics. In the mass analyzer, the ions are separated based on their mass-charge (m/z) ratios and the abundance of different isotopes are measured in the detector, which allows for the quantification of the elements present in the original sample. A simplified illustration of the instrument can be seen in Fig. 4.5.

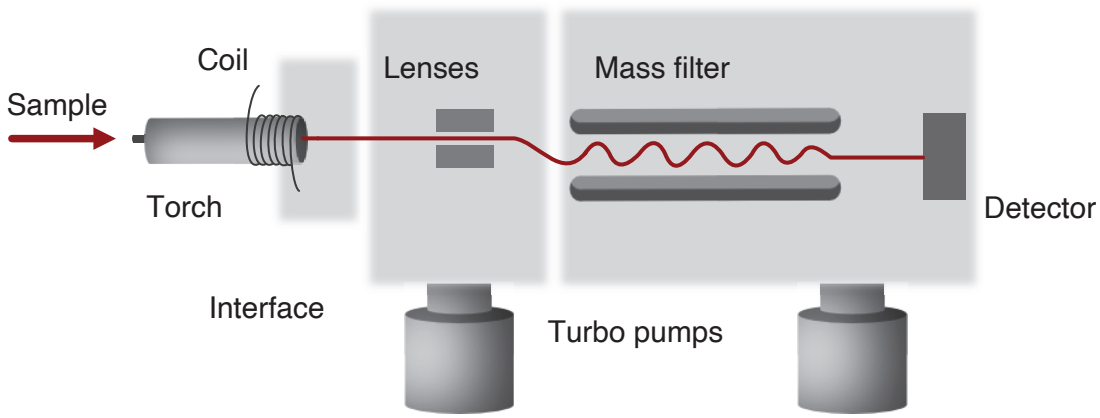

Figure 4.5: Schematic illustration of an ICP-MS instrument, based on data from Ref. 61.

Mercury can be very difficult to analyse in solutions. This extremely volatile element is notorious for its so-called memory effect, where a prolonged signal count for mercury is sustained long after the initial sample has been analyzed and an appropriate washout time carried out [62–64]. This effect can lead to a non-linear calibration of the instrument, reduced sensitivity over time, and a high dependency of the signal on the sample matrix. Even at low mercury concentrations the effect can be prevalent, as mercury can adhere to the walls of both the ICP-MS transfer tube and the spray chamber. Divalent mercury is a soft acid metal cation, and its covalent, and occasionally nonpolar behaviour, allows it to adhere strongly to nonpolar surfaces such as the polymeric tubing of the sample introduction system. In addition, divalent mercury is easily reduced, and in its elemental form, it is neither lipophilic or hydrophhilic, and it can easily stick to any crevices, making it difficult to rinse out [65].

Several steps have been proposed to eliminate the issues associated with the memory effect of mercury, such as the addition of gold and stabilizing agents to the sample, as well as specific acid rinsing solutions [65, 66]. Particularly, for stabilization against mercury reduction during analysis, hydrochloric acid (HCl) can be used to prepare the sample matrix. By using HCl, $HgCl_2$ present in the sample can be adsorbed on hydrophobic surfaces and if sufficient concentrations of HCl is present, mercury can be found predominantly in the water soluble anionic form $[HgCl_4]^{2-}$. If the concentration of the chloride ions is too high, the signal count can however be suppressed by Cl^+ and $ArCl^+$ species formed in the plasma [65].

In **Papers I** and **II**, ICP-MS is used to quantify mercury and other metals of interest in solution. The samples taken from the electrochemical measurements are diluted using 1 M HCl to fall within the ICP-MS instrument's detection limits, ensuring the stability of mercury in the sample and guarantee signal accuracy. Moreover, the standard matrices for the calibration curve are carefully prepared to exactly mirror the samples taken from the electrochemical measurements. Internal standards can be added to all samples to further correct for random errors, such as noise, torch instabilities, and matrix effects. These internal standards possess atomic mass and ionization potential similar to the element of interest, allowing any deviations to be accounted for [67]. By taking these measures, the memory effect during mercury analysis with ICP-MS can be minimized, leading to negligible deviations and eliminating the need for further preventative measures to guarantee precise and reliable results.

Chapter 5

Results

In this chapter, some of the results from **Papers I**, **II**, and **III** are presented.

5.1 Reaction Mechanism

To better understand and optimize electrochemical alloy formation as mercury removal method, it is crucial to gain insights into various aspects of its reaction mechanism. These include, but are not limited to, the onset potential of the alloy formation and its dissolution, as well as kinetic parameters such as its reaction order in mercury ion concentration and the activation energy for the alloy formation.

It is important to note, that there is currently no universally accepted or standardized method for determining the onset potential of an electrochemical process [68]. One commonly used approach is the tangent method, where a tangent line or a linear extrapolation of the current at higher overpotentials is drawn, and the potential at which this extrapolation intersects the baseline is defined as the onset potential. Another approach is the de-visu method, which relies more on subjective visual assessment than the tangent method. In this method, the onset potential is considered the potential value at which the current begins to deviate noticeably from its baseline. Many studies also employ the threshold method, where the onset potential is defined as the point at which the current exceeds a preset value above the baseline current. Despite these methods being commonly used to determine the onset, none are universally applicable, and their accuracy can depend on the specifics of the experimental system. Furthermore, in many instances, the method used to determine the onset potential is simply not specified [68, 69].

5.1.1 Alloy Formation

In **Paper III**, EQCM analysis was used to determine the onset potential for the formation of the $PtHg_4$ alloy using a WE consisting of a crystal quartz sensor coated with 200 nm of platinum (25 mm^2), in 0.5 M H_2SO_4, with initial mercury concentration of 10 mg/L. Using the EQCM, the changes in frequency and dissipation were measured for three different harmonics (3, 5, 7) during a linear potential sweep from 0.73 V – 0.18 V vs. SHE. The potential was scanned in a step-wise manner from a high overpotential, where no alloy formation would occur, to a sufficiently reductive overpotential that enables the formation of the alloy, while avoiding hydrogen evolution (HER). As the alloy begins to form at the electrode surface, the frequency decreases linearly corresponding to the mass uptake at the crystal surface. Throughout the measurement, the dissipation recorded remains relatively low. However, the slight increase, though minimal, might be indicative of the formation of a soft, viscoelastic layer, possibly representing the formation of elemental mercury at the surface. The subsequent rapid decrease in dissipation suggests a transition of these layers into a more rigid state. This is likely due to the insertion of the elemental mercury into the platinum lattice forming $PtHg_4$ and its diffusion through the growing alloy, as suggested in Section 4.1.

Assuming that the formed alloy demonstrates ideal rigid behavior, the Sauerbrey equation (Eq. 4.2) was used to calculate the mass of the alloy formed on the WE surface from the measured frequency changes. In this case, the mass corresponds to the cumulative current, and the tangent method was used to determine the onset potential, where linear extrapolation was made through the data set ranging from 0.56 V to 0.18 V. As shown in Fig 5.1.b, the onset potential for the alloy formation was found to be 0.63 V vs. SHE.

The formation of the $PtHg_4$ alloy is a non-spontaneous process. As indicated by the onset potential, the process proceeds very close to the thermodynamic limit, which, based on the Density Functional Theory (DFT) calculations detailed in **Paper III**, is determined to be 0.77 V vs. SHE at a Hg^{2+} concentration of 10 mg/L. For an effective mercury removal, a sufficiently reductive overpotential is essential, while avoiding excessively high potentials that could instigate undesired side reactions such as HER or degrade the electrode material. Within the potential range of 0.63 – 0.18 V vs. SHE, an optimal potential for the alloy formation can be determined. The identification of this optimal potential is crucial to advance the mercury removal technique, ensuring it is not only efficient in removing mercury but also in its energy consumption, a necessity for practical applications.

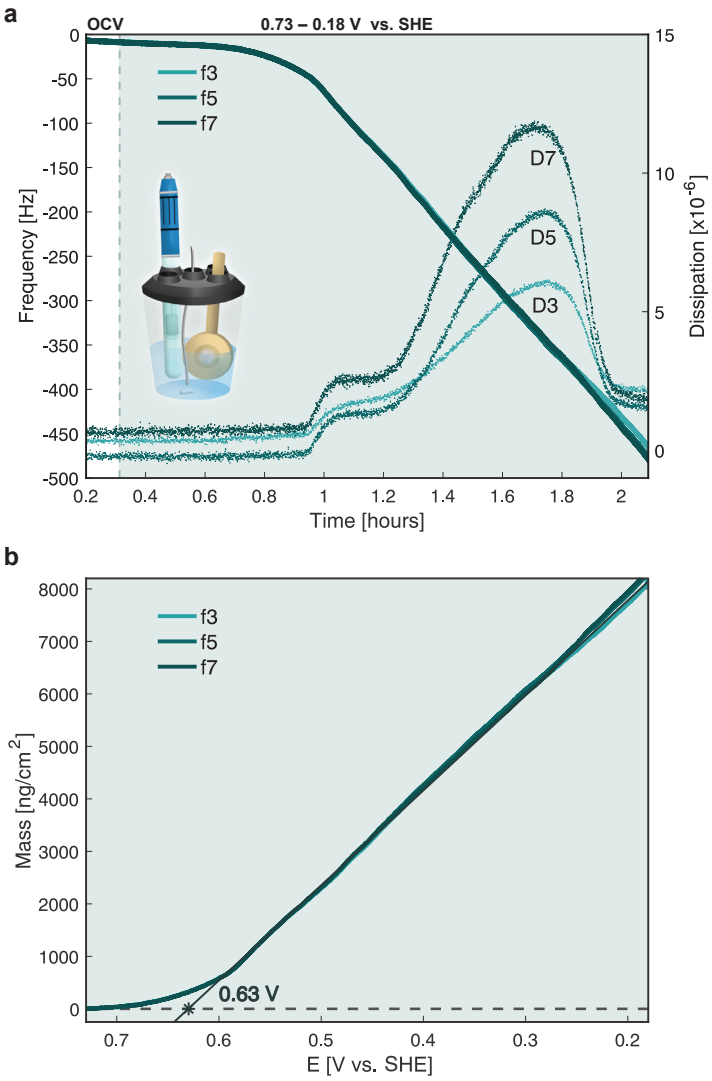

Figure 5.1: (a) The measured frequency changes and dissipation over time for three different harmonics (f3, f5, and f7), as detected with EQCM during alloy formation. (b) The calculated mass as a function of the applied potential, with the onset potential for the alloy formation determined to be 0.63 V vs. SHE.

5.1.2 Regeneration

In **Paper III**, EQCM analysis was used to determine the onset potential for the regeneration of the platinum WE and the release of the bulk $PtHg_4$ alloy back into the solution. As was done in Section 5.1.1, the changes in frequency and dissipation were measured for three different harmonics (3, 5, 7). The experimental process involved the formation of the alloy at a constant potential of 0.18 V, followed by the application of a constant potential of 0.80 V to remove elemental mercury formed at the surface. Finally, a potential scan from 0.80 V to an higher overpotential of 1.16 V vs. SHE was performed to regenerate the platinum WE and release the bulk alloy, see Fig. 5.2.a. The frequencies measured showed a linear decrease as the alloy was formed, followed by a sharp increase as the elemental mercury at the surface was removed. Subsequently, a linear increase was observed as the bulk alloy was released back into the solution, with the frequency eventually plateauing, indicating the completion of the electrode's regeneration. The changes in dissipation during the formation exhibited a similar trend to that observed in Section 5.1.1. However, the dissipation changes were notably lower when a constant potential was applied to form the alloy, as opposed to a slow potential scan. After the elemental mercury at the surface was removed, the dissipation remained consistent throughout the regeneration process.

As previously done in section 5.1.1, the mass of the alloy was calculated from the measured frequency changes, see fig. 5.2.b. The tangent method, was used to determine the onset potential for the regeneration, where a linear extrapolation was made through the data set ranging from 0.96 V to 1.01 V. As illustrated in Fig. 5.2.c, the onset potential for the regeneration process was identified to be 0.93 V vs. SHE.

Identifying the onset potential for the regeneration of the platinum electrode, and the release of the bulk mercury back into the solution, is particularly important for practical applications. Recovering the mercury from the platinum electrode for secure disposal, and enabling the reuse of the electrodes is a vital aspect of the process. The regeneration should be carried out as quickly and efficiently as possible, which can be facilitated by a higher overpotential. However, applying an excessively high potential to the system could lead to unwanted side-reactions and/or degradation of the electrode material. Further research is needed to identify an ideal "Goldilocks" potential, one that is neither too low nor too high, to achieve optimal regeneration.

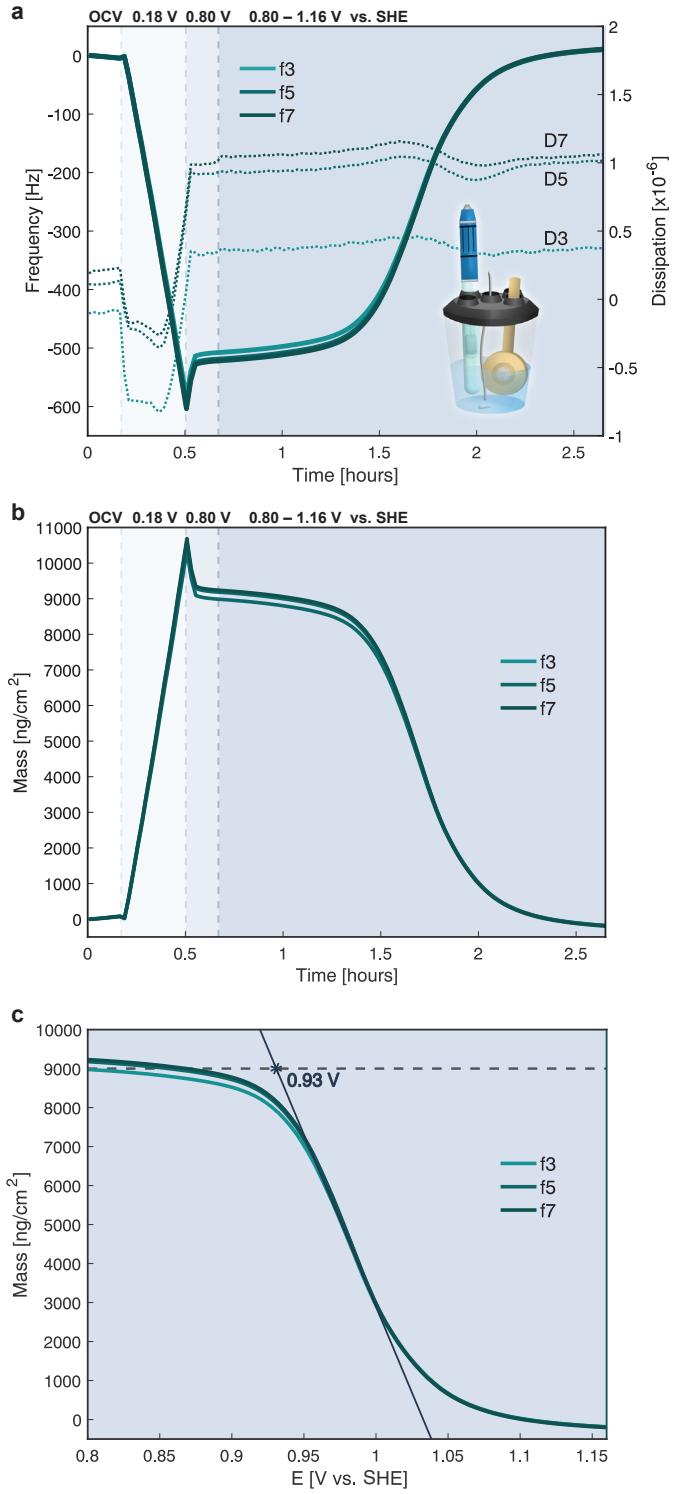

Figure 5.2: (a) Measured frequency changes and dissipation over time, for three different harmonics (f3, f5, and f7), as detected with EQCM. (b) The calculated mass as a function of time, and (c) the mass change as a function of the applied potential. The onset potential for the regeneration was determined to be 0.93 V vs. SHE.

5.1.3 Temperature and Concentration Studies

In **Paper II**, batch experiments were conducted using a 2-electrode setup to maintain a clean system, particularly important at low concentrations of mercury where the system is sensitive to any contamination from the RE. These experiments were carried out using a glass WE plated with 100 nm of platinum (15 x 15 mm), in 0.5 M HNO_3 with initial mercury concentrations ranging from 0.25 to 1000 µg/L, as shown in Fig. 5.3. Notably, over 99% of the mercury was removed from the solution in all cases, or would be, given sufficient removal time. Furthermore, the mercury was reduced to levels far below the WHO's safe limit for drinking water (6 µg/L) within 30 hours. These concentration studies are essential for evaluating the practicality of the electrochemical removal method for real-world environmental decontamination and sanitation scenarios, where the target mercury concentration is often well below the WHO limit. Owing to the current measurement procedures and the detection limits of the used ICP-MS, experiments with initial mercury concentrations lower than 0.25 µg/L could not be carried out. However, it can be expected that the electrochemical alloy formation will also effectively remove mercury from solutions at substantially lower concentrations.

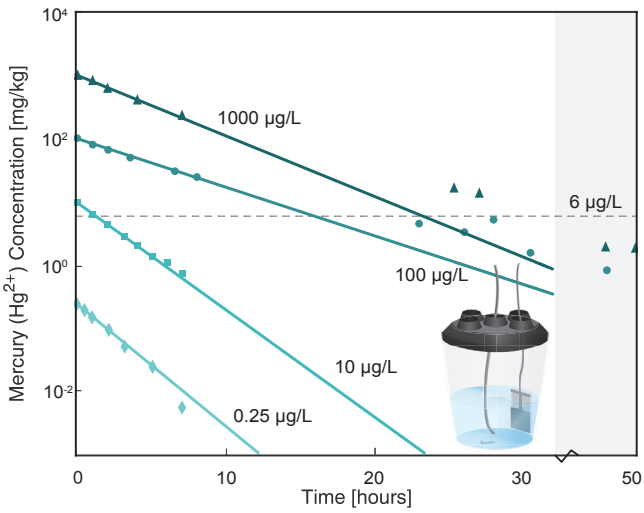

Figure 5.3: Mercury concentration in solution as a function of time for 2-electrode batch measurements. The dashed line corresponds to the WHO guideline for safe drinking water (6 µg/L).

From the concentration studies, the mercury removal rates were estimated, as shown in Fig. 5.4. It can be observed that the absolute rate of mercury removal is larger at higher initial concentrations, demonstrating a clear concentration dependence. Furthermore, from the general rate expression (Eq. 3.6), both the reaction order (α) and the rate constant (k) can be derived.

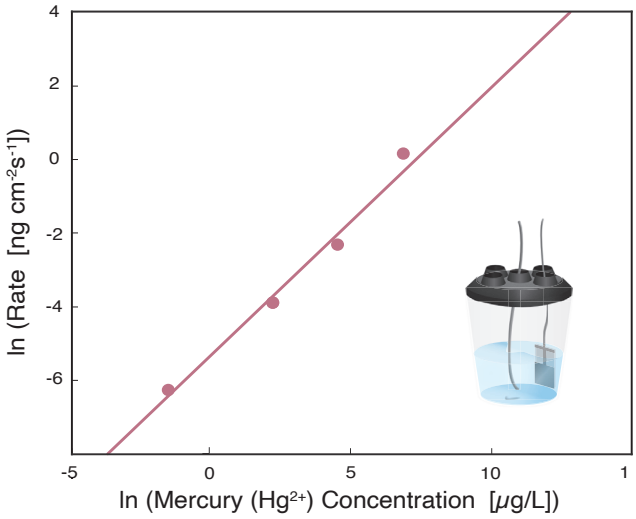

Figure 5.4: Natural logarithm of the mercury removal rate as a function of the natural logarithm of the initial mercury concentrations, for 2-electrode batch measurements.

The apparent reaction order in mercury ion concentration was determined to be 0.7. This reaction order of less than one for Hg^{2+} concentration suggests that the alloy formation process does not directly proceed via Hg^{2+} in the solution, contrary to what is indicated by the overall reaction (Eq. 4.1). Instead, it seems more probable that the reaction proceeds via the formation of elemental mercury on the surface, as proposed by Eq. 5.1, and subsequently followed by the alloy formation Eq. 5.2. If indeed the plating of elemental mercury is faster than the alloy formation, elemental mercury will accumulate on the surface, resulting in an apparent reaction order of less than one in Hg^{2+} concentration.

$$Hg^{2+} + 2e^- \rightarrow Hg^0 \tag{5.1}$$

$$Pt + 4Hg \rightarrow PtHg_4 \tag{5.2}$$

In **Paper II**, further investigations were conducted using EQCM analysis at varying temperatures ranging from 20 to 60°C. An Arrhenius plot (Eq. 3.7) was made to determine the apparent activation energy (E_A) of the overall reaction for alloy formation, as depicted in Fig. 5.5.

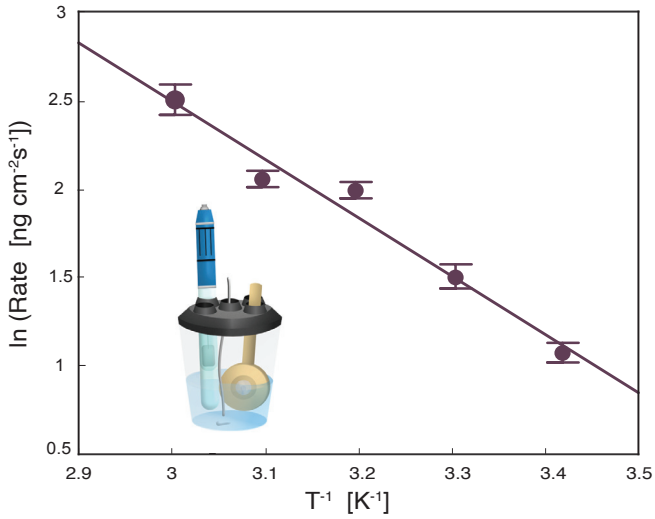

Figure 5.5: Arrhenius plot for temperatures 20 – 60°C using EQCM analysis. The error bars represent the standard error of the data for each temperature.

The apparent activation energy for the electrochemical alloy formation was determined to be 0.29 eV. This value being relatively low, i.e. the threshold energy for the reaction to occur is low, is significant for the selective removal of mercury, as the removal process is favored over other potential competing reactions [70]. Notably, the apparent activation energy for alloy formation between platinum and elemental mercury has been reported differently in two separate studies, with values being 0.35 eV [71] and 0.52 eV [48]. The value determined in **Paper II**, 0.29 eV, is relatively close to 0.35 eV, suggesting that the rate-determining step might be the same for both the reaction between elemental mercury and platinum, and the electrochemical alloy formation between mercury ions and platinum.

5.2 Large-scale Mercury Decontamination

Recognizing the need to further develop the electrochemical alloy formation process as a practical method for large-scale mercury decontamination, **Paper I** investigates, for the first time, its potential to remove mercury from concentrated sulfuric acid. For industrial application, the method should be scalable to treat hundreds or even thousands of tonnes of concentrated sulfuric acid. Furthermore, it should effectively lower the mercury concentration in the acid to levels that are considered technical quality grade (0.30 mg/kg) or high-purity grade (0.08 mg/kg) [72], within specified time frames.

For large-scale decontamination, it is essential for the WE to possess a high surface area support onto which platinum can be deposited, in order to increase the rate of mercury removal, while reducing the amount of platinum needed. Identifying appropriate materials for the WE posed a substantial engineering challenge, primarily due to sulfuric acid's highly corrosive nature. Given their high surface area foam materials emerged as suitable candidates for the WE.

Specifically, Stainless Steel 316L (SS316L) foam, commonly used in the industrial storage and handling of concentrated sulfuric acid, was identified as a potential support material [59, 73]. In this study, five different SS316L foams (25 x 15 mm), listed in Table 5.1, each with varying porosity and coated with 2 µm of platinum from two reputable manufacturers, were evaluated.

Table 5.1: Five different SS316L foams (15 × 25 mm), with different porosity, each coated with 2 µm of platinum. The foams originate from two different manufacturers, referred to as A and B. Additional platinum powder coating was applied to the fifth and final foam, as denoted by (*).

WE foam	**PPI**	**Manufacturer**
F1	45	A
F2	80	B
F3	30	A
F4	60	A
F5	45*	B

Preliminary batch experiments were conducted at lab-scale using the different SS316L foams as support material for the WE. Mercury was successfully removed from samples of authentic sulfuric acid from a zinc smelter, as shown in Fig. 5.6.a. In all cases (F1-F5), mercury was reduced below the technical limit within 80 hours, with F1 outperforming the rest by achieving high purity quality of the acid within 100 hours. However, all SS316L foams exhibited instability in the concentrated acid during mercury removal, as evidenced by iron leaching from the electrodes, see Fig.5.6.b. For all five foams, the iron concentration in the acid exceeded the high purity limit (15 mg/kg). Moreover, for foams F1, F4, and F5, the iron concentration surpassed the technical quality limit (30 mg/kg), with F4 exhibiting the most significant instability. This instability was unexpected and suggests that the foams might not possess the stated high-quality SS316L structure, possibly due to defects from the fabrication or the high-temperature platinum plating process. The observed instability does not appear to correlate with the manufacturer or the pore size of the foam.

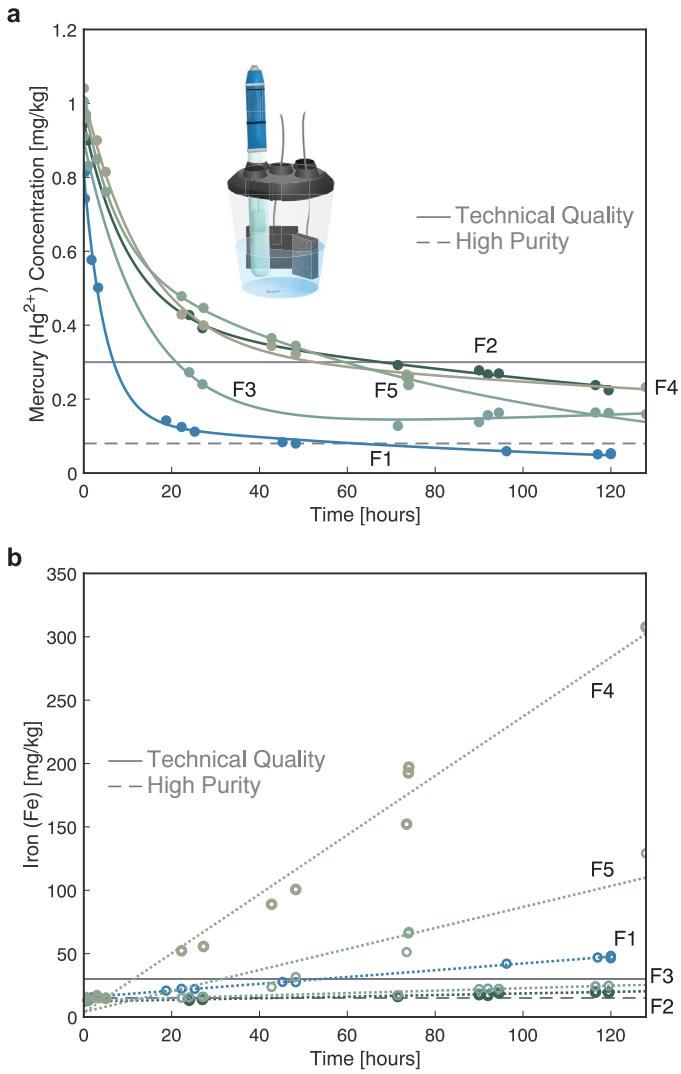

Figure 5.6: (a) Mercury removal from concentrated sulfuric acid at lab-scale (50 mL), using five different SS316L foams (15 x 25 mm). (b) The stability of all five foam during the mercury removal in terms of iron concentration in the acid. The curve fittings serve as a visual aid without representing the best fit of the data spread.

Despite the SS316L foam (F1) lacking stability in the concentrated acid at lab-scale, the mercury removal was still excellent, and thus, the foam was used to further evaluate the scalability of the removal method in a 20 L scale-up. The WE was also up-scaled from one SS316L foam (15 x 25 mm) to two SS316L WEs (200 x 150 mm). The results, which demonstrate the decrease in mercury concentration and the corresponding increase in iron concentration, during the mercury removal process, are shown in Fig. 5.7.

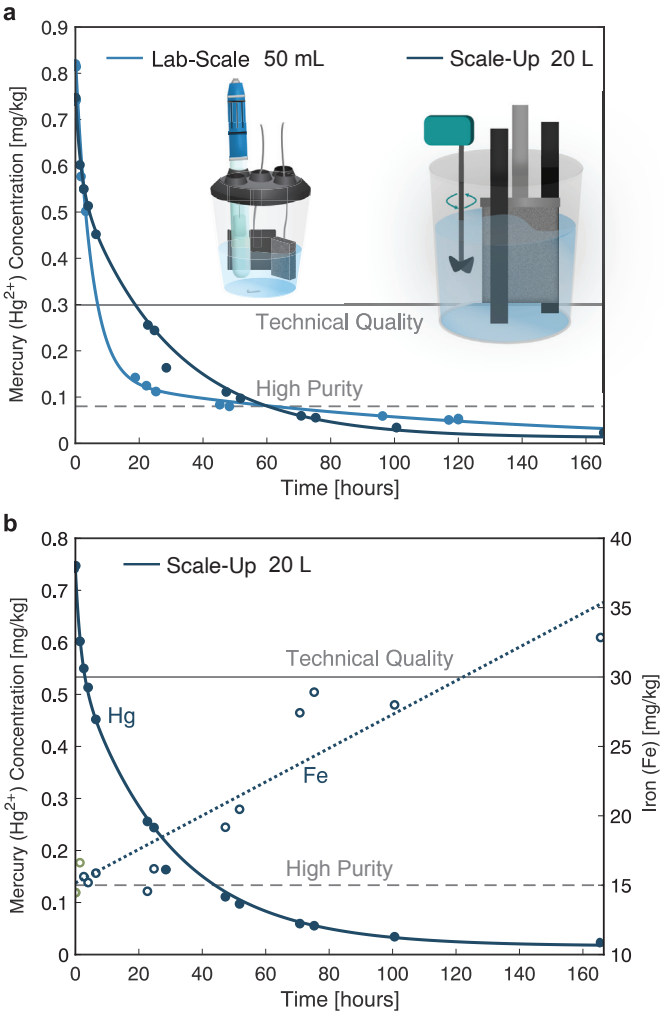

Figure 5.7: (a) Mercury removal from concentrated sulfuric acid using platinum SS316L foam WE, for both mercury removal at lab-scale (50 mL) and in a scale-up (20 L). (b) The mercury removal in the pilot reactor and the corresponding increase in iron concentration. The curve fittings serve only as visual aids without representing the best fit of the data spread.

Mercury was successfully removed from concentrated sulfuric in the scale-up, where over 98% of the mercury content was removed from the acid with initial concentration of approximately 0.8 mg/kg, within 160 hours. Technical quality of the acid was reached after around 20 hours, and high purity quality within 80 hours. The removal trends at the lab-scale and in the scale-up align after 60 hours, with high-purity quality achieved within 80 hours in both cases. Differences in removal behavior can be attributed to factors such as cathode electrode area vs. electrolyte volume, temperature fluctuations, number and size of anode electrodes, and reactor geometry. Despite these differences, the removal process largely follows the same trend and achieves mercury concentrations well below technical and high purity quality. Iron contamination, which initially exceeded high-purity limits, increased above technical quality after 160 hours.

This confirmed scalability indicates that the method has great potential for industrial-scale applications, treating thousands of tonnes of concentrated sulfuric acid, which has never been demonstrated before. However, moving forward, an alternative support material is needed for the WE, as SS316L was discovered to have poor corrosion resistance to the concentrated acid and thus unsuitable for future applications.

To prevent potential iron contamination of the acid, a metal-free candidate, a reticulated vitreous carbon (RVC) was used as an alternative to SS316L [60]. The RVC foam (15 x 40 mm), plated with 100 nm of platinum, demonstrated excellent stability in the concentrated sulfuric acid at lab-scale, where around 90% of the mercury content was removed from the acid within 120 hours, see Fig. 5.8. Technical quality of the acid was reached within 20 hours, however the mercury concentration appears to unexpectedly plateau and not decrease below 0.10 mg/kg, just above the high-purity quality. This may be due to the nature of platinum deposition on porous substrates, which can result in uneven film thickness. As the removal process continues, areas with thinner platinum layers become saturated, leading to less available platinum surface area for mercury absorption and consequently, lower removal rates. Furthermore, the RVC foam was only plated with platinum on one side, limiting the total available surface area compared to the SS316L foam, which was coated on all sites. With improved coating techniques, it is likely that the RVC foam could achieve mercury concentrations below high-purity targets.

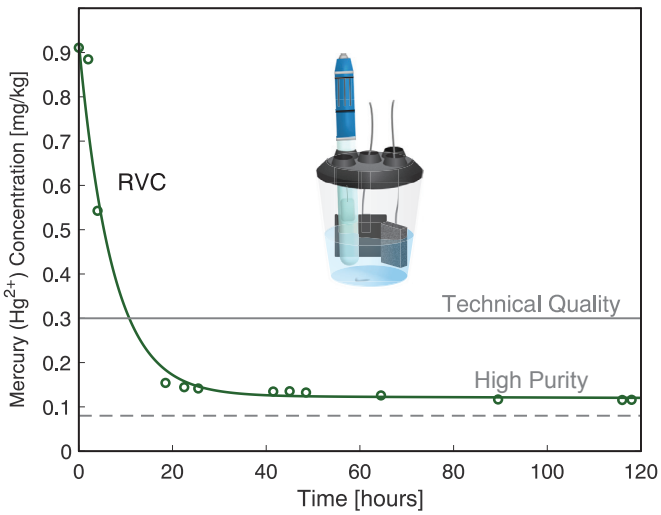

Figure 5.8: Mercury removal from concentrated sulfuric acid at lab-scale (50 mL) using RVC foam (15 × 40 mm) WE. The curve fittings serve as a visual aid without representing the best fit of the data spread.

Chapter 6

Conclusion and Outlook

The research conducted in this thesis provides substantial insights into electrochemical alloy formation as a technique for mercury removal. A series of studies demonstrated effective mercury removal from solutions with initial mercury concentrations as low as 0.25 µg/L. This proves the potential of the method to reduce mercury to extremely low levels in a relatively short amount of time, highlighting its applicability for decontamination of natural waters. In addition, the alloy formation process was found to have an apparent reaction order below one in Hg^{2+} concentration, which is an important kinetic parameter for understanding the alloy formation mechanism and its performance at specific mercury concentrations. The temperature dependence and the determined apparent activation energy of 0.29 eV are also crucial considerations for practical applications, as temperatures can vary significantly across different industrial streams. Furthermore, by using electrochemical alloy formation on platinum, mercury was removed from concentrated sulfuric acid for the first time. Over 98% of mercury was removed from the acid with initial concentration of approximately 0.8 mg/kg, resulting in high quality acid with mercury content below key industrial limits of technical quality (0.30 mg/kg) and high purity (0.08 mg/kg). This method proved effective at both 50 mL lab-scale and in a 20 L scale-up, demonstrating its excellent scalability and potential for large-scale industrial applications.

While this mercury removal technique holds potential, it also comes with its own set of challenges and limitations. One general challenge, not limited to the present method, is that the analysis of mercury in solution is complex, even when sophisticated analytical techniques such as ICP-MS, which is widely used in clinical laboratories, are employed. Mercury is well-known for its memory effect, which can lead to an overestimation of mercury levels. Rigorous sample preparation is therefore essential, including ensuring mercury stability in the samples being evaluated and adjusting for correct dilution within the detection limits of the instrument. Furthermore, it is important to tailor the sample matrices to accurately reflect the environment being studied to ensure dependable and accurate results.

A significant challenge lies in identifying the ideal support material for the platinum electrode in larger-scale applications. While the SS316L foam demonstrated effectiveness in mercury removal, its poor corrosion resistance makes it unsuitable. In contrast, the carbon foam (RVC) displayed both efficient mercury removal and notable corrosion resistance, marking it as a promising candidate for the platinum electrode support material. However, further investigations are necessary to fully evaluate the materials stability, longevity, and effectiveness over numerous cycles of mercury removal and regeneration. This is particularly important as the electrodes must endure repeated mercury extraction processes without performance degradation or contamination of the sulfuric acid, to be considered viable for commercial applications. To develop this removal technique into a viable decontamination solution, every stage of the process, including the regeneration, must be thoroughly designed and optimized. In particular, future research focusing in more depth on the regeneration process is essential for establishing a comprehensive end-to-end mercury removal system.

In conclusion, the electrochemical alloy formation has shown to be a promising method for mercury removal. With further research, optimization, and technological advancements, it has the potential to be an effective solution for mercury decontamination of aqueous systems, with real-life applications in environmental remediation, industrial waste treatment, large-scale decontamination of sulfuric acid in the mining industry, and many more.

Acknowledgment

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