Master Thesis

Enhancing Water Safety in Decentralized Water Reuse Systems with Low-Cost Prussian Blue Amperometric Sensors for Free Chlorine Monitoring

by

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Abstract:

In this Master Thesis, the fabrication, optimization, and testing of a low-cost free chlorine sensor is addressed. The goal is to provide a solution towards lower-cost sensors for monitoring the water quality in decentralized water treatment and reuse systems. These systems represent an interesting solution to provide sustainable and safe water services in regions lacking centralized water infrastructure. However, the considerable expense associated with remote water quality monitoring, imposed by the small scale of decentralized water reuse systems, are hindering widespread implementation of such systems.

This thesis takes the form of a collection of two scientific papers. The first one: “Enhancing Water Safety in Decentralized Water Reuse Systems with Low-Cost Prussian Blue Amperometric Sensors for Free Chlorine Monitoring” has been published in August 2023 in “IEEE Sensors Letters” and describes the optimization of the fabrication process via electrodeposition of Prussian Blue on screen-printed carbon electrodes (SPCE). The sensor is tested in treated greywater (that is water from sinks, washing machine and shower that is treated in a decentralized water reuse system) in controlled laboratory conditions. Sensitivity, linearity, and repeatability are measured and optimized. The second one: “Testing Low-Cost Prussian Blue Amperometric Sensors for Free Chlorine Monitoring in Decentralized Water Reuse Systems”, will be submitted to “Water Science & Technology” in the last trimester of 2023. A first version is presented here and will be revised before submission. In this paper, the fabricated sensor is tested over several days, and evaluated for sensitivity, stability, reliability, repeatability, and linearity in a real water reuse system, for both greywater and municipal wastewater. The relevance of Prussian Blue coated SPCE in the context of water treatment and reuse is evaluated. In addition, a few theoretical elements have been added to this thesis to help readers understand the context of the two articles presented.

Résumé :

Ce travail de master porte sur la fabrication et l’expérimentation d'un capteur de chlore libre à faible coût. L'objectif est de fournir une solution pour des capteurs à faible coût pour la surveillance de la qualité de l'eau dans les systèmes décentralisés de traitement et de réutilisation de l'eau. Ces systèmes représentent une solution intéressante pour une fourniture d'eau fiable et sûre dans les régions dépourvues d'infrastructures d'eau centralisées. Cependant, les dépenses considérables associées à la surveillance à distance de la qualité de l'eau, imposées par la petite échelle du système, empêchent la mise en œuvre généralisée de ces systèmes.

Cette thèse prend la forme d'un recueil de deux articles scientifiques. Le premier : "Enhancing Water Safety in Decentralized Water Reuse Systems with Low-Cost Prussian Blue Amperometric Sensors for Free Chlorine Monitoring" a été publié en août 2023 dans "IEEE Sensors Letters" et décrit l'optimisation du processus de fabrication via l'électrodéposition de bleu de Prusse sur des électrodes de carbone sérigraphiées (ECS). Le capteur est testé dans des eaux grises traitées (c'est-à-dire les eaux provenant des éviers, des machines à laver et des douches qui sont traitées dans certains systèmes décentralisés de réutilisation de l'eau) dans les conditions contrôlées du laboratoire. La sensibilité, la linéarité et la répétabilité sont mesurées et optimisées. Le second article : « Testing Low-Cost Prussian Blue Amperometric Sensors for Free Chlorine Monitoring in Decentralized Water Reuse Systems », sera soumis à « Water Science & Technology » au cours du dernier trimestre 2023. Une première version est présentée ici et sera révisée avant la soumission. Dans cet article, le capteur fabriqué est testé sur plusieurs jours et sa sensibilité, sa stabilité, sa fiabilité, sa répétabilité et sa linéarité sont mesurés dans un système réel de réutilisation de l'eau, à la fois avec de l’eau grise et de l’eau usée municipale. La pertinence des ECS activés par bleu de Prusse dans le contexte du traitement et de la réutilisation de l'eau est évaluée. En outre, quelques éléments théoriques ont été ajoutés en complément pour permettre aux lecteurs de comprendre le contexte des deux articles présentés.

Sommario:

Questa tesi di laurea magistrale tratta la fabbricazione e il test di un sensore di cloro libero a basso costo. L'obiettivo è fornire una soluzione per sensori a basso costo per il monitoraggio della qualità dell'acqua in sistemi decentralizzati di trattamento e riutilizzo dell'acqua. Questi sistemi rappresentano una soluzione interessante per un approvvigionamento idrico affidabile e sicuro nelle regioni prive di infrastrutture idriche centralizzate. Tuttavia, il costo considerevole associato al monitoraggio remoto della qualità dell'acqua, imposto dalla piccola scala del sistema, impedisce la diffusione di questi sistemi.

Questa tesi si presenta come una raccolta di due articoli scientifici. Il primo: "Enhancing Water Safety in Decentralized Water Reuse Systems with Low-Cost Prussian Blue Amperometric Sensors for Free Chlorine Monitoring" è stato pubblicato nell'agosto 2023 su "IEEE Sensors Letters" e descrive l'ottimizzazione del processo di produzione mediante elettrodeposizione del blu di Prussia su elettrodi di carbonio serigrafati (ECS). Il sensore è stato testato in acque grigie trattate (cioè l'acqua di lavandini, lavatrici e docce che viene trattata in alcuni sistemi decentralizzati di riutilizzo dell'acqua) in condizioni controllate di laboratorio. La sensibilità, la linearità e la ripetibilità sono state misurate e ottimizzate. Il secondo lavoro: “Testing Low-Cost Prussian Blue Amperometric Sensors for Free Chlorine Monitoring in Decentralised Water Reuse Systems”, sarà inviato a “Water Science & Technology” nell'ultimo trimestre del 2023. Qui viene presentata una prima versione, che sarà rivista prima della pubblicazione. In questo lavoro, il sensore fabbricato viene testato per diversi giorni per verificare la sensibilità, la stabilità, l'affidabilità, la ripetibilità e la linearità a lungo termine in un sistema reale di riutilizzo dell'acqua con acque grigie e acque reflue urbane. Viene valutata la rilevanza degli elettrodi attivati con blue di Prussia nel contesto del trattamento e del riutilizzo delle acque. Inoltre, sono stati aggiunti alcuni elementi teorici per aiutare i lettori a comprendere il contesto dei due articoli presentati.

Index

1 Introduction

The availability of clean water for various purposes, is crucial for human well-being (Murray et al., 2020). However, due to increasing water scarcity caused by factors such as climate change (Angela et al., 2022), population growth (Flörke et al., 2018), and pollution (Liu et al., 2016), there is a need to find alternative water sources (DeOreo et al., 2016; Mekonnen & Hoekstra, 2016). Water reuse, especially through decentralized systems that treat local wastewater for non-potable uses, has gained a lot of attention recently (Reynaert et al., 2021b; Salgot & Folch, 2018). In such systems chlorination is a common disinfection method (Ikehata et al., 2018), but its effectiveness must be continuously monitored to ensure safety (Schoen et al., 2018). Affordable water quality sensors are essential for such systems, but current options are often costly (Banna et al., 2014). This observation formed the basis for this Master Thesis. The development of low-cost electrodes for free chlorine monitoring has been recently explored by several of preliminary studies, demonstrating new promising amperometric (Olivé-Monllau et al., 2010; Salazar et al., 2015) or chemiresistive (Hoque et al., 2017; Hsu et al., 2014) sensors. However, few of these sensors have been tested outside of controlled laboratory conditions, and none to our knowledge in water reuse systems, and it is therefore not clear whether these new low-cost sensing technologies are applicable for water reuse.

A very promising approach is based on Prussian Blue coated screen-printed carbon electrodes (SPCE), as electrocatalytic properties of Prussian Blue are well established, and that it is a low-cost catalyst (Itaya et al., 1984), for instance with respect to platinum. SPCE are also widely available, easy to manufacture (Oliveira et al., 2023) and allow good reproducibility between electrodes. The present thesis builds on this work, with the aim to optimize the fabrication process for chlorine monitoring in water reuse systems.

Chapter 2 present the theoretical background, including Prussian Blue and free chlorine chemistry or electrode degradation as well as water separation and reuse.

Chapter 3 presents the optimization of the Prussian Blue electrodeposition process for sensitivity and reproducibility in treated greywater based on existing research that showed good results in laboratory conditions (Salazar et al., 2015; Salazar et al., 2012). We optimized the electrodeposition process for sensitivity and reproducibility in greywater. This work was published in the journal “IEEE Sensors Letters” in August 2023 (Herold et al., 2023).

In Chapter 4, we test the electrodes in a real water reuse system in the Water Hub at NEST building. Chapter 4 is the preliminary version of a scientific publication that will be submitted to the journal “Water Science & Technology”.

Finally, Chapter 5 presents the overall conclusions from this Master thesis.

2 Theoretical additional background

2.1 Amperometric sensing

2.1.1 Bases of amperometric sensing

The electrochemical sensing of Free-Chlorine via the Prussian Blue coated Screen-Printed Carbon Electrodes (SPCE) relies on amperometric sensing, more specifically on single potential amperometry. Amperometric sensing is a type of electrochemical sensing technique used to detect and quantify the concentration of a specific analyte in a sample solution. It relies on the measurement of current generated by a redox reaction (oxidation-reduction reaction) involving the analyte on an electrode surface (Carrara, 2012). The relationship between the concentration of an analyte and the current generated follows Fick's law of diffusion, which describes how the concentration gradient of a species influences its rate of diffusion in an electrochemical reaction at the electrode interface and the Nernst equation, that permits the calculation of the reduction potential of a reaction. Both are used to determine the quantitative relationship between the concentration of the analyte and the resulting current generated by the redox reaction at the electrode surface. When reaching the steady state[1], the current is directly proportional to the concentration of the analyte (see annex I for demonstration). (Carrara, 2012)

In the case of single potential amperometry, a specific potential is applied to measure the current generated by the corresponding oxidation or reduction reaction. The applied potential can be adjusted to maximize the signal coming from the analyte of interest with respect to the signal coming from interfering analytes. Usually, before amperometry, cyclic voltammetry is performed to determine the potential of the redox reaction related to the analyte of interest. (Settle, 1997)

For electrochemical measurements, the most commonly employed setup is based on he three electrodes configuration. This is composed by working electrode (WE), counter electrode (CE), and reference electrode (RE). Theoretically, a minimum of two electrodes (WE and RE) is required for the measurement, however, the use of only two electrodes, practically, is not sufficient to obtain a reliable measure (Carrara, 2012). The utilisation of the three electrodes configuration permits to measure the faradaic current flowing from the WE to the CE at the right applied potential between RE and WE (Carrara, 2012). The potential applied to the electrochemical cell, generates the electron transfer mechanism due to the presence of the analyte of interest. (Chugh et al., 2022)

2.1.2 Prussian Blue chemistry and its use in amperometric sensors

Iron(III) hexacyanoferrate(II), whose common name is Prussian Blue, is a deep blue pigment and a coordination compound, that is a molecule with a central metal atom/ion bonded to surrounding molecules/ions (ligands) through coordinate covalent bonds (Lawrance, 2013), with a complex chemical structure. His chemical formula is $Fe^{III}_4[Fe^{II}(CN)_6]_3$. It has been historically significant as both an artist's pigment and as a material with various practical applications, including in chemistry, medicine, and dye in the clothing industry, where it

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[1] By steady state, we mean equilibrium with respect to the electrochemical reaction occurring at the electrode surface. This means that the rate of diffusion of the analyte to the electrode and the rate of its electrochemical reaction are balanced, resulting in a constant current over time for constant concentration.

replaced the expensive lapis lazuli due to its easy synthesis, lasting colour, insolubility, non-toxicity and low cost (Feller & FitzHugh, 1997).

Prussian Blue has a face-centered cubic structure (Fig.1). The ideal structure consists of Fe^{II}–C–N–Fe^{III} sequences forming the cubic framework. One-fourth of $Fe(CN)_6$ sites are randomly vacant and filled with water molecules coordinated to Fe^{III}. Fe^{II} centers are low spin and surrounded by six carbon ligands in an octahedral arrangement, while high-spin Fe^{III} centers are typically surrounded by about 4.5 nitrogen atoms and 1.5 oxygen atoms (from coordinated water).

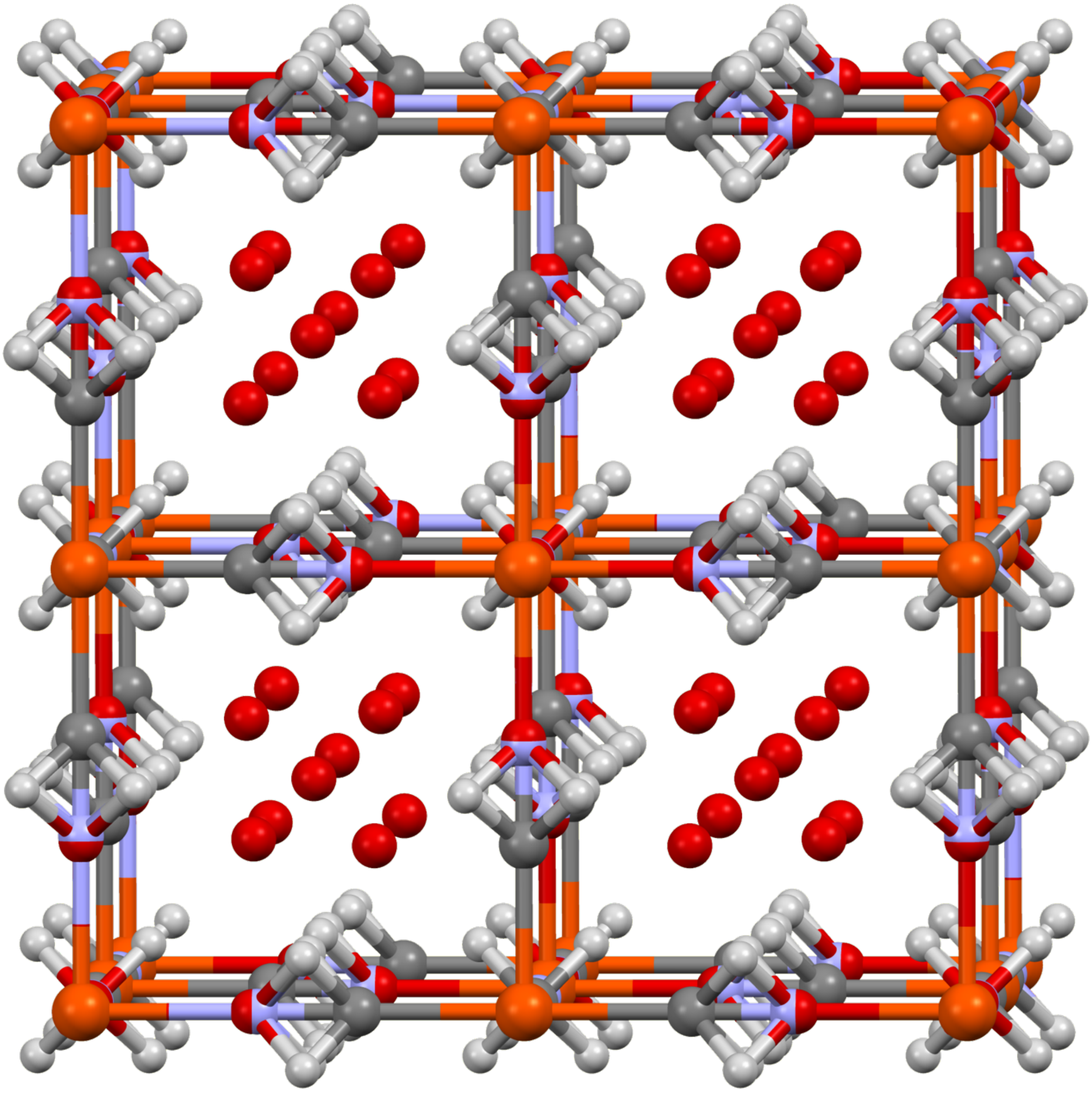

Figure 1: Ball-and-stick model of the unit cell of the crystal structure of hydrated Prussian blue, $Fe_4[Fe(CN)_6]_3 \cdot xH2O$ where x = 14-16, as reported in (Herren et al., 1980). One fourth of the $Fe(CN)_6$ groups shown will be missing supposedly at random and replaced by water. This illustration superimposes both possibilities at each site — water molecules or cyanide ions. The cyanide and water positions are disordered.(Mills, 2021) Colour code: Fe: orange C: grey N: blue H: white O: Red

Although cyanide groups are present, the pigment does not pose a toxicity risk to humans. (Estelrich & Busquets, 2021) Prussian Blue's intense blue colour is due to its ability to selectively absorb red and yellow wavelengths of light, reflecting the blue colour we perceive.

Beyond all these properties, Prussian Blue exhibits excellent electrocatalytic activity as a sensing material, with a low redox potential (Itaya et al., 1984). Its structure enables it to act as an electrocatalyst, facilitating redox reactions at the electrode surface (Itaya et al., 1984). Prussian Blue is a redox-active material, meaning that it undergoes a reversible redox reaction, which is of capital importance for its use as a catalyst in sensors allowing the sensor to be used for extended periods of time. The Fe(III) centres within the crystal structure can be reduced to Fe(II), and oxidized back to Fe(III) (Fe(III) + e^- → Fe(II) / Fe(II) → Fe(III) + e^-). (Yagi et al., 2014) These properties have been demonstrated to be useful for the sensing of Free-Chlorine by reduction of HOCL (Salazar et al., 2015), as good catalytic properties are necessary to obtain a distinct peak, which intensity is proportional to concentration, and that reversibility provides the necessary longevity of the modified electrode.

2.1.3 Free chlorine equilibrium and compensated raw value

The measured current I_{raw} of the redox reaction on Prussian Blue coated SPCE is proportional to the concentration of only HOCl. The speciation between hypochlorite (OCl-) and hypochlorous acid (HOCl) is a function of the pH and the temperature of the solution (Gray, 2014). By scaling the measured signal by the dissociation constant, we can compensate for hypochlorite ions to obtain the concentration of free chlorine, which is the sum of concentrations [HOCl] and [OCl-].

The relationship between the pH compensated raw value I_{eq} (in nA) and the free chlorine concentration is linear and can be expressed as

$$C_{out} = m * I_{eq} + c, I_{eq} = \frac{I_{raw}}{\alpha}$$

, where

$$\alpha = \frac{10^{-pH}}{10^{-pH}+10^{-pKa}}, \quad pKa = -0.009 * T + 7.765 \text{ (Gray, 2014)}$$

and m and c are calibration variables. We see on (Figure 2) that proportion of HOCl decreases quickly for basic pH, which leads to smaller I_{raw} and consequently more difficult to detect.

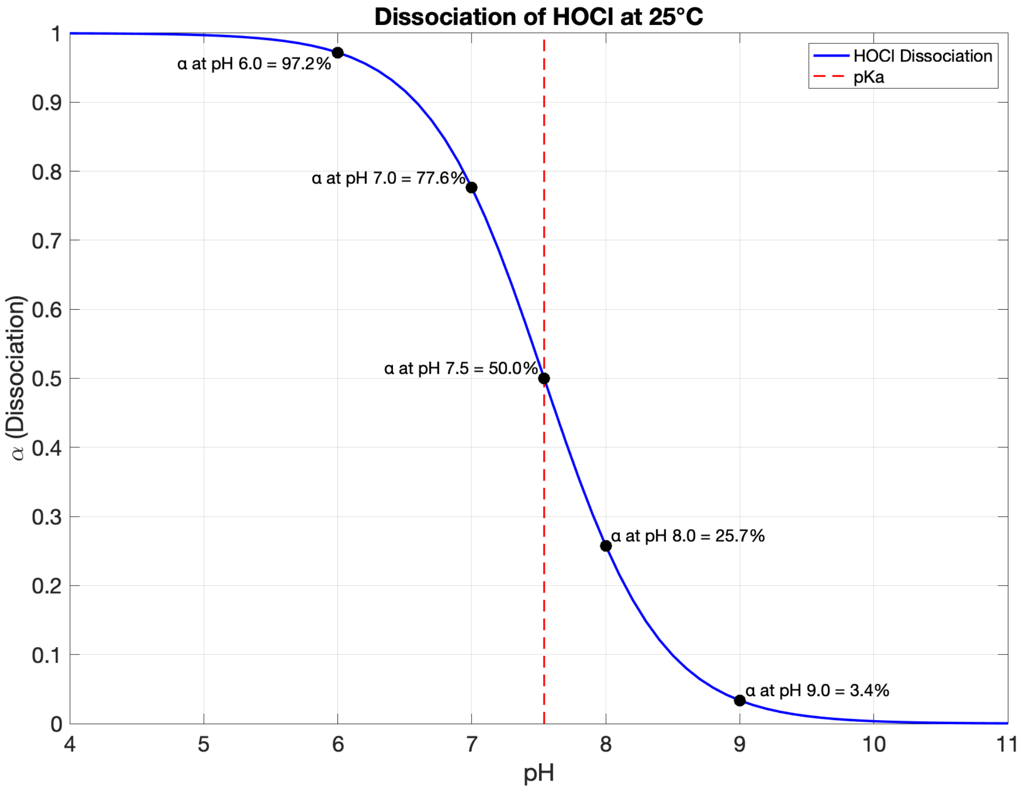

Figure 2: Dissociation constant for Hypochlorous acid at 25°C for pH values ranging from 4 to 11.

2.1.4 Phenomenon limiting life expectancy of amperometric sensors.

Several phenomena can limit life expectancy and impinge long-term sensitivity of electrodes. Among them, we report the three that we expect to have more significant impact on the sensitivity of our electrodes.

- Electrode Fouling: it refers to the accumulation of unwanted deposits or substances on the surface of electrodes used in electrochemical processes. This build-up can hinder the efficient transfer of electrons and ions, leading to reduced performance. Regular cleaning or maintenance is often necessary to mitigate electrode fouling and maintain optimal functionality. (Hanssen et al., 2016) In wastewater treatment, it is especially challenging as biological processes can lead to the formation of biofilm and prevent the analyte to reach the electrode surface. (Qi et al., 2022) However, for our electrode, biofilms are less of a concern since they are designed to be used in the chlorinated part of the treatment plant, where biological organisms should not be present.
- Leaching of Prussian Blue coating: it refers to the process where the coating or electrode material is dissolved by the analysed water. Since none of the materials (Prussian Blue, carbon, silver) are soluble in water, and that our pH is expected to remain in a 7-9 range, we expect the abrasion by the particle in the treated water can be the mean factor of wear, especially with treated wastewater, which is not filtered, but only sedimented.
- Electrochemical Degradation: repeated redox cycles and exposure to harsh analytes can cause the electrode surface to degrade over time, leading to a decline in electrochemical

activity and stability. However, Prussian Blue coating is stable when exposed to free-chlorine (Salazar et al., 2015), and Prussian Blue redox process is theoretically fully reversible, preventing chemical degradation (Yagi et al., 2014).

2.2 Introduction to Decentralized Wastewater Treatment and Reuse Systems (DWRS)

2.2.1 Principle and Description

Decentralized wastewater treatment and reuse systems (DWRS) represent a fast-developing and promising approach to water management. These systems provide on-site wastewater treatment and reuse at the scale of individual households to entire neighbourhoods. Localised water treatment reduce strain on centralized treatment plants and reuse reduce reliance on freshwater sources. (Hardy et al., 2015) Due to sanitary requirements, water is most often reused for non-potable applications such as toilet flushing or landscaping. (Reynaert et al., 2021a; Sanz & Gawlik, 2014) These systems offer in any case a possibility of addressing water safety problems where centralized water infrastructure is not provided (Reynaert et al., 2021a).

2.2.2 Technical description, advantages, and challenges

Treating wastewater near the source of generation provides several advantages, apart from smaller initial investment and saving infrastructure cost, it is an excellent barrier against environmental pollution from untreated wastewater diffusion in environment (Ghernaout, 2018). DWRS have been suggested as a solution that can be cheaper and more energy efficient compared to other solutions to address water scarcity, as for instance desalinisation. (Ghernaout, 2018)

One of the challenges of water reuse is the need for strict compliance with water quality standards (Reynaert et al., 2020; Sanz & Gawlik, 2014) These standards are different in and also depend on the type of reuse (e.g., potable use, or different types of non-potable uses)

Another challenge is that community engagement and proper maintenance are required. (Exall, 2004; Reynaert et al., 2020). For instance, some systems need consumables or spare parts, and training of local operators is required.

2.2.3 Greywater, blackwater and wastewater

Separating different types of wastewaters according to their degree of contamination can facilitate water reuse easier as each type of wastewater can be treated according to the type of contaminants it contains. This can lead to improvement in term of greenhouse gas emissions and energy consumption (Mathilde et al., 2021).

A common separation of wastewater types is the separation between greywater and blackwater. Greywater is wastewater from bathroom sinks, showers and washing machines (WHO, 2006). Before being treated, it is not safe for human use or contact. After adequate treatment, it can be recycled for non-potable purposes such as garden irrigation, toilet flushing, handwashing, etc. Greywater is less contaminated than blackwater, especially because it contains fewer biological contaminants and substantially fewer bacteria of faecal origin. Proper safety managements and standards are necessary for treatment and reuse (Vuppaladadiyam et al., 2019). In contrast to greywater, blackwater is highly contaminated wastewater from toilets and kitchen sinks (tough some authors describe water from kitchen sinks as heavy greywater, introducing a second separation line (Etter et al., 2017)). Blackwater contains human waste, and not safe for contact. It requires complex and extensive treatment before safe disposal or reuse. The separation of wastewater into differently contaminated streams aims to avoid that all wastewater has to go through these more complex processes. (WHO, 2006)

2.2.4 Water Hub at NEST Water-Hub installation

The Water Hub at NEST (Eawag/Empa campus, Dübendorf, Switzerland) is a building that implements a water separation system that collects wastewater streams separately, including urine, blackwater, less concentrated greywater, more concentrated greywater, and rainwater (Etter et al., 2017). NEST collects and treats greywater separately as 'light' and 'heavy' greywater from bathrooms respectively kitchens. NEST also introduced a new urine-diverting flush toilet to separate urine at the source. It allows treatment of urine and production of fertilizer containing all major nutrients.

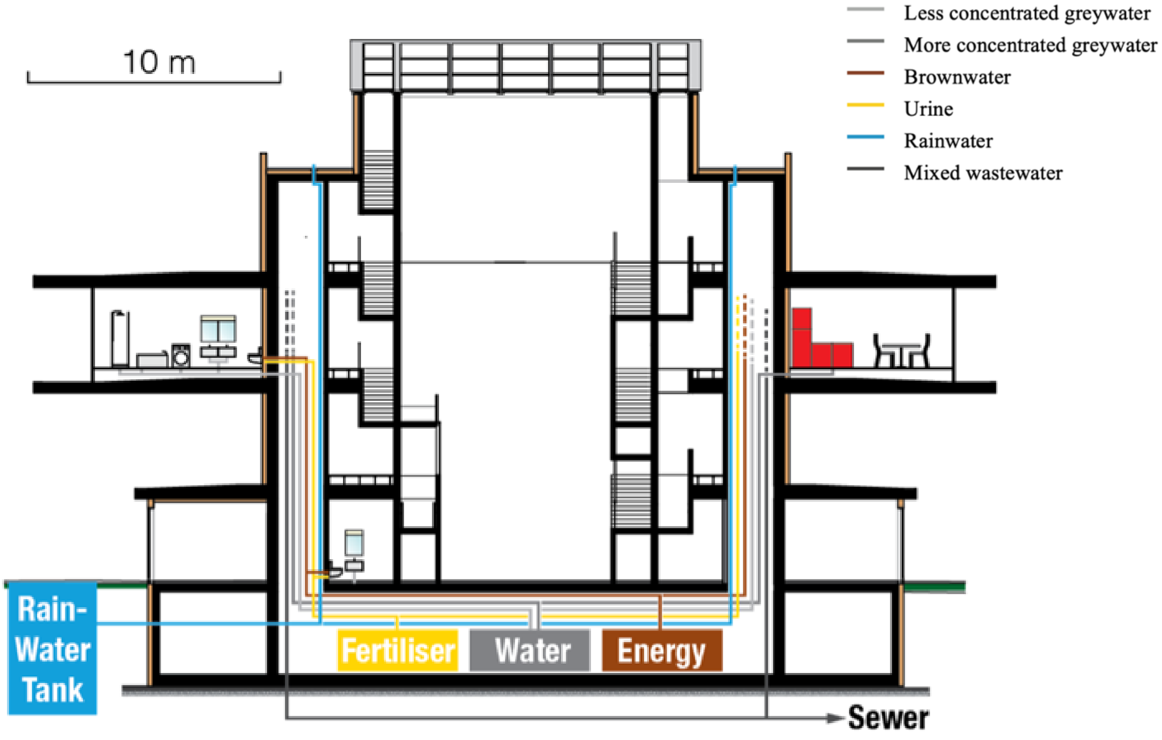

Figure 3: Cross-section of the NEST building indicating the main waste-water flows separated at the source, then collected and treated.(Etter et al., 2017)

3 First paper: electrode fabrication and optimisation

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Sensor Application

Enhancing Water Safety in Decentralized Water Reuse Systems with Low-Cost Prussian Blue Amperometric Sensors for Free Chlorine Monitoring

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Abstract— The challenge of providing sustainable and safe water services in regions lacking centralized water infrastructure can be addressed through the utilization of on-site treatment and reuse of wastewater. However, the widespread implementation of decentralized water reuse systems is currently hindered by the considerable expenses associated with remote water quality monitoring. Specifically, when using chlorination for treatment, the fabrication and maintenance costs of free chlorine sensors pose significant drawbacks to their implementation. In this study, we present an alternative solution by mitigating the sensor cost through the utilization of electrochemical sensing coupled with a cleanroom-free sensor fabrication process. We meticulously optimized the electrodeposition process to enhance sensor stability and ensure reproducibility, achieved through precise control of reactant concentrations. Our findings demonstrate the feasibility of obtaining consistent measurements in treated greywater by employing controlled Prussian Blue electrodeposition on readily available screen-printed electrodes, resulting in variation as low as 7.44% (n = 6). Furthermore, cyclic voltammetry experiments reveal a distinct peak at -0.11 V, indicating the presence of free chlorine in treated greywater samples. This characteristic is leveraged in chronoamperometric sensing, enabling robust chemical detection with a wide dynamic linearity range ($R^2 = 0.9933$) spanning from 0.06 to 6.28 ppm of free chlorine in treated greywater samples and a competitive sensitivity reaching 7.6 μA/cm^2 per ppm.

Index Terms— Decentralized water treatment and reuse, chemical sensors, free chlorine, Prussian Blue, remote monitoring.

I. INTRODUCTION

Access to safe water is of major importance for human health and well-being. Disturbingly, projections indicate that by 2030, 2.8 billion will lack access to adequately managed sanitation, and 1.6 billion people will still be deprived of safely managed drinking water [1]. The repercussions of such deficiencies are dire, as contaminated water and inadequate sanitation directly contribute to the spread of life-threatening diseases such as cholera, typhoid, and other diarrheal diseases [1], causing more than 1.4 million lives lost in 2019 [2]. Climate change additionally challenges freshwater availability and quality due to rising temperatures, altered precipitation patterns, and extreme weather events [3].

Recently, decentralized wastewater treatment and reuse systems have gained recognition as a promising approach to improving access to safe water in regions lacking centralized water and wastewater infrastructure [4]. Such systems are designed to treat wastewater from individual households or buildings to achieve a quality suitable for non-potable applications. Stringent regulations and guidelines specifying water quality requirements for various intended uses have been established [5]. In particular, ensuring the protection of human health necessitates removing pathogens present in the wastewater through adequate treatment [4].

Chlorination is a widely adopted method for disinfection, primarily due to its cost-effectiveness and efficiency in removing pathogens [6]. However, maintaining an appropriate chlorine concentration is crucial to ensure pathogen inactivation while avoiding the formation of harmful by-products [7]. Thus, the monitoring of chlorine concentrations is a critical aspect of ensuring safety in water reuse systems employing chlorine disinfection [5]. In decentralized systems lacking on-site operators who can manually analyze samples and adjust operations, online remote monitoring becomes essential to automate chlorination and issue alarms when water quality requirements are unmet [4]. Consequently, the development of chlorine sensors capable of continuously monitoring chlorine concentrations in treated water is indispensable. Nevertheless, the high cost of commercially available chlorine sensors poses a significant barrier to the implementation of decentralized water reuse systems, especially in resource-limited countries. Indeed, chlorine sensors can account for a substantial portion of the expenses associated with household-scale water reuse systems, disproportionately inflating the cost of monitoring treated water quality [8].

Several approaches have been employed for the quantification of chlorine concentrations, including colorimetric, optical, voltammetric, and amperometric methods [7]. However, optical techniques necessitate the use of reactants, impeding real-time monitoring and requiring extensive handling procedures [9]. Similarly, non-electroanalytical systems rely on costly selective membranes, limiting their feasibility for low-cost applications. To tackle the issue of expensive chlorine sensor techniques, alternatives such as chemo resistive sensors that eliminate the need for reference electrodes [10], [11] or amperometric sensors that offer enhanced sensitivity [12] have been proposed to enable more economical electronic readouts. Nonetheless, challenges persist concerning the stability of such systems and sensing materials in aqueous environments, as well as the accuracy and reliability of measurements [13]. To address these

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challenges, previous studies have already demonstrated the reliable and selective capabilities of Prussian Blue-coated screen-printed carbon electrodes (SPCEs) in detecting free chlorine in buffer solutions, with sensitivity up to 16.2 μA/cm^2 per ppm [14]. Furthermore, the utilization of specific surfactants to enhance the electrodeposition process of Prussian Blue allows a better deposition and durability. [15], [16]. However, the application of Prussian Blue-coated electrodes in diverse water matrices, particularly in the context of wastewater treatment plants, and the assessment of interelectrode repeatability in such complex water matrices remain unexplored. Therefore, here, we introduce an enhanced electrode fabrication process, optimizing the sensitivity and stability of the measurement by examining various reactant concentrations and controlling the homogeneity and concentration of the solution during the electrodeposition process. Initially, the performance of these sensors was evaluated in phosphate-buffered saline (PBS), followed by their validation in treated natural greywater originating from showers, washing machines, and sinks, excluding toilet flush water.

II. METHODOLOGY

A. Chemicals, Reagents and Treated Greywater

Sodium hypochlorite (NaOCl, 4.00–4.99%), iron(III)chloride ($FeCl_3$, ≥ 97%), potassium hexacyanoferrate(III) ($K_3[Fe(CN)_6]$, ≥ 99.0%), benzethonium chloride ($C_{27}H_{42}ClNO_2$, ≥ 97%), potassium chloride (KCl, ≥99%), hydrochloric acid (HCl, 1 mol/L, reagent grade), and PBS (1x) were purchased from Sigma-Aldrich (MilliporeSigma, Switzerland). Two 4 L samples of treated greywater were received from an implemented greywater reuse system at Eawag Water-Hub (Dübendorf, Switzerland) with 5 days of an interval to evaluate the impact of variations of treated greywater matrix on the measurement and stored at 4°C. Total organic carbon (TOC), NO_3^- (N weight) and PO_4-(P weight) were respectively 1.06 mg/L, 10.1 mg/L and 0.30 mg/L for sample 1 and 1.44 mg/L, 10.6 mg/L and 0.25 mg/L for sample 2.

B. Instrumentation

Electrochemical measurements were conducted using Autolab PGSTAT302N potentiostat (Metrohm, Switzerland). Data were analyzed using Matlab (MathWorks, USA) and Origin (OriginLab, USA) software. The SPCEs used were DRP-110 models purchased from DropSens (Metrohm, Switzerland), and they have a conventional three-electrode configuration. The working electrode, with a disc-shaped design measuring 4 mm in diameter, and the counter-electrode were fabricated using carbon inks. The pseudo-reference electrode was constructed using silver. Raman spectroscopy was performed using a confocal backscattered microscope with a 514 nm laser with 10 mW of laser power measured at the sample location (MonoVista, Germany). Digital microscopy was conducted using the KH-8700 microscope with the MXG-2500REZ optic (Hirox, Japan).

C. Electrodeposition and Measurement

To ensure precise control over the electrodeposition process, concentrated solutions were prepared in advance. A 150 mmol/L $FeCl_3$ solution, 150 mmol/L $K_3[Fe(CN)_6]$, 200 mmol/L benzethonium chloride, and 1 mol/L KCl were used. These solutions were then diluted in demineralized water (18.2 MΩ·cm, type 1 ultra-pure water unit, Siemens, Germany) to prepare the electrodeposition solutions. The standard electrodeposition solution contained 1.5 mmol/L $FeCl_3$, 1.5 mmol/L $K_3[Fe(CN)_6]$, and 2 mmol/L surfactant (benzethonium chloride) using a buffer solution of 0.02 mol/L HCl and 0.1 mol/L KCl. Different multiples of electrodeposition solution concentrations were utilized for optimization. A total volume of 10 mL of electrodeposition solution was prepared, the electrode immersed in it, and the solution stirred continuously to ensure homogeneity of reactant concentration. The electrodeposition process was carried out by cycling between -0.6 and 1 V at a scan rate of 0.1 V/s.

Free chlorine concentration was determined using a portable spectrophotometer (DR 1900, Hach, Loveland, USA) with corresponding test kits (DPD, 0–2 mg/L free chlorine, Hach, Loveland, USA). Cyclic voltammetry experiments were conducted in PBS and treated greywater to find the oxidation and reduction potentials and assess the impact of the water matrix on the voltammetric response. The potential range used was -0.4 V to 0.6 V at a scan rate of 0.01 V/s for PBS and -0.8 to 1 V at a scan rate of 0.01 V/s for treated greywater. Two scenarios were considered: one without any free chlorine and the other with 50 ppm of free chlorine. Amperometry was performed in PBS, and treated greywater to calibrate the sensors using a potential of -0.11 V. The experiments were carried out in 100 mL beakers under stirring conditions. A 600 mL beaker was employed for the calibration curve, where the large volume allowed for more 3,3'-Diaminobenzidine (DPD) reference measurements. Free chlorine was gradually added to the sodium hypochlorite solution. The pH of both PBS and treated greywater was maintained at 5.7 to keep the free chlorine in a more active HOCl form.

III. RESULTS AND DISCUSSION

A. Formation of Prussian Blue on Carbone Electrodes

The Raman spectrum (Fig. 1) confirmed the successful electrodeposition of Prussian Blue on the surface of carbon electrodes, as evidenced by Fe-C stretching vibrations 598 cm^{-1} and its prominent peak observed at 2154 cm^{-1} corresponded to the $1A_g$ mode of C-N stretching vibration and the vibrational state of [Fe(II), Fe(III)]. The 2154 cm^{-1} peak exhibited a first shoulder at around 2120 cm^{-1}, indicative of CN^- presence, and a second shoulder at 2090 cm^{-1}, corresponding to the E_g mode of C-N stretching vibrations in the [Fe(II), Fe(III)] state [17]. Peaks observed at 1580 cm^{-1} and 1350 cm^{-1} were attributed to the sp^2- and sp^3-type carbon bonding on the bare carbon working electrodes [18]. A bare carbon and Prussian Blue-coated working electrode were compared with a digital optical microscope (Fig. 1, inset). Blue color, texture change, and particle clusters-like apparitions confirmed the homogeneous deposition of Prussian Blue [19].

B. Amperometric Free Chlorine Sensing

Fig. 2. illustrates the I-V curve induced from cyclic voltammetry from chlorine concentrations of 0 and 50 ppm in water and treated greywater samples. In PBS, adding chlorine led to an oxidation peak at 0.08 V and a reduction peak at -0.11V (Fig. 2a).

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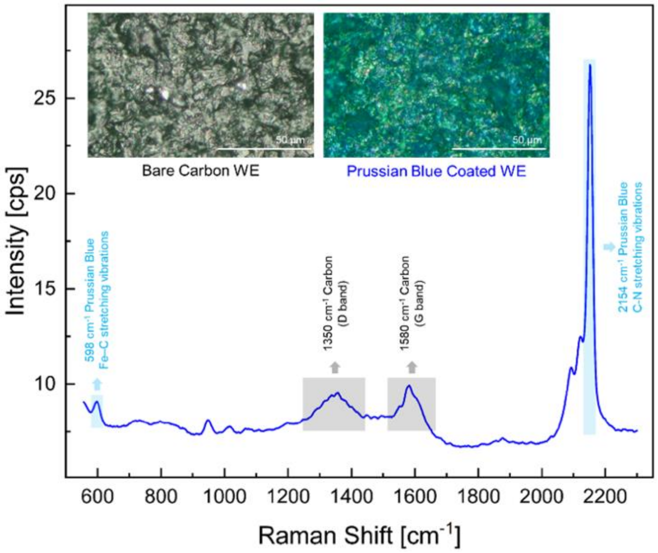

Fig. 1: Raman spectrum of the fabricated sensor showing the development of Prussian Blue on carbon substrate and digital microscope image with 3500x magnification from the surface of the bare and functionalized electrodes.

In treated greywater, the cyclic voltammetry presented much more crowded peaks due to numerous chemical species present in the treated greywater (Fig. 2b). However, analysis of the second derivative of the current showed the presence of the same peak caused by the addition of chlorine (Fig. 2c). Therefore, the potential of -0.11 V can be used for amperometry in treated greywater samples. Fig. 3 presents the calibration curve obtained in amperometric free chlorine analysis in treated greywater samples with this potential. To assess the sensor performance, we measured concentrations exceeding the typical range of free chlorine for greywater disinfection. Remarkably, we observed a high level of linearity in both treated greywaters ($R^2 = 0.9932$) and PBS ($R^2 = 0.9920$) on the tested range, from 0 to 6.28 ppm, indicating a strong linear correlation between the sensor current output and free chlorine concentration as well as the selectivity of such chemical sensing. In addition, the computed sensitivity was determined to be 0.935 ppm/µA, with a theoretical limit of detection (LOD) of 0.407 ppm.

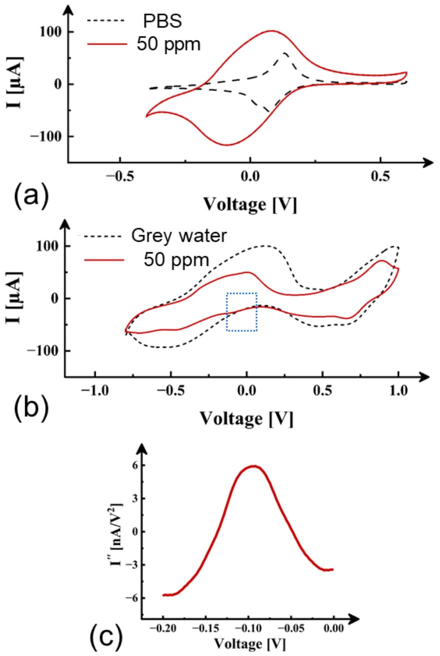

Fig. 2: Cyclic voltammetry in (a) PBS (b) treated greywater for 0 and 50 ppm free chlorine and (c) second derivative of (b) at 50 ppm, which clearly shows the reduction peak of free chlorine at -0.11 V.

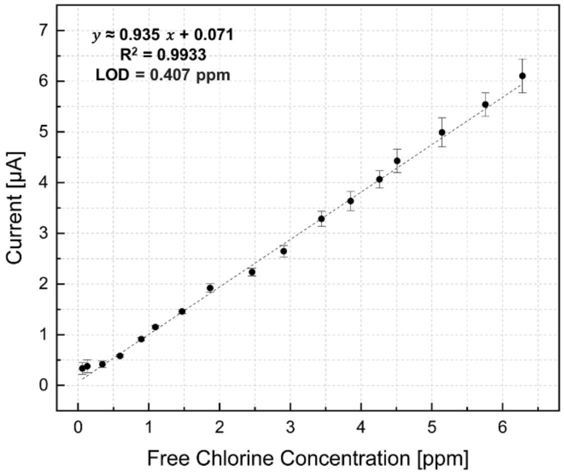

Fig. 3: Calibration curve in treated greywater of free chlorine amperometric sensing. Error bars are composed of mean ± STD (n=3).

C. Reproducibility Enhancement

The potential impact of Prussian Blue membrane thickening on sensitivity is reportedly due to diffusion-dominated processes [15]. Reproducibility is especially important for low-cost applications as minimal calibration should be required. After achieving almost perfect linearity (Fig 3.), we conducted multiple repetitions of the process using various multiples ranging from 0.125x to 2x (Fig. 4) to determine the optimal reactant concentration for electrodeposition, which will result in the deposition of different thicknesses. As anticipated, a decrease in reactant concentration led to increased sensitivity, which is evident in 1 ppm free chlorine measurement with 0.5x to 2x in Fig. 4. However, we found out that the measurements in the sub 2 ppm levels exhibited high instability with a lower concentration of the electrodeposited standard solution. Notably, the standard deviation for three consecutive measurements with three different fabricated electrodes (but with identical processes) at 1 ppm significantly increased (172%) when electrodeposition was performed with reactant concentrations below 0.5x of the standard concentration (Fig. 4). This has clear consequences in reducing measurement stability. Therefore, an optimum trade-off between stability, sensitivity and LOD should be achieved with Prussian Blue-based chemical sensing. Here, an optimal trade-off was achieved with a concentration of 0.5x of the standard, corresponding to 750 µmol/l $FeCl_3$, 750 µmol/l $K_3[Fe(CN)_6]$, and 1 mmol/l benzethonium chloride. Furthermore, three SPCE were coated using the optimized electrodeposition process to evaluate inter-electrode reproducibility. Each electrode was tested in two greywater samples, demonstrating good reproducibility and sensitivity with a mean of 0.955 µA/ppm and a standard deviation of 71.1 nA/ppm (Fig. 5).

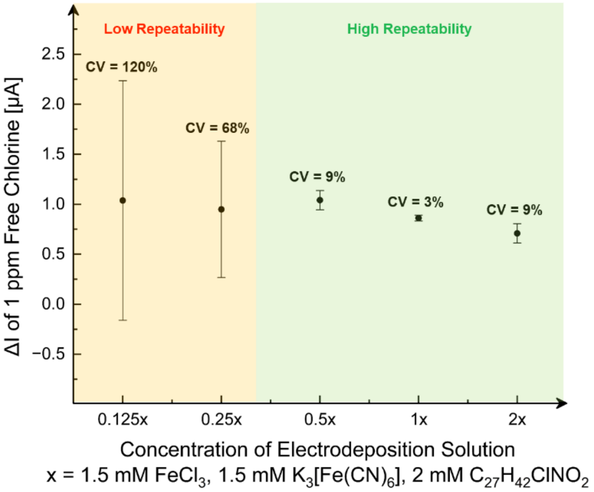

Fig. 4. Measure of 1 ppm free chlorine sample using 3 electrodes for each concentration of electrodeposition solution.

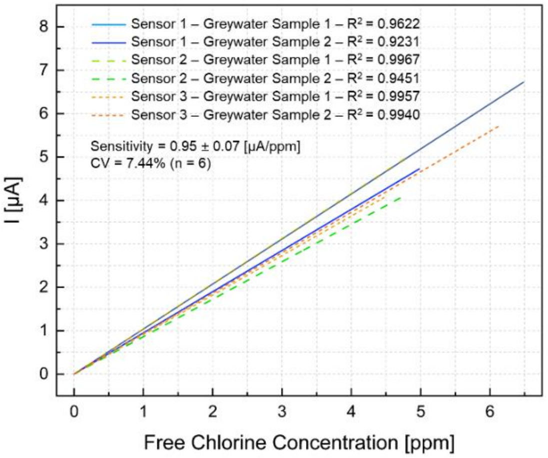

Fig. 5. Calibration curves of different measurements with optimized formulation with different electrodes and greywater samples.

Considering the electrode surface area of 0.1256 cm^2, the sensitivity obtained is 7.6 $\mu A/cm^2$ per ppm, comparable to state-of-art electrochemical free chlorine sensors [13].

IV. CONCLUSION

This study presents an innovative approach using cost-effective electrochemical sensors coated with Prussian Blue for the monitoring of free chlorine in decentralized water reuse systems. The optimized fabrication process ensures stable and highly sensitive detection capabilities, achieving low detection limits in treated greywater for the first time in literature. The sensors exhibit well-defined oxidation and reduction peaks in cyclic voltammetry, while calibration experiments establish a robust linear relationship between the sensor output and free chlorine concentration. The next phase involves conducting continuous testing within an implemented decentralized greywater reuse system to evaluate the long-term sensitivity and reliability of the sensors. By eliminating the necessity for expensive selective membranes, these affordable electrodes hold promise as a practical solution for remote water quality monitoring, particularly in regions with limited resources.

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4 Second paper: real conditions electrode testing

Testing Low-Cost Prussian Blue Amperometric Sensors for Free Chlorine Monitoring in Decentralized Water Reuse Systems

1. Introduction

Access to sufficient quantities of safe water is essential for human health and well-being. While the most fundamental requirement for clean water is for drinking, the bulk of residential water usage pertains to other activities such as personal hygiene, laundry, irrigation, and, where water-based sanitation infrastructure exists, toilet flushing (DeOreo et al., 2016). Unfortunately, freshwater to meet this water demand is becoming increasingly scarce. A recent study estimated that two thirds of the global population are exposed to severe water scarcity for at least one month every year (Mekonnen & Hoekstra, 2016). Freshwater scarcity is expected to further increase in many regions in the future, as a consequence of changes in the global climate (Gosling & Arnell, 2016), rapid population growth and urbanization (Flörke et al., 2018), and widespread environmental pollution (Liu et al., 2016). Consequently, we will need to reconsider for what applications we use freshwater.

In recent years, water reuse has gained increasing attention as a reliable alternative water source (Salgot & Folch, 2018). In particular, decentralized water reuse has been proposed as a flexible approach for supplying reclaimed water without the need for the large-scale infrastructure from centralized water reuse schemes (Reynaert et al., 2021). These decentralized systems are designed to treat locally-collected wastewater at the scale of a household or a building to a standard enabling reuse for non-potable purposes. Decentralized systems have been designed to treat both, separately collected greywater with low faecal contamination, or mixed wastewater that additionally contains toilet flush water (Reynaert et al., 2020). In order to ensure user safety, it is essential that pathogens be reliably removed from the wastewater (Sharvelle et al., 2017), making some form of disinfection imperative.

Globally, chlorination is the most widely-used disinfection method, due to its broad-spectrum efficacy, low cost and formation of a residual (Ikehata et al., 2018). Unfortunately, recent studies have demonstrated that undetected failures of the chlorination in decentralized systems can significantly increase the risk of water reuse on human health (Schoen et al., 2018). At the same time, it is also important to avoid adding excessive amounts of chlorine to the water, to reduce the formation of potentially toxic by-products (Sedlak & von Gunten, 2011). Thus, the online monitoring of the chlorination efficacy, for instance through free chlorine concentrations, is a critical aspect for ensuring safety in water reuse systems employing chlorine disinfection, in order to automate chlorination (Reynaert, Gretener, et al., 2023) and issue alarms when water quality requirements are not met (Reynaert, Steiner, et al., 2023).

Unfortunately, the costs of commercially available water quality sensors tend to be prohibitively high (Banna et al., 2014), especially for implementation in decentralized water reuse systems that do not benefit of economies of scale, i.e., where one sensor is needed independently of the quantity of water produced. To allows economically feasible water reuse systems, low-cost sensors are needed to assess water quality.

Various techniques have been utilized to measure chlorine concentrations, including methods such as optical (colorimetry being the most used), voltammetry, and amperometry (Kruse, 2018). Yet, optical methods require the utilization of reactants, which hinders the ability to monitor in real-time and demands complicated handling procedures (Golparvar et al., 2023). Similarly, systems which do not rely on advanced electroanalytical methods need costly selective membranes, making them ill-suited for low-cost applications (Williams, 2005). To tackle these issues, more economical solutions have been proposed such as chemoresistive sensors to eliminate the need for reference electrodes (Hoque et al., 2017; Hsu et al., 2014), or amperometric sensors optimized for maximum sensitivity, allowing for simpler electronic signal readout. (Olivé-Monllau et al., 2010). Challenges persist in the development of stable sensing systems and materials that can accurately and reliably measure parameters in aqueous environments (Heikenfeld et al., 2018).

To address the challenges mentioned, previous studies have already demonstrated the reliable and selective capabilities of Prussian Blue-coated screen-printed carbon electrodes (SPCEs) in detecting free chlorine in buffer solutions (Salazar et al., 2015). Additionally, the utilization of specific surfactants has been found to enhance the electrodeposition process of Prussian Blue, resulting in better deposition and durability of the sensor (Salazar et al., 2015; Salazar et al., 2012).

A major limitation of these studies is that they typically evaluate these sensors in laboratory conditions, often with buffered solutions to maintain optimal pH for the detection of free chlorine (Salazar et al., 2015). Some studies have also tested low-cost chlorine sensors for drinking water production, providing promising results in more variable water matrices (Zubiarrain-Laserna et al., 2022).

However, these water matrices are not representative of the more complex reclaimed water matrices, which typically contains higher concentration of organics (Nguyen et al., 2018), and a wide range of other constituents, including varying concentrations of chloride, nitrate, nitrites, or phosphate ions (Zhao et al., 2006). Many of these compounds have been shown to cause interferences with the chlorine measurement (Alam et al., 2021). As an additional challenge, the focus of these studies has been on showing the accuracy of the chlorine sensors over short periods of times (a couple of hours at most) (Pan et al., 2015; Salazar et al., 2015). However, to be useful for the implementation in decentralized water reuse systems, these sensors need to continuously work over longer periods of time. There is thus need for low-cost chlorine sensor that have been demonstrated to reliably work for the continuous monitoring of chlorine concentration in realistic reclaimed water matrices.

When miniaturizing sensors for lower cost, there is a trade-off between the sensor material and fabrication cost and the cost of required electronics (Aliofkhazraei & Ali, 2014), due to the increased complexity required for measuring smaller electric currents. In a previous paper, we optimized a Prussian blue-coated SPCE-based free chlorine sensor for maximum current, in order to allow for the use of off-the-shelf electronics. (Herold et al., 2023) We demonstrated that, in laboratory conditions, this sensor exhibited an excellent linearity and sensitivity both in PBS ($R^2 = 0.9920$) and treated greywater ($R^2 = 0.9933$) from 0 to 6 ppm. In the present paper, we test the sensor performance under continuous operation in real-life water reuse systems, with both treated greywater and treated household wastewater in order to assess the accuracy and reliability.

2. Methodology:

2.1. Prussian Blue amperometric sensing

The detection of free chlorine using Prussian Blue-coated SPCE relies on single potential amperometry, a form of electrochemical sensing. Single potential amperometry quantifies analyte concentrations by measuring the current generated through a redox reaction of analyte at the electrode surface. The relationship between analyte concentration and current follows Fick's law of diffusion, predicting a direct proportionality when the system reaches equilibrium. (Carrara, 2012). Prussian Blue (iron^{III} hexacyanoferrate^{II}) demonstrates remarkable electrocatalytic activity and redox behaviour, making it an excellent candidate for amperometric sensing applications. Its structure, featuring $Fe^{II}–C–N–Fe^{III}$ sequences forming a cubic framework, allows reversible redox reactions at the electrode surface(Yagi et al., 2014). The Fe(III) centres within the crystal structure can be reduced to Fe(II), and oxidized back to Fe(III) (Yagi et al., 2014). This distinctive property allows the detection of hypochlorous acid (HOCl), one species of free chlorine, through the reduction of HOCl when suitable potential applied (Salazar et al., 2015). Notably, the low redox potential of Prussian Blue further enhances its catalytic performance in electrochemical systems (Itaya et al., 1984). It's structural stability and low toxicity assure their suitability for water analysis (Estelrich & Busquets, 2021).

2.2. Free chlorine equilibrium and compensated raw value

The measured current of the reaction I_{raw} is proportional to the concentration of only HOCl. The speciation between hypochlorite (OCL-) and hypochlorous acid is a function of the pH and the temperature of the solution (Gray, 2014). The free chlorine concentration is retrieved with the following formula.

$$C_{out} = m * I_{eq} + c, I_{eq} = \frac{I_{raw}}{\alpha}$$

, where

$$\alpha = \frac{10^{-pH}}{10^{-pH} + 10^{-pKa}}, \quad pKa = -0.009 * T + 7.765 \text{ (Gray, 2014)}$$

and m and c are calibration variables.

2.3. Electrode fabrication

All chemicals were bought from Sigma-Aldrich (MilliporeSigma, Switzerland). To ensure precise control over the electrodeposition process, concentrated solutions were prepared in advance. 150 mmol/L $FeCl_3$ (from $FeCl_3$≥ 97%), 150 mmol/L $K_3[Fe(CN)_6]$ (from $K_3[Fe(CN)_6]$, ≥ 99.0%), 200 mmol/L benzethonium chloride (from $C_{27}H_{42}ClNO_2$, ≥ 97%) and 1 mol/L KCl (from KCl, ≥99%) solutions were prepared. These solutions were then diluted in demineralized water (18.2 MΩ·cm, type 1 ultra-pure water unit, Siemens, Germany) before starting the electrodeposition process. In accordance with the optimised process we presented in our previous paper (Herold et al., 2023), these were diluted in a buffer solution of 0.02 mol/L HCl (from HCl, 1 mol/L, reagent grade) and 0.1 mol/L KCl to obtain concentration of 750 µmol/l $FeCl_3$, 750 µmol/l $K_3[Fe(CN)_6]$, and 1 mmol/l benzethonium chloride. A total volume of 10 mL of electrodeposition solution was prepared, the electrode immerged in it, and the solution stirred continuously to ensure homogeneity of reactant concentration. The electrodeposition process was carried out by cycling the electrode potential (cycling voltammetry process) between -0.6 and 1 V at a scan rate of 0.1 V/s. The substrate electrode were DRP-110 models purchased from DropSens (Metrohm, Switzerland). they have a conventional three-electrode configuration with a 4mm diameter disc-shaped working electrode. The cyclic voltammetry was done using Autolab PGSTAT302N potentiostat (Metrohm, Switzerland).

2.4. Sensor characterization and testing

Previous research (Salazar et al., 2015), including our own (Herold et al., 2023) demonstrated high repeatability of the fabrication process. Characterization was then focused in verifying that the electrodeposition curves were identical for each electrode, to confirm an identical deposition process, since that electrodeposition current allows a good estimation of surface coverage. (Salazar et al., 2012)
For wear and tear characterization, Electrodes were observed with digital optical microscope KH-8700 (Hirox, Japan) and lens MXG-2500REZ (Hirox, Japan).

2.4.1. Test setup

To evaluate the Prussian Blue coated electrodes in different types of water matrices, we tested its performance it in (A) treated greywater, and (B) treated municipal wastewater.

2.4.2. Greywater and wastewater treatment

The greywater treatment unit was located in the Water Hub at NEST, an experimental building in which source-separated wastewater streams are treated separately (Etter et al., 2016). The greywater originates from a fitness unit, flats, and public bathrooms. The aim is to produce treated water that is suitable for toilet flushing, but to allow for the testing of different technologies without endangering toilet user safety, reuse is currently not implemented. The greywater is treated in three steps prior to chlorination: (1) a moving bed membrane bioreactor (MBBR) is followed by (2) ultrafiltration, and (3) a biological activated carbon filter (Figure 1.A).

The MBBR and ultrafiltration unit are part of a commercial greywater recycling system (Intewa GmbH, Aachen, Germany), and the biological activated carbon filter has been described in Hess and Morgenroth (2021).

For the chlorination, the treated greywater was collected in a storage tank, from where 39.35 ± 0.06 mL/min were continuously pumped with a Beta® BT4a (ProMinent GmbH, Germany) solenoid dosing pump into a chlorination tank (50 L, Figure 1.C). In the chlorination tank, a concentrated sodium hypochlorite solution (45.3 - 51.6 mg/L) was continuously added to the water also by means of a solenoid dosing pump (same model). A stirrer operated at 300 rpm ensured mixing in the tank. The chlorinated water exited the chlorination tank through an overflow. The chlorination unit was operated with the aim of reaching ~1 ppm of free chlorine, although the concentrations varied due to variations of the composition of the treated water quality and manual adjustments to the dosing in order to test the sensor on a range wider than the natural variations.

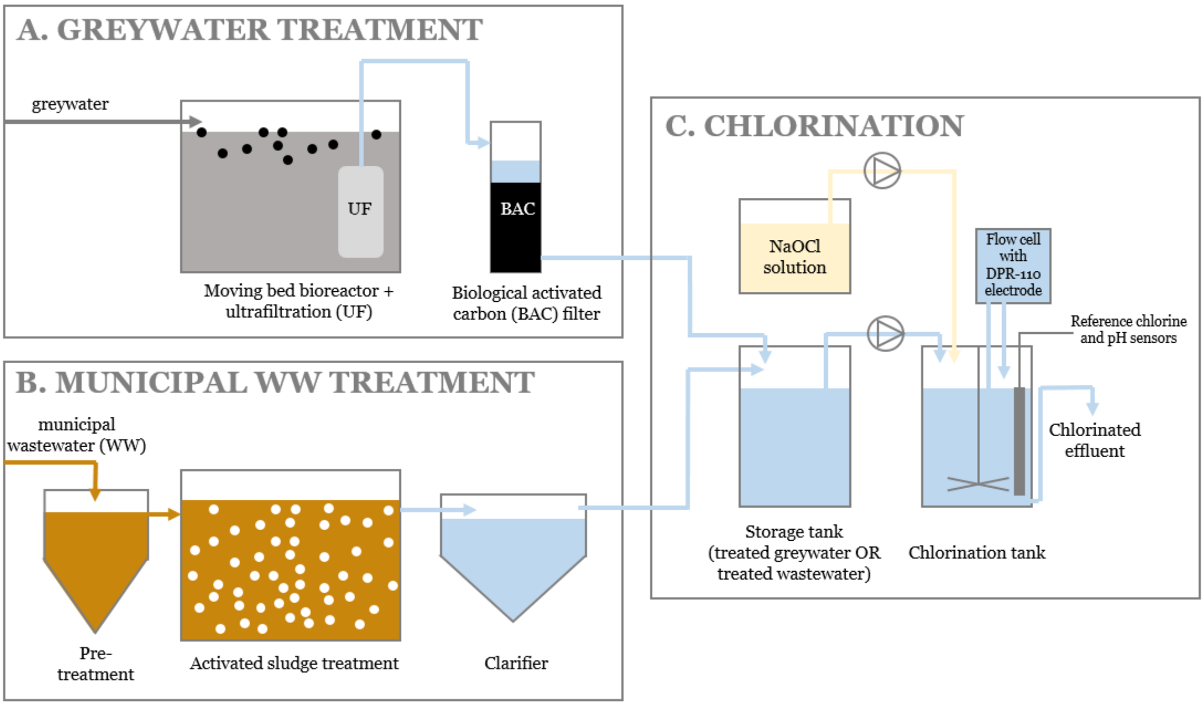

Figure 1. Simplified representation of the greywater (A) and wastewater (B) treatment units, along with the chlorination setup (C).

For the experiments with municipal wastewater, we collected effluent from a small wastewater treatment plant located on Eawag campus in Dübendorf. Treatment included primary clarification, activated sludge treatment, and secondary clarification (Figure 1.B). The water was then chlorinated in the same setup as described above, where the effluent storage tank was filled with treated municipal wastewater instead of treated greywater.

2.4.3. Water quality analyses

There are multiple potential interfering ions for chlorine measurement with electrochemical sensors, including nitrite, nitrate, sulfate, and chloride (Alam et al., 2021). To characterize the test water quality, these ions were measured in the treated water (before chlorination). Samples were filtered at 0.45 µm (Nanocolor Chromafil membrane filter GF/PET 0.45 µm, Macherey Nagel, Düren, Germany) for sample conservation and stored at 4°C before analysis by means of ion chromatography (Metrohm 881, Herisau, Switzerland).

Note: While the composition of the treated greywater varied during the experiments, as the water in the storage tank was continuously replaced, the composition of the treated municipal wastewater was not subject to such variations, as the storage tank was filled in batches.

2.4.4. Implementation of the Prussian Blue coated free chlorine sensor

Water from the chlorination tank was constantly recirculated through a DropSens FLWCL methacrylate wall-jet flow cell (Metrohm, Switzerland) at a rate of 26.78 mL/min. The circulation time through the deviation circuit is 64 seconds of which 38 seconds were spent from the chlorination tank to the sensor. The sensor was connected to a Autolab PGSTAT302N potentiostat (Metrohm, Switzerland). The potentiostat was set to a potential of -0.12[V] between working and reference electrode, which we determined to be the most selective reduction potential for HOCl free chlorine on these electrodes (Herold et al., 2023). Current was measured at a frequency of 10Hz.

2.4.5. Reference chlorine measurements

Reference chlorine measurements were done through a commercially available free chlorine sensor (CCS51D, Endress+Hauser, Reinach, Switzerland). The reference free chlorine sensor is based on a closed amperometric 2-electrode measuring cell with PVDF membrane (Endress+Hauser, 2018). HOCl diffuses through the PVDF membrane and is reduced to chloride ions (Cl^-) at the gold cathode. At the silver anode, silver is oxidized to silver chloride. The resulting electrical current is proportional to the concentration of HOCl. The HOCl concentration is transformed into a free chlorine concentration based on a pH compensation (pH sensor CPS16E, Endress+Hauser, Reinach, Switzerland). The commercial free chlorine and pH sensors were placed directly in the chlorination tank, measurements were stored each 10s. The Endress+Hauser reference chlorine sensor was calibrated using a spectrophotometer (DR 3800 VIS, Hach, Loveland, USA) with corresponding DPD test kits (0–2 mg/L free chlorine, Hach, Loveland, USA).

3. Results and discussion

Understanding the physicochemical quality of the treated water is important to assess the performance of the Prussian Blue chlorine sensor. The pH will determine the fraction of free chlorine present as HOCl, while the concentration of ions can provide information on potential interferences. During the experiment, an average pH of 8.52 was measured in treated greywater, as well as an average temperature of 24.22°C, which resulting in a dissociation coefficient α between 0.10 and 0.29 with an average of 0.17 (Figure 2). Treated municipal greywater had a higher pH, with an average of 8.84 (Figure 3). The higher temperature of, in average, 26.70°C, was due to the filling of the tank by batches and the temperature of NEST building at time of measurement. Therefore, the dissociation coefficient was almost three times smaller, in average at 0.06, which minimum at 0.05 and maximum at 0.09.

3.1. Physicochemical water quality and dissociation coefficient

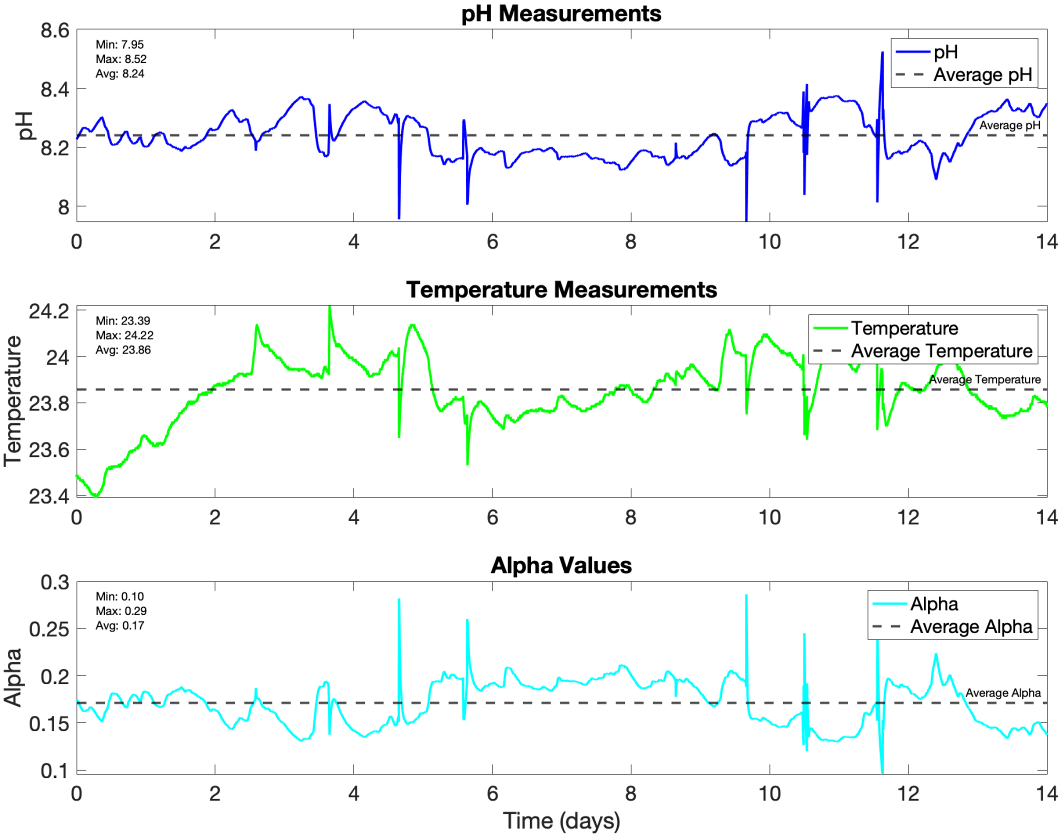

Figure 2: Temperature, pH, and dissociation coefficient during experiment in greywater

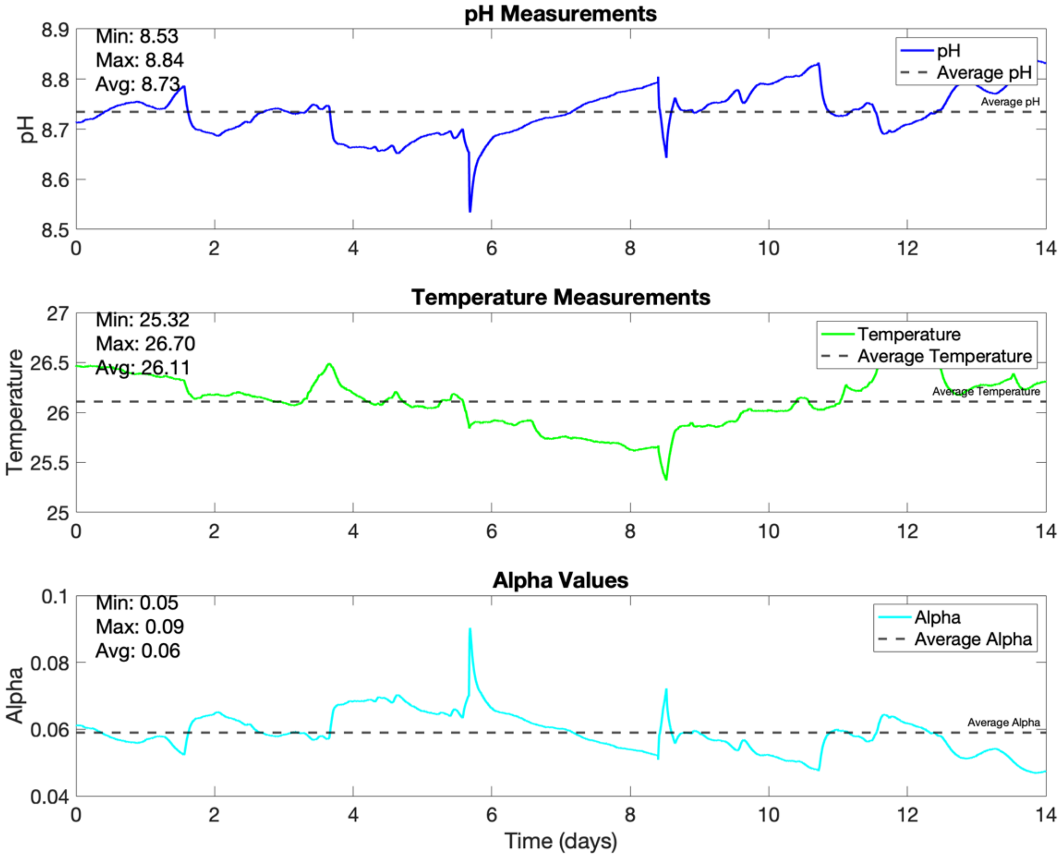

Figure 3: pH, temperature, and dissociation coefficient in treated municipal wastewater during the experiments.

Parameter	Unit	Treated greywater	Treated municipal wastewater
Dissolved organic carbon	$\mathrm{mg_C/L}$	1.4	13.3
Chloride	mg/L	152	121
Nitrite	$\mathrm{mg_N/L}$	<0.15	<0.15
Nitrate	$\mathrm{mg_N/L}$	17.82	7.38
Phosphate	$\mathrm{mg_P/L}$	1.62	1.65
Sulfate	mg/L	n/a	35.6
Ammonium	$\mathrm{mg_N/L}$	0.15	0.19

Table 1: Concentration of ions and other components in both used water matrices

Water quality measurement before chlorination shows similar water matrices between treated greywater and treated municipal wastewater (Table 1), containing non negligeable concentration of potential disturbing ions, as Chloride, Nitrate and Phosphate. It has to be noted that there are still some differences as concentration of dissolved organic carbon is one order of magnitude higher in treated municipal wastewater and nitrate concentration more than twice higher in greywater.

3.2. Sensitivity decrease

The stability of sensitivity is necessary to achieve long-term linearity between the measured electrical current and the HOCl concentration. Our results show a considerable decrease of the sensitivity before a stabilisation after 28 to 78 hours (Figure 4).

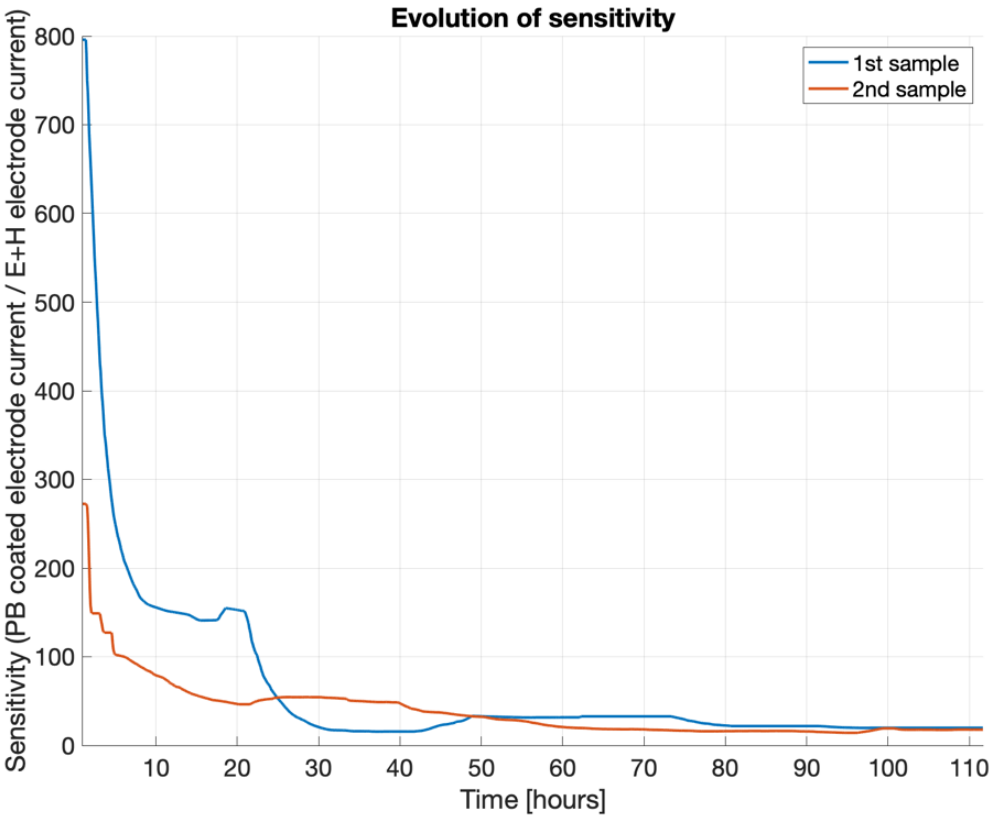

Figure 4: Sensitivity over 110 hours, samples with observed fast and slow stabilization.

After 83 hours, average sensitivity over 4 samples is 1.9275x the sensitivity of reference E+H electrodes, standard deviation is 0.2275x. After 111 hours, sensitivity is 1.925x thus of reference E+H electrodes (std=0.12556x). (Figure 5)

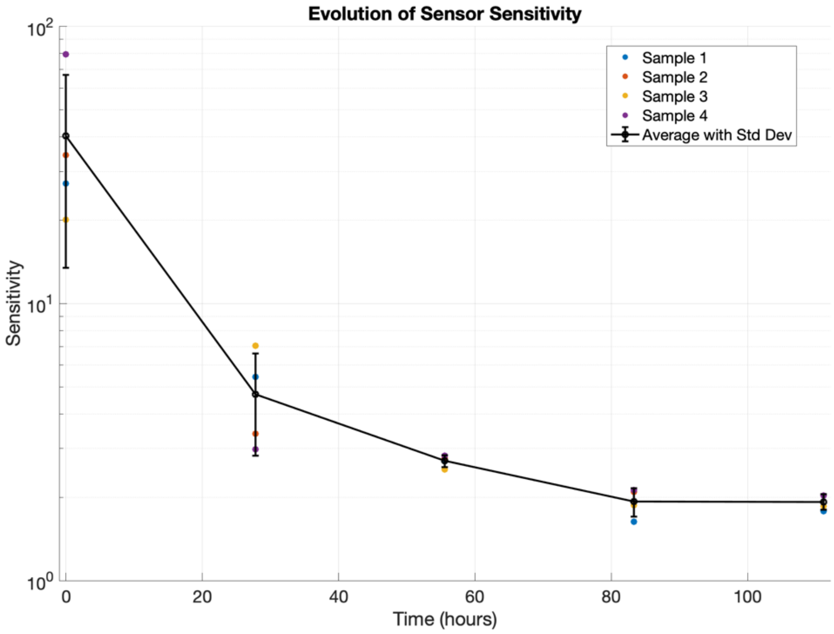

Figure 5: Evolution of sensor sensitivity (raw current of Prussian Blue electrodes, over raw current of E+H Electrodes), over 111 hours, 4 measurements points on 4 samples

3.3. Linearity and reproducibility

After the maximal stabilisation period of 78h, compensated raw current I_{eq} was recorded for 24 hours and compared to the chlorine concentration measured with the Endress + Hauser reference sensor, C_{out}. Results proved the sensor to be highly linear, with R^2 values systematically over 0.95 and reaching up to 0.9855. (Figure 6).

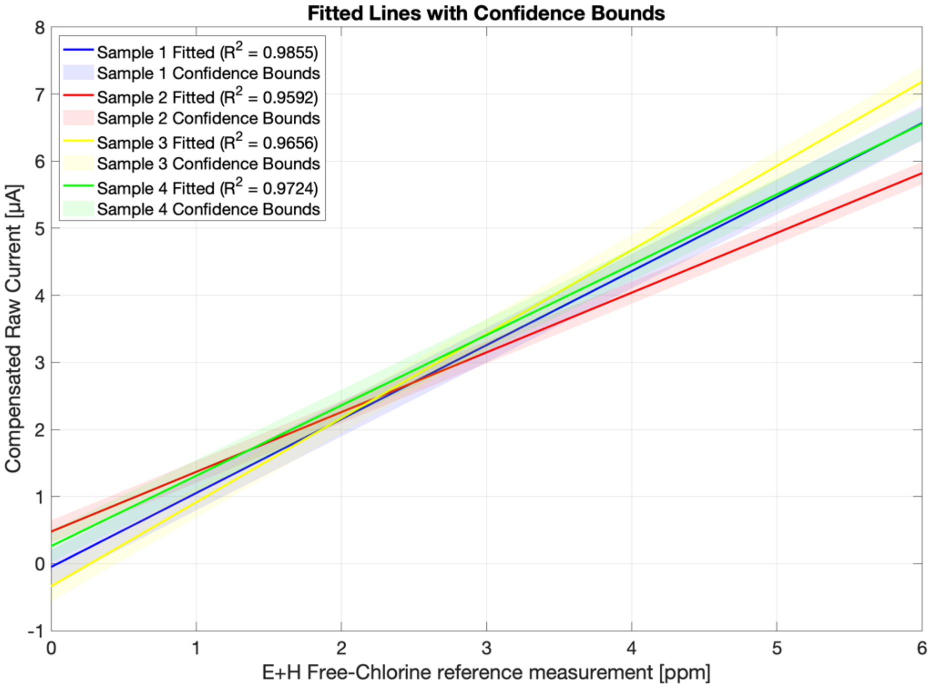

Figure 6: Calibration curve of Prussian Blue sensor w.r.t. E+H reference measurement

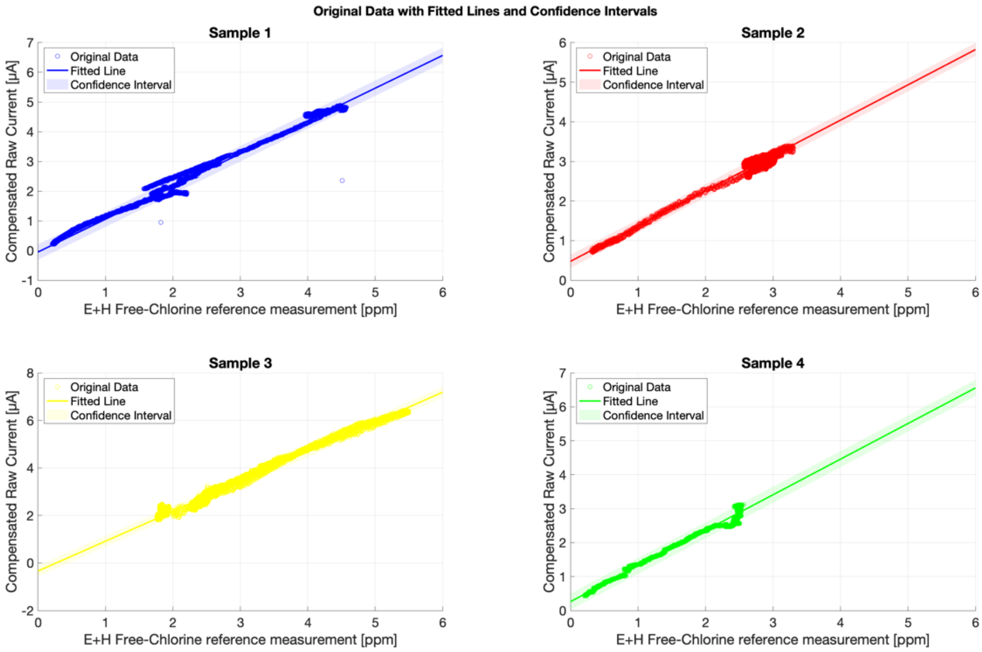

Figure 7: Data, fit line, and 95% confidence interval for 4 samples

Good reproducibility was achieved with an average slope on 4 samples of 1.0739 $\frac{\mu A}{ppm}$, a standard deviation of the slope of 0.1499 $\frac{\mu A}{ppm}$, which correspond to a surface sensitivity of 8.5461 $\frac{\mu A}{ppm*cm^2}$ and a standard deviation of surface sensitivity of 1.1925 $\frac{\mu A}{ppm*cm^2}$. If they number seems better that those obtained in our previous work with new electrodes (Herold et al., 2023), they shouldn't be compared as here, flow conditions where optimized. Moreover, due to the very low concentration of HOCl with respect to total free chlorine at the high pH values present in these water matrices, we are measuring very low HOCl concentration, and are in a totally new range, unexplored in our previous study. The α coefficient between 0.05 and 0.29 (see section 3.1) means that we measured a raw current 3.3 to 20x smaller than it would have been with the same free chlorine concentration at a controlled pH of 5.2 similar to the laboratory conditions.

3.4. Signal processing and noise values

Analysis of the data over 72h was performed with Matlab (Mathworks, USA). We applied a moving average with window size of 10 s (100 measurements point) and a median filter of order 300 to smooth peaks with anormal deviation. The difference between the raw and the processed signal was considered as noise. Fitting with an iterative Expectation-Maximization (EM) algorithm determined that the noise was composed of two Gaussians, both with negligeable mean and standard deviations of 12.9 nA and 28.4 nA, respectively. (Figure 8).

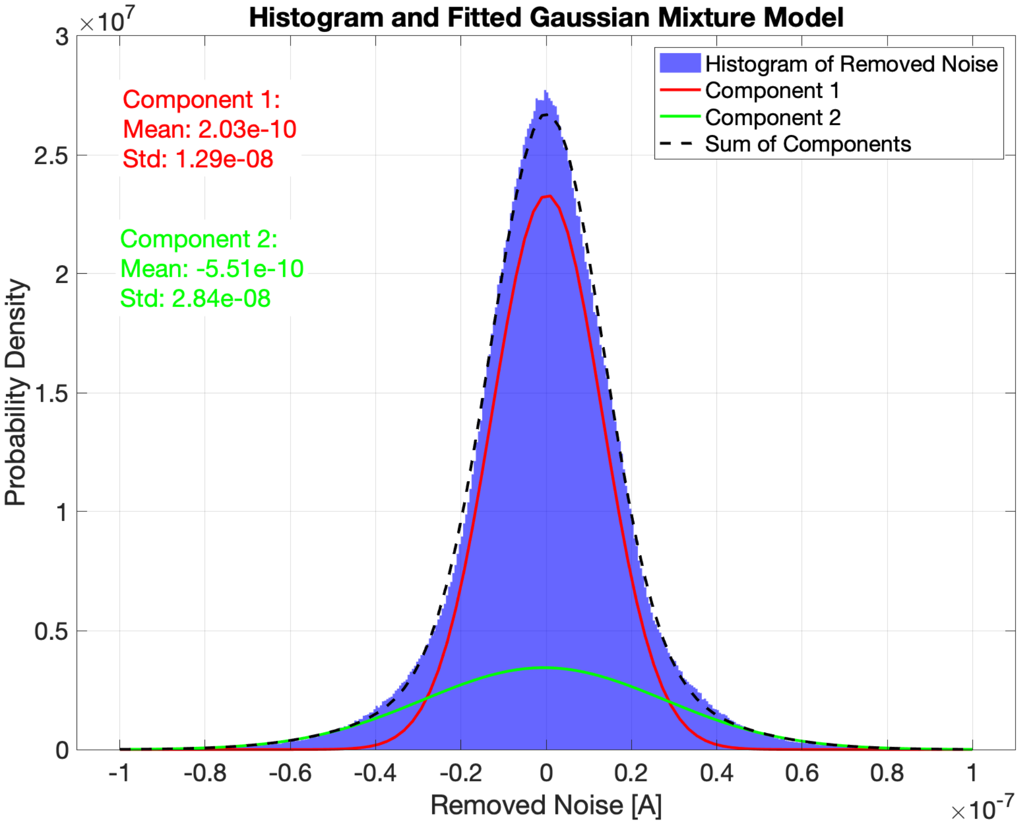

Figure 8: Histogram of noise and fitted Gaussian Mixture Model

These two Gaussians can probably be associated to two different electrical or chemical phenomena. For this data, values of free chlorine from 0.13ppm to 20.28 ppm have been detected with a median of 2.85ppm. The corresponding raw current on the Prussian Blue electrodes varied between -3.43 nA and -1.65 µA, with a median of -447.20 nA. We have then a significant noise level. With 10 s windows, the average of maximum variation of current on one window is 30% on the whole data with peak at 10'800% variation on 10 second that does not reflect actual variations of the free chlorine concentrations. The average of the maximum variation on one window drops to 1.74% with the moving average and to 0.64% with median filter (Figure 9).

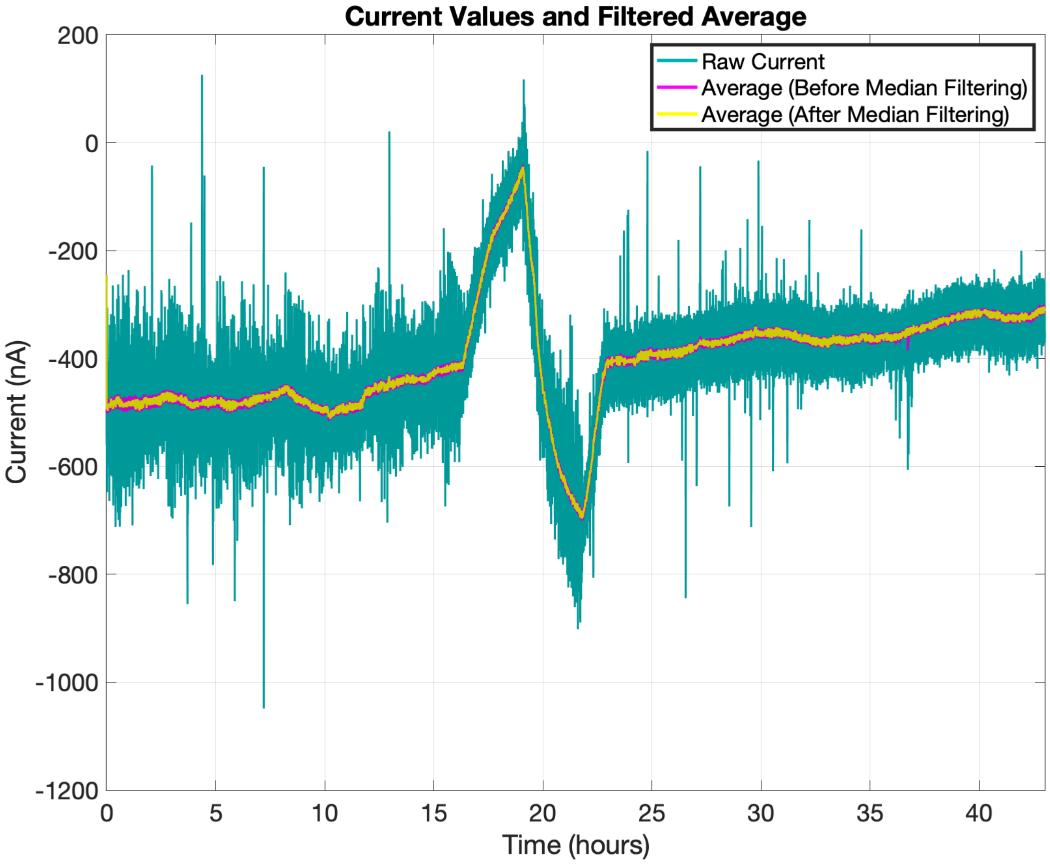

Figure 9: Raw current, average, and average with median filter over 43 hours

3.5. Electrode wear and long-term sensitivity

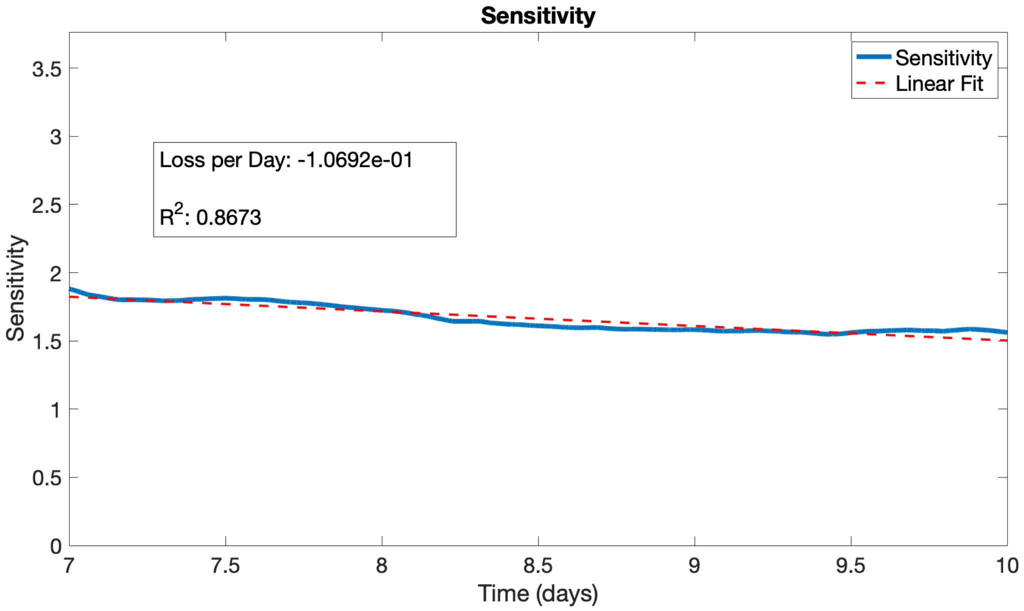

Figure 10: Sensitivity on one sample from day 7 to day 10 of continuous working

Due to the continuous flow of water on the electrode a mechanical wear of the electrodes was expected. A sensor has been let in flow for a longer time, in treated greywater for 0 to 8.5 days, and then in treated municipal wastewater. A constant linear loss of sensitivity of -0.107 per day was observed (R^2=0.87), which is 5.55% of the initial stable value. This is probably due to the mechanical wear of the electrode by the constant flow of water.

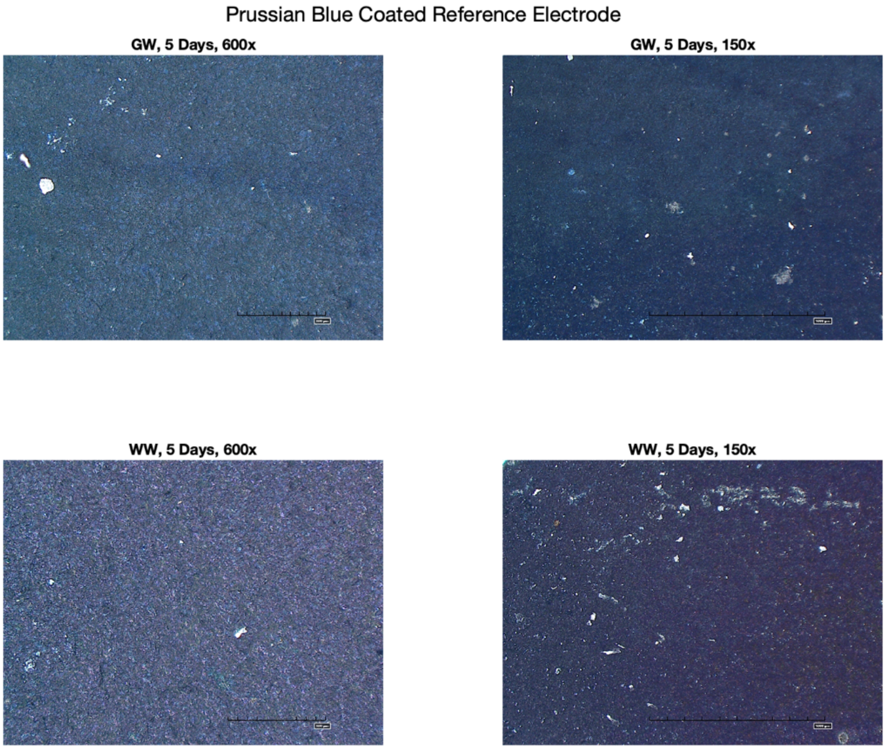

Figure 11: Prussian Blue coated carbon working electrode after 5 days in treated wastewater (WW) and treated greywater (GW)

On the working electrode, the Prussian Blue layer was still present, and the carbon substrate did not present traces of wear and tear. Some impurities can, however, be observed. (Figure 11). The counter electrode showed more traces of wear, especially with wastewater, with parts ceramic substrate exposed (Figure 12). The reference electrode showed traces of wear and oxydation (Figure 13). The external electrodes being more worn could be an effect of the configuration of the flow cell. It is probable that the observed residual long-term loss of sensitivity without loss of linearity is due to the wear of the counter electrode. Indeed, substantial degradation of the performances of Prussian Blue layer, or of reference electrodes would lead to a decrease of selectivity, and by consquence to a loss of linearity due to variations in the water matrix.

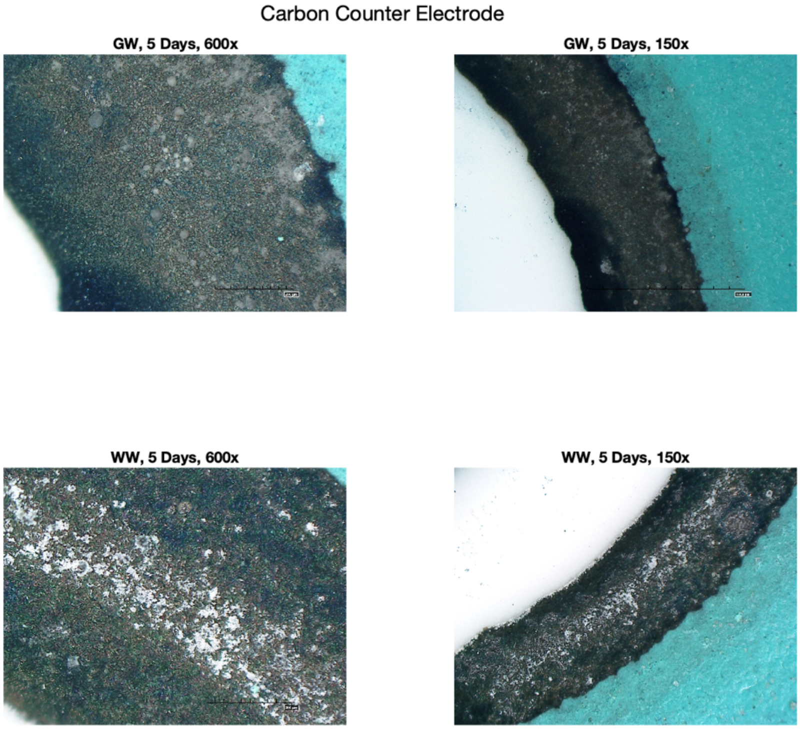

Figure 12: Carbon counter electrode after 5 days in treated wastewater (WW) and treated greywater (GW)

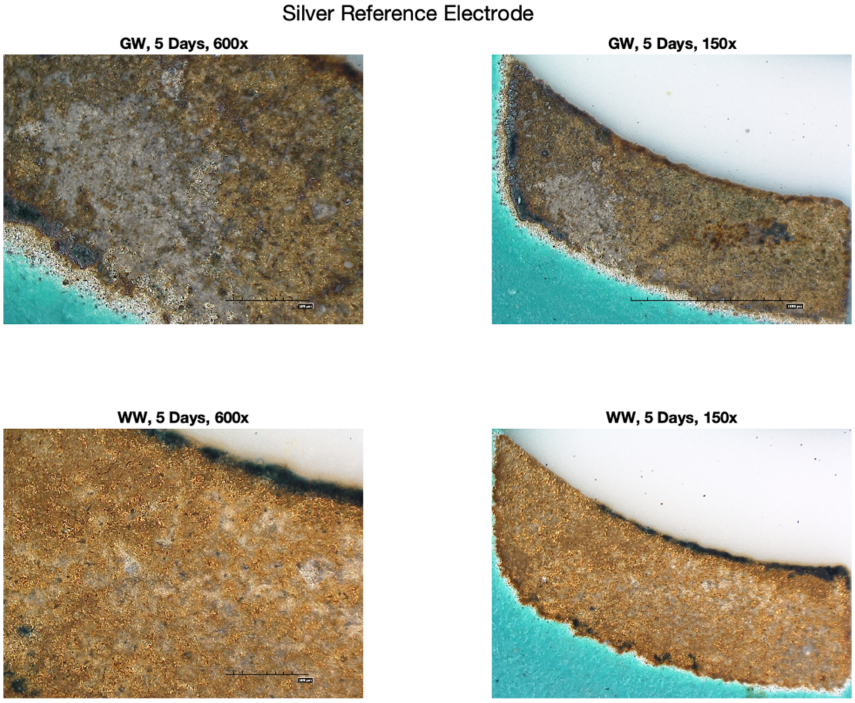

Figure 13: Silver reference electrode after 5 days in treated wastewater (WW) and treated greywater (GW)

3.6. Cost assessment

Linear loss of sensitivity could be easily compensated by signal processing to increase life expectancy of the electrodes (linear amplification of the signal). However, it is difficult to determine a cut-off signal to noise ratio that is acceptable for water reuse applications, as this depends on the pH and the temperature, as well as from the noise sources. For an arbitrary cut-off of 0.5x the sensitivity of commercial electrodes, the obtained life expectancy is 13 days. This is relatively low, but given the prices of the DRP-110, which have been acquired for about 1 CHF each, and that of the used chemical, of less than 0.20 CHF by electrodes, this can still be a very cost-efficient solutions, at about 25$ of consumables per year, given that sufficient effort is put in industrializing the process of production, which is very simple and clean-room free. This could lead to the use of cheaper substrate electrodes, using for instance paper-based or textile electrodes, or more resistant one, using carbon nanotubes or graphene electrodes. As size of electrodes is not a constraint, increase of sensing surface could also be a path towards cheaper sensing electronics. As we obtained excellent repeatability in real conditions, industrializing the process could also lead to the production of a calibration-free sensor, which will require additional development and testing.

4. Conclusion

In conclusion, this study represents a significant step in demonstrating the viability of low-cost Prussian Blue amperometric sensors for real-time monitoring of free chlorine concentrations in decentralized water reuse systems. Despite an initial sensitivity reduction within the first 72 hours, the sensors stabilized and displayed sensitivities comparable to or even surpassing those of reference Endress+Hauser electrodes. Moreover, the sensors consistently demonstrated strong linearity, with R^2 values consistently exceeding 0.95. Notably, these results were obtained by testing the sensors in a real water reuse system, treating both greywater and household wastewater. These findings emphasize the substantial potential of Prussian Blue sensors as practical and cost-effective solutions for continuous chlorine monitoring in decentralized water reuse applications.

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5 Conclusion

This Master Thesis and the two papers that are part of it demonstrated that low-cost electrochemical sensors, in particular Prussian Blue coated carbon electrodes are a promising alternative to expensive sensors for treated greywater and treated municipal wastewater monitoring in decentralised system. Good sensitivity and linearity have been achieved for test periods up to 10 days in real decentralised water reuse system. Fabrication process proves easy and demonstrate good repeatability. Next steps before real life applications include further testing on longer time periods, as well as finding substrate and fabrication method more adapted to mass production. Sensitivity could be increased by increasing the electrode surface and adequate electronics should be developed to set amperometry potential and process the electrodes signal without using a potentiostat.

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Annex I: Proportionality to reactant concentration

Fick's law of diffusion (Carrara, 2012): Fick's First Law of Diffusion, describes the rate at which a substance diffuses through a medium. It is commonly used in physics and chemistry to understand how molecules move from areas of high concentration to areas of low concentration. The law is expressed as:

$$J = -D \cdot \frac{dC}{dx}$$

Where:

J is the diffusion flux, which represents the amount of substance crossing a unit area perpendicular to the direction of diffusion per unit time.

D is the diffusion coefficient, a property of the substance and the medium through which it is diffusing.

$\frac{dC}{dx}$ is the concentration gradient, representing the change in concentration (C) of the substance over a change in distance (dx).

Nernst equation (Carrara, 2012): The Nernst equation relates the electrode potential of an electrochemical cell to the concentration of ions involved in the cell's reaction under non-standard conditions.

$$E = E^0 + \frac{RT}{nF} \ln[\mathrm{Q}]$$

E is the cell potential under non-standard conditions.
E^0 is the standard cell potential (cell potential under standard conditions, usually at 25°C and 1 atm pressure).
R is the ideal gas constant (8.314 J/(mol·K)).
T is the temperature in Kelvin.
n is the number of moles of electrons exchanged in the balanced cell reaction.
F is the Faraday constant (96,485 C/mol, which is the charge of 1 mole of electrons).
Q is the reaction quotient, which is the ratio of the product concentrations to the reactant concentrations, each raised to their respective stoichiometric coefficients.

Combining these two equations, we can derive a relationship between the concentration of the analyte and the current generated:

Let's assume the current I is proportional to the diffusion flux J at the electrode surface. In other words, $I = k * J$, where k is a proportionality constant.

Substituting Fick's law into the equation for current:

$$I = -k * D * \frac{\partial C}{\partial x}$$

Now, the concentration gradient $\frac{\partial C}{\partial x}$ can be related to the concentration C and the thickness of the diffusion layer δ near the electrode surface:

$$\frac{\partial C}{\partial x} = \frac{C_{bulk} - C_{surface}}{\delta}$$

Where C_{bulk} refers to the bulk concentration of the analyte in the solution being analysed, away from the electrode surface and $C_{surface}$ refers to the concentration of the analyte at the electrode surface where the electrochemical reaction is occurring.

Substituting this into the equation for current:

$$I = -k * D * \frac{C_{bulk} - C_{surface}}{\delta}$$

Now, substituting the Nernst equation for the surface concentration $C_{surface}$:

$$C_{surface} = C_{bulk} * \exp\left((E^0 - E) * \frac{nF}{RT}\right)$$

Putting it all together:

$$I = \frac{-k * D * C_{bulk}}{\delta} * \left[1 - \exp\left((E^0 - E) * \frac{nF}{RT}\right)\right]$$

Which shows the proportionality to C_{bulk}, the concentration of analyte.