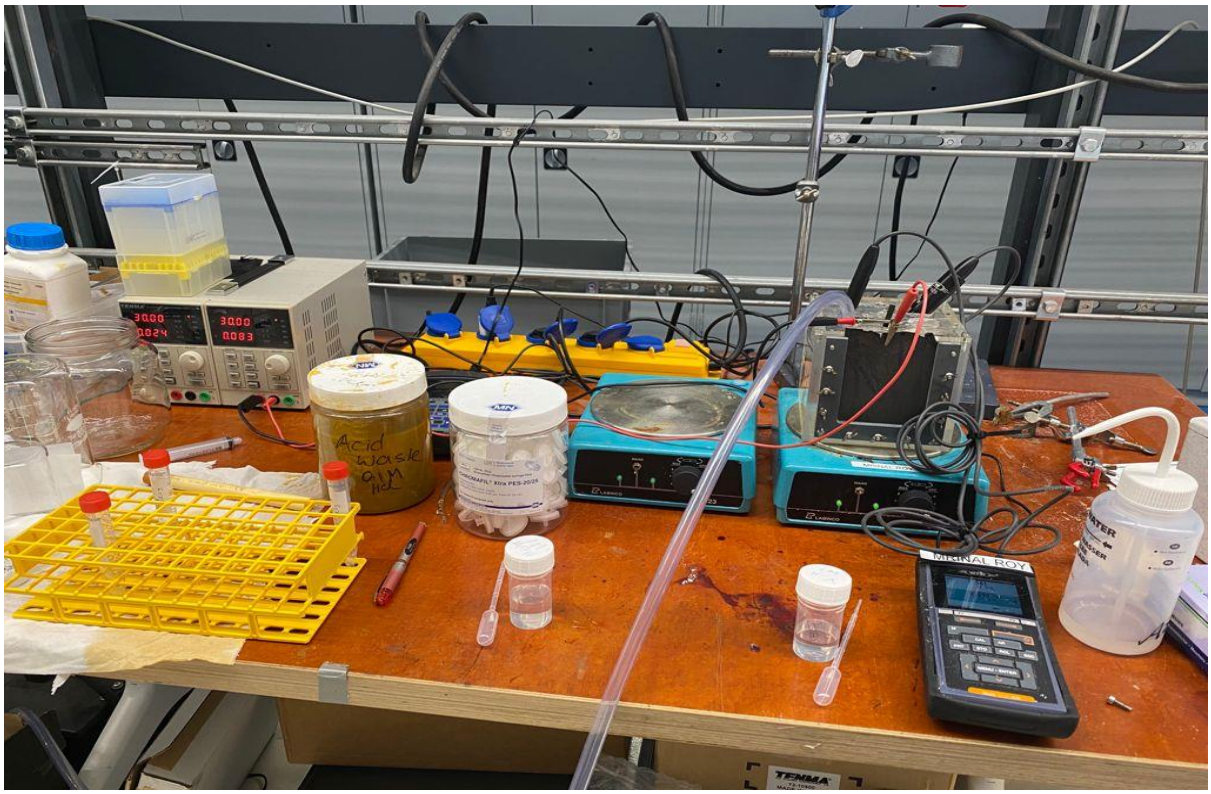
Development of air-cathode reactor to electro-chemically generate hydrogen peroxide (H_2O_2) anaerobically

(CIE 5050-09: Additional Thesis)



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January 2022

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Abstract

Groundwater is a major source of drinking water containing various elements out of which arsenic(As) is one of the toxic elements present. It is present in the form of arsenite, Conventionally, As(III) can be effectively removed if it is pre-oxidized to arsenate, As(V), thereby not involving any chemical dosage. There are various techniques to remove arsenic from drinking water like membrane filtration, electro-coagulation, filtration, adsorption and ion exchange. Among these the iron electro-coagulation technique of arsenic removal is one such technique which can be done by electrochemically generating oxidizing compounds like hydrogen peroxide, H_2O_2. Instead of dosing H_2O_2 anaerobically, it can be generated before the aeration step and can improve the As(III) oxidation with the groundwater native Fe(II).

The in-situ electrochemical generation of H_2O_2 was done by means of an air-cathode reactor setup, which reduces atmospheric oxygen O_2 to H_2O_2, under anoxic water. This H_2O_2 then reacts with ferrous iron, Fe(II) to produce ferric iron Fe(III) and reactive oxidizing species(ROS)/intermediate products/fenton products. These ROS mainly form poorly ordered solids, which have higher adsorption capacities than the products of aeration. The oxidation of As(III) is 4 times more by H_2O_2, than the oxidation by O_2.

By varying the applied charge dosage (CD) and the rate of dosage (Charge Dosage Rate, CDR), the faradaic efficiencies of both Fe and H_2O_2 were analyzed. It was found that as the CDR increased, the overall faradaic efficiency of H_2O_2 generation also increased from 76.32% to 92.07%. However, there might have been discrepancies in the faradaic efficiencies of Fe due to acid & base dilutions, human errors or the difference in the operational values of the current. In theory, 1 mole of H_2O_2 oxidizes 2 moles of Fe(II), and in the absence of O_2 the main Fe(II)-oxidant is the generated H_2O_2.

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Chapter 1

1. Introduction

Groundwater is a common source of drinking water. And arsenic, which is a toxic element, is present in groundwater all over the world, mostly in countries like India, Bangladesh, Cambodia, China, Argentina, Vietnam, Mexico and the United States. From figure 1, it can be seen that the highest among these are from Asia and parts of Europe, followed by regions like Africa, North America, South America and Australia (Shaji et al.,2021).It has been estimated that about 220 million people worldwide have been exposed to arsenic via consumption of groundwater from drinking water(Podgorski and Berg, 2020), which is a global threat.

In water sources, As is mainly present in two inorganic forms: arsenite (As(III)) and arsenate (As(V) (Cubadda et al., 2010),(Wan et al., 2011), with the As(III) species being more toxic and more prevalent in reduced groundwater aquifers than As(V) (Katsoyiannis and Zouboulis, 2004; Nicomel et al., 2015). If one consumes arsenic contaminated water, they may be exposed to various diseases like cancer, which are collectively called Arsenicosis (Cubadda et al., 2010), (Quansah et al., 2015). As a result, it is very important to remove arsenic from drinking water. The WHO has recommended on guidelines to consumption of water having concentrations less than 10 µg As/L(WHO,1993).

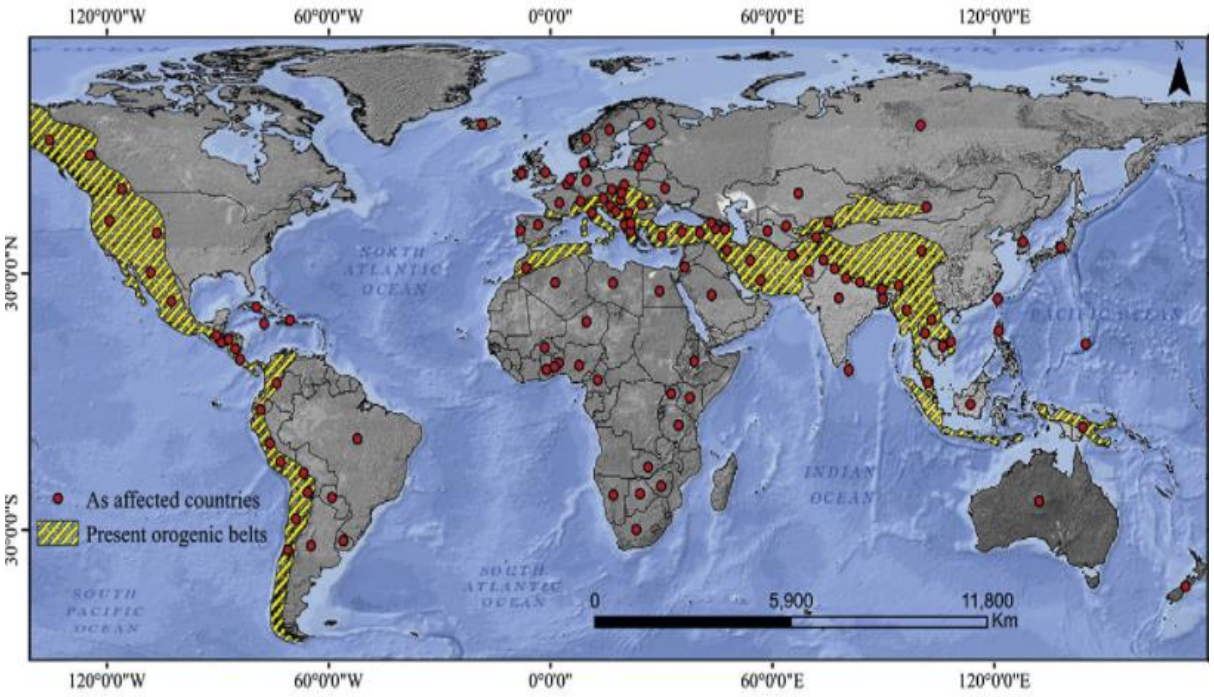

Figure1: World Map showing the As affected countries with the organic belts (Shaji et al.,2021).

Many techniques have been proposed to remove As from drinking water, such as coagulation and flocculation, ion exchange, adsorption to activated alumina or iron based sorbents and reverse osmosis (Feenstra et al., 2007; Mondal et al., 2013). One of the most conventional forms of arsenic removal is the passive treatment of anaerobic groundwater (figure 2). In a conventional basic treatment scheme, the anaerobic groundwater is passed through an aeration then followed by a filtration step, but in this process, the oxidation of As(III) is incomplete as the rate of oxidation of As(III) by just O_2 is quite slow. To enhance this oxidation of As(III), chemical oxidants and Fe is added to oxidize and remove the remaining As(III). Taking into account the expenses, the amount of unwanted by-products produced, if the oxidation of As(III) along with the natural Fe prior to aeration-filtration step can be done, then the addition of external Fe can be minimized(Jackman & Hughes,2010),(Katsoyiannis & Zouboulis, 2004).

The groundwater has nearly anaerobic conditions, with a low O_2 content, and presence of Fe(II) and As(III), which when aerated, with a series of cascade aerators forms Fe(III)solids and the arsenic tends to adsorb around these solids. These Fe-As solid complexes can then be filtered out via rapid sand filters and the effluent is treated water. This passive removal of As

has been proven to completely remove Fe but only 8-50% removal efficiencies of As, depending on few factors like the initial As/Fe ratios, the competing ions, etc (van Genuchten & Ahmad, 2020; Holm & Wilson, 2006; Li et al., 2016). Arsenic in groundwater is present in the form of arsenite, As(III), which are neutrally charged As species. These neutrally charged As species have a very low affinity towards the absorption sites of the Fe(III) solids which are formed post aeration. However, if we can oxidize arsenite, As(III) to arsenate, As(V), which is negatively charged As species, it has high affinity to the adsorption sites of the Fe(III) solids.

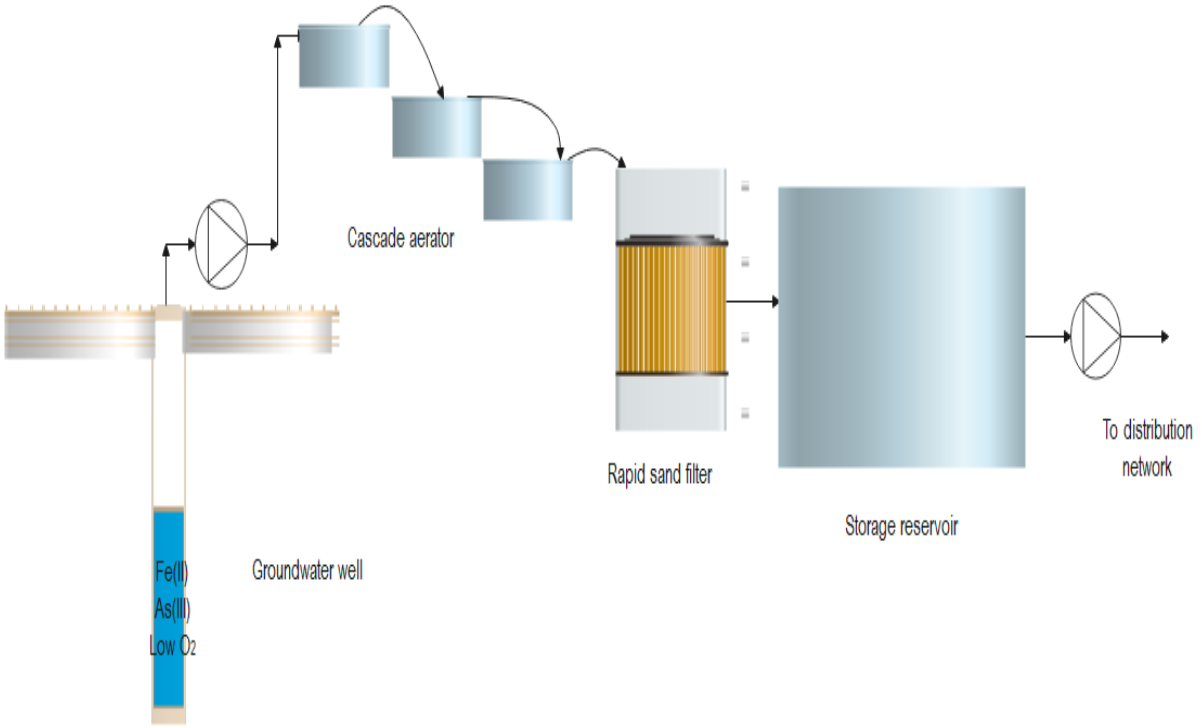

Figure 2: Passive treatment of anaerobic groundwater

When it comes to As(III) oxidation of As(V) using O_2, then there is only partial oxidation occurring. In this case, aeration takes place not only with O_2, but it is catalyzed by Fe(II). When Fe(II) is oxidized to Fe(III) by O_2, a cascade of reactions take place and it generates certain reactive oxidizing species(ROS), which oxidizes the arsenic. So, as a whole, we can say that, due to impartial oxidation of As(III), majority of the unoxidized As(III) doesn't get adsorbed on the freshly generated Fe(III) solids, and thus, still remain in the water. Secondly, it is also dependent on the solids that are generated. It has been reported that when we oxidize Fe(II) with O_2, the Fe(III) solids that are generated are moderately crystalline. On the other hand, when we oxidize this Fe(II) with strong oxidants like H_2O_2, then it generates

Fe(III) solids that are poorly ordered crystalline structures, which is of great advantage for adsorption. The decreased crystallinity, the increase in specific area and the increase in adsorption capacity of these solids enhances arsenic removal efficiencies. But in the presence of only O_2, there is no generation of such poorly ordered solids. Hence, we can say that, optimization of the co-removal of As(III) with groundwater native Fe(II) can be achieved if we can effectively co-oxidize As(III) as well as generate poorly ordered solids.

As mentioned above, indeed we get partial oxidation of As(III) with the generation of ROS in combination with Fe(II). But if we take H_2O_2, as a ROS, it rapidly oxidizes Fe(II) to form Fe(IV) or OH radicals which are great As(III) oxidizers. Based on literature of Fe based As removal studies, it was observed that in aerobic conditions, when Fe(II) was oxidized to Fe(III) in presence of H_2O_2, there is increase in As(III) co-removal than that of Fe(II) oxidized by O_2 only. The oxidation rate of H_2O_2 is of magnitude 4 orders more than O_2 and hence, even with the presence of oxygen, the oxidation is predominantly done by H_2O_2. Due to this rapid oxidation, the solids that are generated are poorly ordered solids compared to O_2 allowing higher As adsorption. Also, another important thing observed here is that, when you directly oxidize Fe(II) by H_2O_2, the stoichiometric yield of ROS per mole of oxidized Fe(II) is higher (^{o}OH/Fe(IV):Fe(II)= 1:1 for H_2O_2 than that of 1:3 for O_2(Bandaru et al., 2020) (Hug & Leupin, 2003).

Hence, in this research, the concept of electro-Fenton process is applied by the in-situ generation of H_2O_2 and Fe by passing current through a Fe anode and air-cathode(Bandaru et al., 2020). The air-cathode is made of carbonaceous material that generate H_2O_2 electrochemically due to O_2 reduction (Roy, 2020), as follows:

$$O_2+2e^-+2H^+ \rightarrow H_2O_2$$

The Electro-Fenton reactions are to be used to oxidize As(III) in H_2O by electrochemical generation of H_2O_2(Bandaru et al., 2020). H_2O_2 generated shall react with the Fe(II), which is the anode, to generate ROS(OH or Fe(IV)), and Fe(III) in the product side.

$$Fe(II) + H_2O_2 \rightarrow Fe(III)+INT$$

Where INT= intermediate products/fenton products/reactive oxidizing species(ROS)

The main advantage of the electro-Fenton process is that here the H_2O_2 is generated electrochemically without any chemical usage, and in a controlled rate and at a very low current requirement.

Based on the above ideas, the research hypothesis of this study can be introduced as, instead of oxidizing the groundwater native Fe(II) with O_2, oxidizing it directly with H_2O_2, which is eventually generated, oxidizing it directly with H_2O_2 anaerobically, before the aeration step, can improve As(III) co-removal, due to higher generation of poorly ordered solids as well as higher As(III) co-oxidation. However, in this research, an Fe based air cathode is used to effectively generate H_2O_2 anaerobically, and the main research hypothesis lies on the question that *: "Whether the faradaic efficiencies of both Fe and H_2O_2 increase with the overall increase in the Charge Dosage Rates(CDRs)?"*

One of the main research objectives of this research is to study the electrochemical generation of H_2O_2 by using air cathode under anaerobic conditions and also to determine the influence of different H_2O_2 dosages/ concentrations on the As removal efficiency of the system. To achieve the research objectives, few research questions where specified, such as, *"What is the Faradaic efficiency of H_2O_2 production by air-cathode?", "What is the impact of H_2O_2 concentrations in the oxidation of As(III)?"*. But for our research, the main focus is on *"How does the Charge Dosage(CD) to Charge Dosage Rate (CDR) ratios impact the Faradaic Efficiencies of both H_2O_2 and Fe?"*

A stock solution of $NaHCO_3$ and NaCl was prepared and the solution was poured to the air cathode chamber. To maintain an anoxic condition inside the air cathode chamber, N_2 gas was dosed into it and a dissolved oxygen(DO) of less than 0.3 mg/L was maintained by covering the open holes of the chamber with parafilm, so that there is hardly any O_2 present to oxidize the Fe(II) inside the chamber. Hence, all the Fe(II) will be predominantly oxidized by H_2O_2 produced by the air cathode. A circumneutral pH of 7-7.5 was maintained throughout the experiments to optimize the rate of the experiments as at neutral pH, As(V) in contrast to As(III), is negatively charged and is therefore more efficiently removed via adsorption to hydrous ferric oxides, HFO (Bissen M. et. al, 2003), (Kim M. J. et. al,2000). Fe anode was inserted in the same chamber before the start of the experiment. Both the CDR and CD where varied throughout the experiment as the set up was connected to a DC supply, by varying the applied current to the system.

Chapter 2

2. Literature Review

In water treatment, oxidation which is followed by co-precipitation with iron(hydr)oxides is one of the most efficient and economical arsenic removal technologies. (Hug S & Leupin O, 2003), observed that As(III) is co-oxidized with Fe(II) by O_2 and by H_2O_2 respectively. The As(III) oxidation is not inhibited by • OH radical scavengers, at a neutral pH, which is significant for the understanding of arsenic redox reactions in the environment, in arsenic removal processes and for the understanding of Fenton reactions in general. • OH radical is formed only at low Ph and in contrast, the oxidation of As(III) in Fenton and photo-Fenton reactions appears to be possible at neutral pH. It was observed that there was complete oxidation at pH 5 in the presence of H_2O_2, whereas only 20-30% oxidation at higher Fe(II) concentrations with O_2. Also bicarbonates increased the fraction of oxidized As(III), possibly by formation of carbonate radicals or by changing speciation of Fe(II). The protonation equilibrium between INT and INT-OH leads to a pH-dependent partitioning of the reactions into • OH radicals at low pH and more weakly oxidizing Fe(IV) species a higher pH. The model states that the yield of • OH formation drops sharply between pH 5 and pH 6 and 10-fold with each pH unit increase above pH 6. Compounds that only react with • OH can still be oxidized in the Fenton reaction at pH 7, although with low yields. At pH 7, the naturally present dissolved organic matter would also not significantly affect As(III) oxidation by scavenging • OH.

(Maitlo et. al., 2019) studied the treatment of arsenite (As(III)) by an air-breathing cathode electrocoagulation (ACEC) process, with a sacrificial aluminum anode. Air cathodes have hydrophobic gas diffusion properties and can easily promote passive atmospheric oxygen diffusion inside the reactor through the air cathode. As(III) removal efficiency of the ACEC increased from 81 to 86% with an increase in NaCl concentration from 10 to 20 mM. It was observed that during the operation of ACEC, aqueous As(III) was subsequently oxidized into the As(V). The produced As(V) was then removed by a co-precipitation reaction of As(V) with aluminum oxides. Furthermore, they observed the oxidation of As(III) into its corresponding ions as well as the production of an aluminum oxide hydroxide in the form of boehmite. Also the As(III) removal efficiency increased with an increase in the applied voltage. This study

describes ACEC as one of the most energy-efficient treatment methods for As(III) removal based on its performance evaluation.

(Bandaru et al., 2020), describes the Air Cathode Assisted Iron Electro-coagulation, ACAIE system , which was followed in this research, especially the preparation method of the air-cathode. According to this paper, an air cathode comprises a porous carbon cloth with a hydrophobic gas diffusion layer on the air-facing side and a catalyst layer facing the electrolyte. In-situ generated H_2O_2 oxidizes Fe(II) nearly 4 orders of magnitude faster than O_2 and also produces higher stoichiometric yields of selective reactive intermediates (Fe(IV)) compared to O_2 , which enhances the kinetics of As(III) oxidation and removal by orders of magnitude. The dissolved iron levels were also significantly lower when air cathode was used instead of Fe electrode. The efficiency of H_2O_2 production by the air cathodes used in the ACAIE experiments was lowest at the lowest CDR of 1.5 C/L/min (48 ± 9% of the theoretical value), but increased steadily with increasing CDR (>80% of the theoretical H_2O_2 at CDR> 60 C/L/min). A drastic removal of arsenic was shown by the ACAIE system, where rapid oxidation of Fe(II) and complete oxidation and removal of As(III) were achieved. The Iron Electrocoagulation system, FeEC and the ACAIE for removing As(III) from an initial concentration of 1464 µg/L, was compared, aiming for a final concentration of less than 4 µg/L. They demonstrated that at short electrolysis times (0.5 min), i.e., high charge dosage rates (1200 C/L/min), the ACAIE consistently outperformed FeEC in bringing arsenic levels to less than WHO-MCL of 10 µg/L.

(Si Y et. al, 2018) developed a self-powered iron electrocoagulation that coupled with iron corrosion anode with oxygen reduction air cathode for simultaneous As(III) oxidation and removal. Activated carbon (AC), which favored the four-electron oxygen reduction reaction (ORR, $O_2+4e^-+4H^+\rightarrow 2H_2O$, $E^{0\prime} = 0.816$ V), and carbon black (CB), which favored two-electron ORR ($O_2+2e^-+2H^+\rightarrow H_2O_2$, $E^{0\prime} = 0.283$ V), were evaluated for As(III) removal efficiency and current production performance. The comparison showed a tradeoff between higher current (i.e., higher iron corrosion rate) attributed to the higher reduction potential with four-electron ORR, and higher H_2O_2 production for improved As(III) oxidation with two-electron ORR yet the lower reduction potential. The AC cathode showed that the highest maximum power density of 230 ± 12 mW m^{-2} was with lower As(III) removal of 91.3 ± 1.3%. The AC/CB cathode was a promising option that had an effective As(III) removal (above 99%), and a comparable power generation (209 ± 3 mW m^{-2}).

(Dong H et. al, 2011) discussed that while undergoing economic analysis, it revealed that the cost of the H2O2–Fe(II) process was only 17–32% of that of conventional Fe(III) coagulation process to achieve arsenate concentration below 10 µg/L in treated solution. The results suggested that the H2O2–Fe(II) process is an efficient, economical, selective and practical method. Arsenate removal by the H2O2–Fe(II) process was strongly dependent on pH and the optimum removal was achieved at pH 5. The arsenate removal significantly improved at pH 7 and at low Fe/As ratio.

(Yuan Z et. al, 2019) has studied upon the abio-oxidation of Fe(II) and As removal in As-rich Acid Mine Drainage, AMD. They found out that the As removal efficiency was strongly controlled by pH, which increased from 33% to 96.2% when pH was increased from 2 to 7. Also they described that the fenton-like reaction between Fe(II) and O_2 with reactive oxygen species (ROS) as oxidizers was the probable mechanism for Fe(II) and As(III) oxidation.

Chapter 3

3. Materials and Methods

The complete procedure of all the experiments, the materials used to construct the experimental setup, necessary chemicals and mandatory equipments as well as the experimental conditions are described in this particular chapter. The methods to compare the values with the measured ones and hence, finding out the efficiencies are also shown here. The research experiments were duly performed at the TU Delft Water Lab of the Civil Engineering & the Geosciences Department from 7th of July, 2021 to 7th of September, 2021.

3.1 Chemicals

1L of Ultrapure water, 0.21g $NaHCO_3$ and 7g NaCl were mixed together to prepare the stock solution. Besides this, 1M HCL and 1M NaOH were used for maintaining the pH between 7-7.5. N_2 gas was dosed by a gas cylinder to maintain DO less than 0.3mg/L, thereby maintaining an anoxic condition during the experiment. A pH meter and a DO meter was used to check whether both the pH and DO levels were at stable levels throughout the experiment. Both initial and final filtered and unfiltered samples well collected, before and after each set of experiment which were collected over 10mL sample tubes. Filters of about 0.2µm were used to collect the filtered samples. Concentrated 100 µL HNO_3 was pipetted in all of these sample tubes initially, so that it controls the additional reactions happening inside, basically stopping the Fe(II) oxidation reactions.

3.2 Experimental Setup

3.2.1 Air-cathode batch reactor setup

Batch experiments with air-cathode was performed in a custom-built rectangular batch reactor of 1 L capacity. The reactor was closed on all sides (with perforated openings on the top) and fitted with a carbon-based air cathode on one side of the reactor. The air cathodes were fabricated according to (Bandaru et al., 2020). A rectangular Fe served as the anode and was placed in the same 1 L glass beaker containing the stock solution. A DC power supply was used to generate current at an applied voltage and the circuit was completed. For proper mixing, a magnetic stirrer was used. As mentioned, 10mL sample tubes, 10mL syringes, 0.2µm filters, fitting fiber pipes, cuvettes and pipettes were also used. For the additional experiments with As

(from sodium meta arsenite, $NaAsO_2$), the solution contained As(III) of 500µg/L and 100 µM of Fe(II) and samples were kept for HPLC/ICP-MS(Inductive Coupled Plasma Mass Spectrometry) analysis. Similarly, additional experiments were done in a controlled setup with two Fe electrodes connected together, put into the same stock solution containing As, in presence of atmospheric oxygen(aerobic condition). The spectrophotometric method was used for determination of the H_2O_2 concentrations , and the determination of both Fe(II) and Fe(Total) concentrations as well(Appendix Figure 10). Figure 3 shows the image taken from the laboratory set up of a typical air cathode chamber showing both the atmosphere facing side as well as the side facing towards the electrolyte. Figure 4 shows the top view of the experimental set up of this air cathode chamber showing the insertion points of the DO, pH meter, nitrogen gas dosage and the Fe electrode.

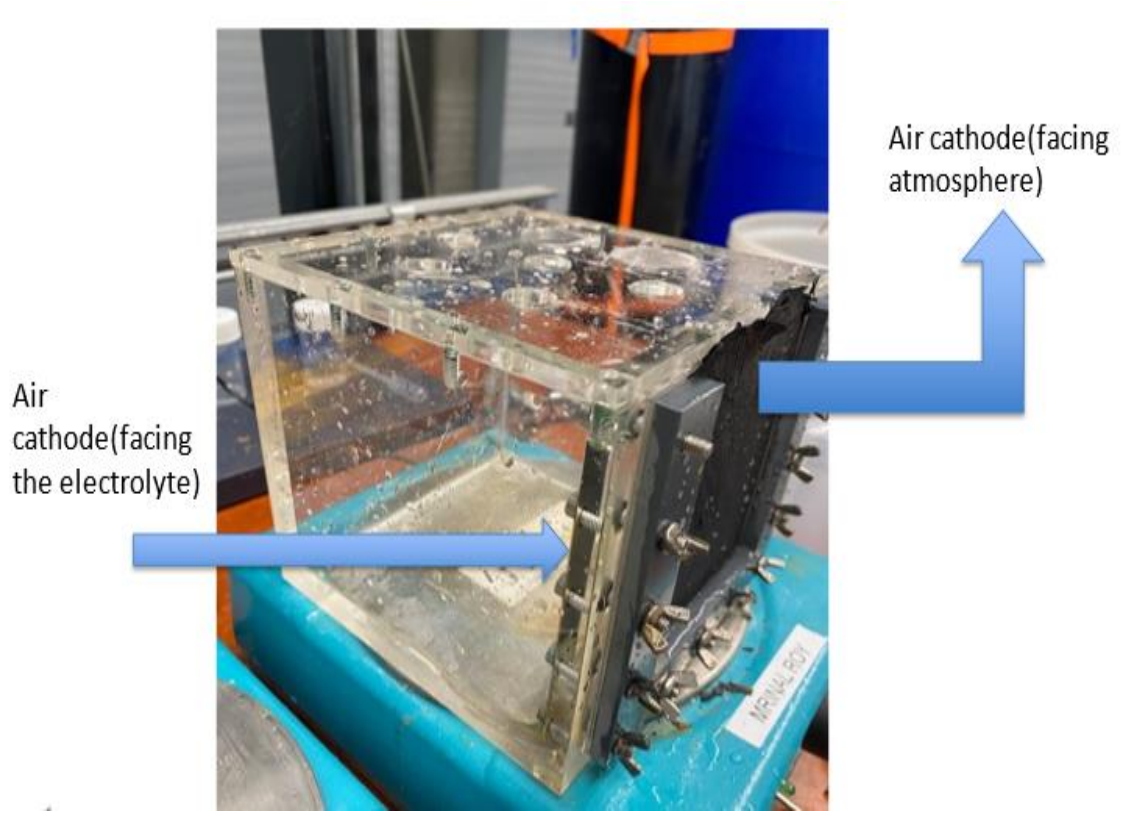

Figure 3: Typical air cathode chamber

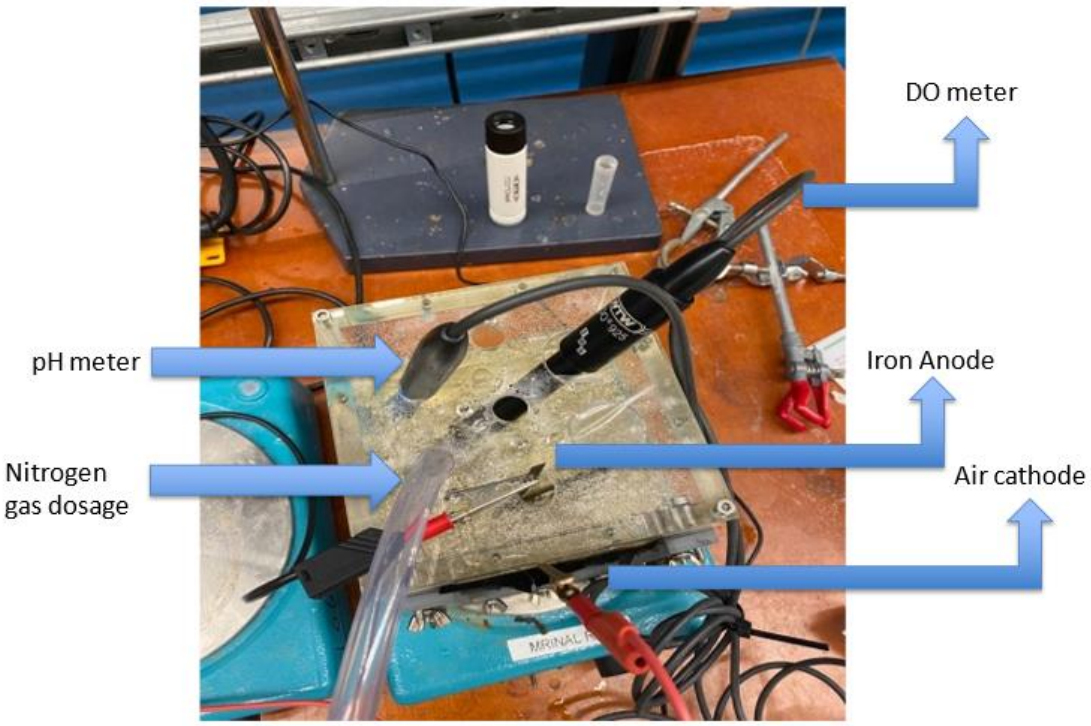

Figure 4: Top view of the experimental setup of the air cathode

3.2.2 Experimental conditions

The experiments with the air-cathode in the cathode reactor was performed by generating H_2O_2 electrochemically.

In the cell, the amount and rate of H_2O_2 generated is proportional to the charge dosage (CD), (q in C/L) and charge dosage rate (CDR), (dq/dt in C/L/min) by Faraday's law (eq. 1 and 2).

$$W = qM/nF = itM/nFV \quad (1)$$

$$dq/dt = i/V \quad (2)$$

where, W = amount of H_2O_2 generated (mg/L); i = current (mA); t = electrolysis time (min); M = molecular weight of H_2O_2 (mg/mol) = 55845; F = Faraday's constant (96485 C/mol); n = number of transferred electrons; V = solution volume (L).

Based upon calculations from equations (1) & (2) (Appendix A); the CDR was varied from 5C/L/min, 40 C/L/min, 80 C/L/min at calculated H_2O_2 concentrations of 100 µM, 250 µM and 500µM. Therefore, in this study, the CD was varied from 19.28 to 96.5 C/L to generate H_2O_2 concentration varying from 100 µM to 500 µM. Further three CDRs values were used in these experiments, which are 5, 40 and 80 C/L/min. For the external DC

power supply (TENMA 72–10,500) was operated in galvanostatic mode to deliver the specified currents to the air-cathode. An overview of the different operational parameters during the experiments is given in Table 1. These experiments were performed with the stock solution of 1L Ultrapure water, 0.21g $NaHCO_3$ and 7g NaCl to determine the faradaic efficiencies of H_2O_2 as well as Fe at different CD and CDRs, also to maintain adequate conductivities throughout the experiments.

Table 1: List of operational parameters varied during air-cathode batch experiments(V=1L).

H_2O_2 generation (in µM)	CD(C/L)	CDR(C/L/min)	Time (mins & sec)	Theoretical CDRs(µM/min)	Current i (Ampere)
100	19.28	5	3min52sec	25.92	0.083
		40	29sec	207.47	0.67
		80	15sec	414.93	1.33
250	48.22	5	9min39sec	25.92	0.083
		40	1min12sec	207.38	0.67
		80	36sec	415.28	1.33
500	96.5	5	18min42sec	26.73	0.083
		40	2min25sec	207.25	0.67
		80	1min13sec	414.51	1.33

Table 1 shows the entire list of operational parameters which was varied throughout the air-cathode batch experiments, which was conducted for a capacity of 1L volume of the electrolyte.

As mentioned earlier, the CD was varied from 19.28 to 96.5 C/L as per calculations, to generate H_2O_2 concentration varying from 100 µM to 500 µM. The CDR values used in these experiments were 5, 40 and 80 C/L/min for each set. The table also shows the calculated time interval, the calculated applied current as well as the theoretical CDRs for each case.

Water samples were collected (from cathode chamber only) before and after electrolysis time (without additional mixing time or precipitate settling) and analyzed for total As and Fe, aqueous As(III) and As(V), as well as for H_2O_2.

Also, theoretically;

[Fe] produced=W=qM/Nf=96.5*55.845/2*96485C/L*g/mol*mol/C

=>W=28mg/L=5.01*10^(-4)mol/L=500µM

Hence, we are also generating 28mg/L of Fe.

Also; in theory;

1 mole of H_2O_2 oxidizes 2 moles of Fe(II),

OR/ (½) mole of H_2O_2 oxidizes 1 mole of Fe(II).

In addition to this, we also had to consider the following steps carefully during the experiments:

- We need to take 1L of solution and apply current of 0.083A for 18min42sec to generate 500µM of H_2O_2.
- 1 L ultrapure water with 2.5 mM(0.21g) $NaHCO_3$ and 10 mM(0.5884g) NaCl solution. Although later on for all the experiments, we had to increase the NaCl dosed to about 7 g in order to increase the conductivity.
- A circumneutral pH range between 7-7.5 was maintained during the experiment and a DO of 0.1-0.3 mg/L was maintained by dosing nitrogen gas at approximately 1.5 atm pressure to maintain the anoxic condition inside the chamber.

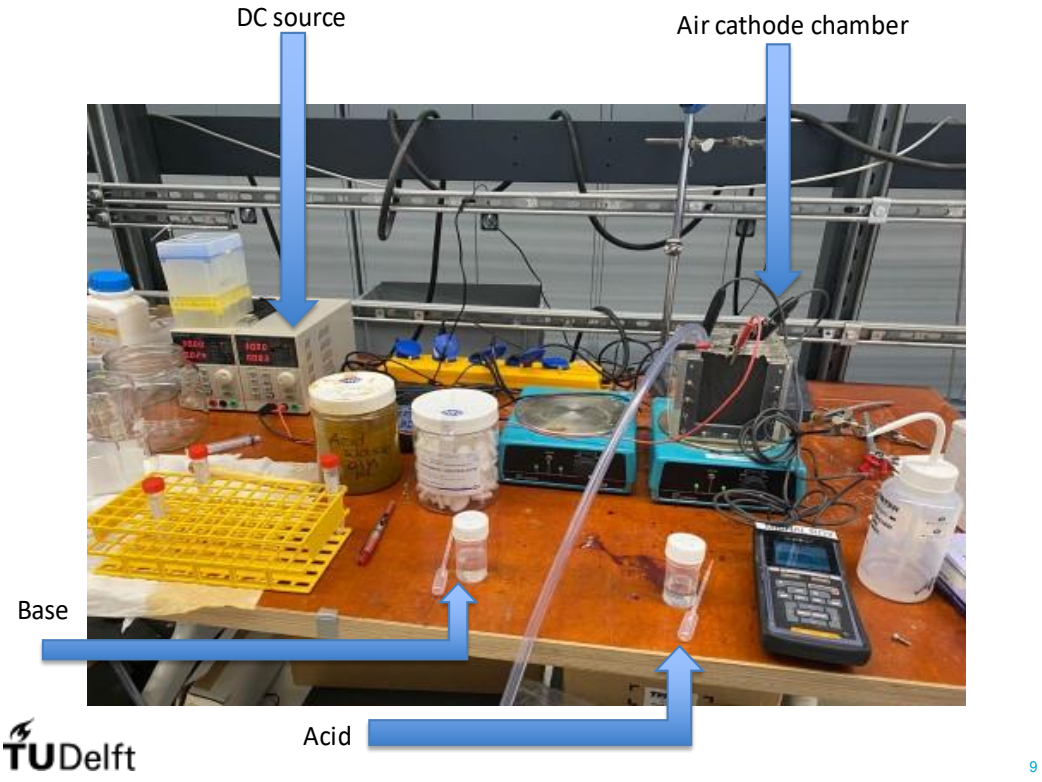

Figure 5: The experimental setup

Sampling was done both at the start and at the end of the electrolysis period. When the pH and DO was maintained at the desired levels mentioned above, the initial sampling was done. In the acidified 10ml sample tubes, containing 100 µL of concentrated HNO_3, unfiltered initial sample was taken out with a 10ml syringe. After the calculated time of each experiment, both filtered and unfiltered samples were taken out in the same manner, in separate sample tubes, except for the filtered sample, a 0.2µM filter was attached to the syringe.

3.2.3 Analytical procedure for the determination of H_2O_2 concentrations

After the final sampling, the cuvette samples were prepared for inserting into the spectrophotometer. A total of 8 cuvette samples were prepared, one for the blanc, the next three for the filtered initial samples and the last three for the filtered final samples. In a cuvette(2.5ml), 1000 microlitres of 0.1M KI is added. After this, 20 microlitres of 0.01M of Ammonium heptamolybdate tetrahydrate was added into all the sample tubes. Finally, 200 microlitres of the sample was added into each cuvette, leaving the first one to be filled with distilled water instead, for measuring the blanc, and the wavelength of the spectrophotometer was set to 350nm. First the blanc was measured and the apparatus was set to it. After this the absorbance of each sample was measured and the corresponding H_2O_2 concentrations were calculated using the calibration graph(appendix Fig 1). According to graphical analysis, the value in y axis(y) corresponds to the concentration of H_2O_2 in mg/L and the x axis(x) corresponds to the absorbance in nm. From the graphical analysis, y=5.7686x(Appendix Figure 10) and hence, with every corresponding x value, the y value, that is the corresponding H_2O_2 values can be determined. Finally the faradaic efficiency of H_2O_2 can be determined as:

$$\text{Faradaic efficiency} = \frac{W_{experimental}}{W_{theoretical}} \text{ x } 100\%$$

3.2.4 Analytical procedure for the determination of Fe(II) and Fe(III) concentrations

For the Fe(II) and Fe(Total) determination, use of Fe kits were used to do the speciation of Fe(II) and Fe(III) by photometric method. For this, total 6 samples were made, two for initial filtered samples, final filtered samples and final unfiltered samples each. For each set, first sample was prepared by pipetting out 1ml sample into the cuvette, and then adding one dose of the chemical inside the iron test kit and then shaking it nicely after closing it properly, for

determination of the Fe(Total). For the second sample, 1ml was pipetted out from the sample tube to the other cuvette and shaking it properly. After this, the samples are kept undisturbed for 30 mins after which the spectrometer measuring the Fe concentration will directly give the measurement based on the absorbance.

Apart from these experiments, some experiments were additionally done with a stock solution of As(III) at 500µg/L and 100µM of Fe(II). (Later on taken for ICP-MS Analysis: Appendix Table 22). Also some controlled experiments were done with this same stock solution in the presence of atmospheric oxygen.(Appendix Table 22)

Chapter 4

4. Results and Discussions

4.1 Air-cathode batch reactor setup

This section defines all the parameters measured as well as some necessary calculation details to obtain the final faradaic efficiencies of both Fe and H_2O_2, and its dependency with the CD/CDR ratios. Duplicates for each experiment were performed and the average values were directly plotted for the graphical analysis.

Table 2 shows the overall calculated faradaic efficiency of Fe and H_2O_2 with the time required for each electrolysis process, with the defined parameters of the H_2O_2 concentrations of 500 µM, 250 µM and 100 µM at CDRs 5C/L/min, 40C/L/min and 80C/L/min, for each set of experiment. It is seen that as the electrolysis time reduces, the faradaic efficiencies of both the Fe and H_2O_2 overall increases. In other words when time, which is basically the ratio of CD/CDR, decreases, the faradaic efficiencies of both Fe and H_2O_2 increases. However, it is still not clear about the optimum set for efficiencies, but an overall dependency relationship of the faradaic efficiencies on the CD/CDR ratio can be obtained.

Table 2 : Overview of the measured data with respect to time

Parameters	Faradaic efficiency Fe	Faradaic efficiency H202	Time(seconds)
H2O2= 500µM CDR= 5C/L/min	98.1	60.56	1122
H2O2= 500µM CDR= 40C/L/min	102.5	67.26	145
H2O2= 500µM CDR= 80C/L/min	95.58	76.32	73
H2O2= 250µM CDR= 5C/L/min	88.94	55.75	579
H2O2= 250µM CDR= 40C/L/min	96.44	88.79	72
H2O2= 250µM CDR= 80C/L/min	107.78	94.28	36
H2O2= 100µM CDR= 5C/L/min	99.11	78.19	232
H2O2= 100µM CDR= 40C/L/min	95	79.99	29
H2O2= 100µM CDR= 80C/L/min	111.02	92.07	15

4.2 Chemical analysis for H_2O_2 detection and Fe(II) & Fe(III) speciation

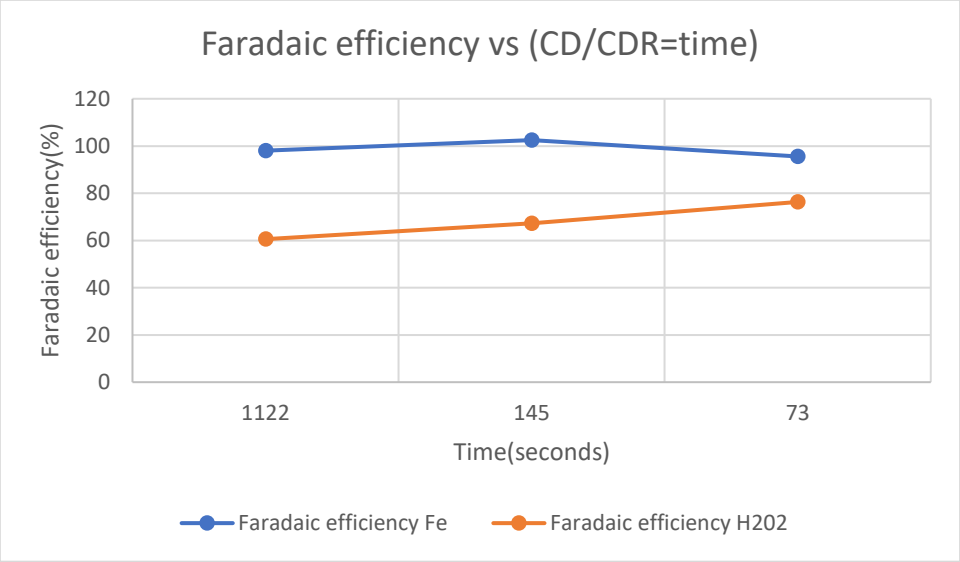

Figure 6: Variation of the faradaic efficiencies of H_2O_2 and Fe in percentage for [H_2O_2]=500µM & CDR=5C/L/min, 40C/L/min and 80C/L/min with calculated time interval in seconds

Figure 6 shows that both the Fe and H_2O_2 concentrations have gradually increased when the electrolysis time has decreased. Although there is not much change in the overall faradaic efficiencies, but it can be said that it has increased on an overall basis.

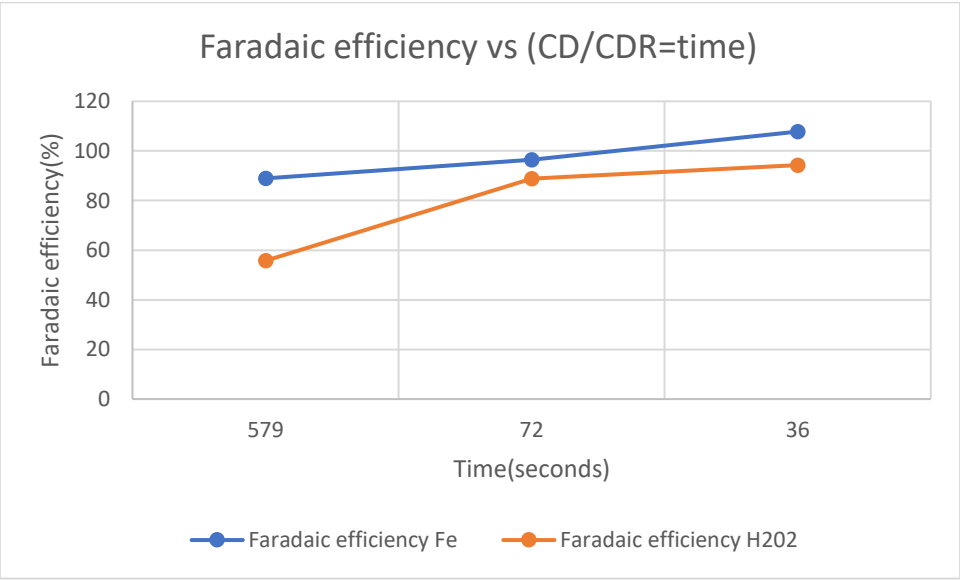

Figure 7: Variation of the faradaic efficiencies of H_2O_2 and Fe in percentage for [H_2O_2]=250µM & CDR=5C/L/min, 40C/L/min and 80C/L/min with calculated time interval in seconds

In figure 7, the increase in the faradaic efficiencies of both the Fe and H_2O_2 concentrations is steeper and hence, the rate of increase can be said to be faster than compared to figure 6. Efficiency has increased up to 107.78% in case of Fe and 94.28% in case of H_2O_2.

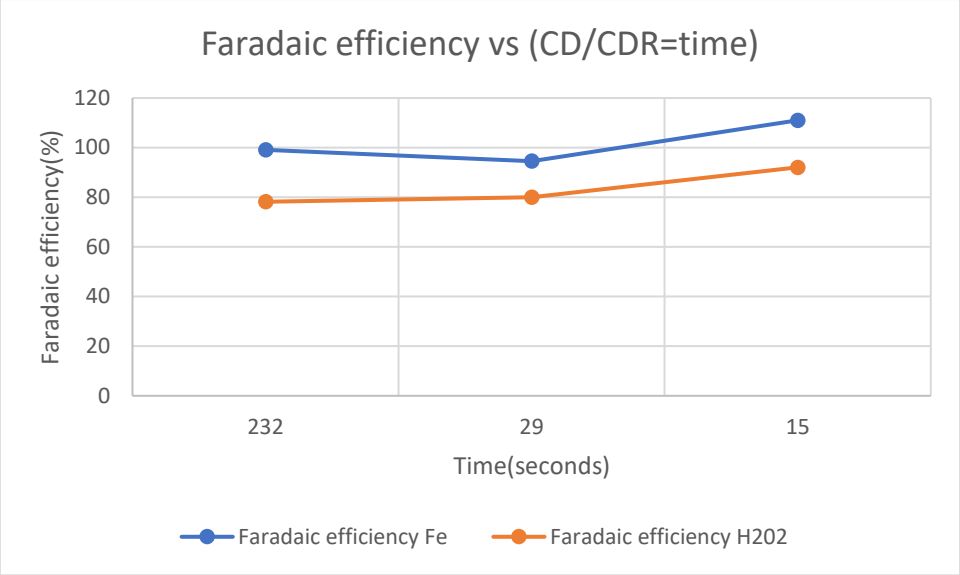

Figure 8: Variation of the faradaic efficiencies of H_2O_2 and Fe in percentage for $[H_2O_2]$=100µM & CDR=5C/L/min, 40C/L/min and 80C/L/min with calculated time interval in seconds

Figure 8 also shows the increase of the faradaic efficiency of Fe from 99.11% to 111.02% and that of H_2O_2 from 78.19% to 92.07%, as the CD/CDR ratio decreases, although the increase in the efficiencies is not so much.

Table 3: Average faradaic efficiencies of H_2O_2 and Fe for $[H_2O_2]$=500µM, $[H_2O_2]$=250µM and $[H_2O_2]$=100µM with calculated CDs

H2O2 concentrations	Faradaic efficiency Fe(Average)	Faradaic efficiency H202(Average)	CD(C/L)
H2O2= 500µM	98.72	68.05	96.5
H2O2= 250µM	97.72	79.61	48.22
H2O2= 100µM	101.71	83.41	19.28

Table 3 shows the average faradaic efficiencies for Fe and H_2O_2 at concentrations of 500 µM, 250 µM and 100 µM and at CDs 96.5 C/L, 48.22 C/L and 19.28 C/L respectively. Hence, also with the decrease in CD, there is overall increase in efficiencies in both the cases, from 98.72% to 101.71% for Fe and from 68.05% to 83.41% for H_2O_2. Therefore, about 15.36% increase in the faradaic efficiency of H_2O_2 is observed.

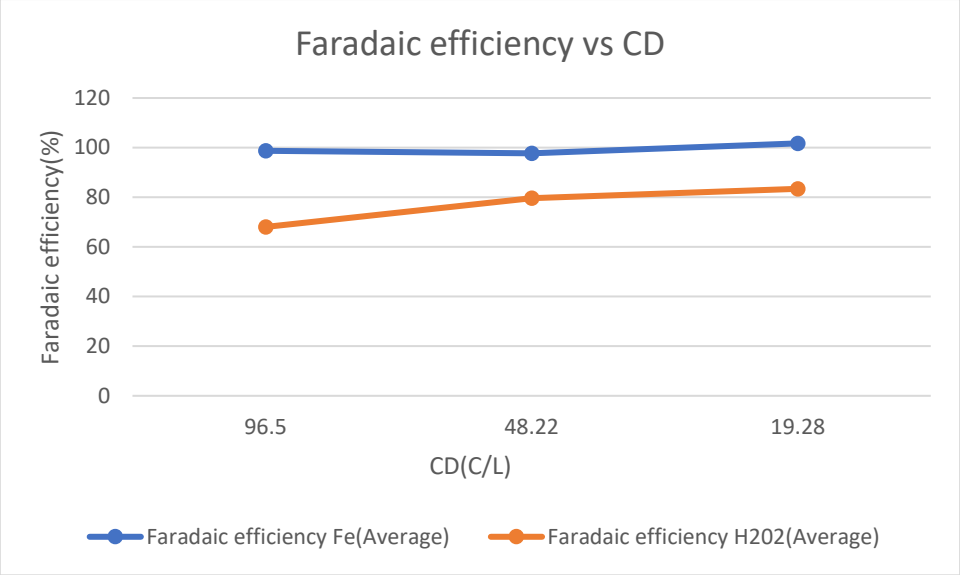

Figure 9 :The variation of the average faradaic efficiencies of H_2O_2 and Fe for $[H_2O_2]$=500µM, $[H_2O_2]$=250µM and $[H_2O_2]$=100µM with calculated CDs

In figure 9, the graphical depiction of what is shown in table 12 has been represented. We can say that there is an overall increase in the average faradaic efficiencies of H_2O_2 and Fe for all concentrations of H_2O_2=500µM, H_2O_2=250µM and H_2O_2=100µM with calculated CDs, decreasing from 96.5C/L, 48.22C/L to 19.28C/L respectively.

Chapter 5

5. Conclusion and Recommendations

The following points can be concluded and discussed based on the above results and the analysis of it:

- Yes! As the CDR increases, the faradaic efficiencies of both H_2O_2 and O_2 increases.

- The factors like little dilution, occuring due to acid/base addition, human error, current value being 0.001A-0.002A lower than the applied current value during the experiments must have reduced the faradaic efficiency of Fe.

- In theory;

  1 mole of H_2O_2 oxidizes 2 moles of Fe(II);

But there remains no oxygen to oxidize Fe(II) in anoxic condition, so there has to be some amount of H_2O_2 generated in the solution to oxidize it.

Total H_2O_2 (produced) = [(H_2O_2 used in Fe(II) oxidation)

+

(Dissolved H_2O_2concentration in the filtered sample)]

Hence, from this research, according to its challenges and limitations, while performing the experiments, the following future recommendations can be discussed :

- To investigate how the increase in the amount of Nacl dosed in the electrolyte solution increases to 7 g with the increase of CDR from 5 to 80 C/L/min.
- To see whether an inert anode, which doesn't corrode like Fe can be used in the chamber.
- To study the possibility of using some other form of cathode that can be used to generate H_2O_2 instead of this air cathode.
- To perform HPLC/ICP-MS with solutions highly containing As, to check how much As(III) is removed depending when the CDR is increased.(Appendix: table 22).

6. Acknowledgements

I am thankful to Dr. Ir. Doris van Halem for giving me this golden opportunity to work on this topic. Obliged to have all the conceptual discussions and guidance throughout the period of my additional thesis. Really grateful to Ir. Mrinal Roy for supervising me with the experiments, and for the constant support in guiding me amidst all sort of difficulty faced in the research work. Also thankful to the lab-in-charge Mr. Armand Middeldorp, Ms. Jane Erkemeij, Ms. Patricia van den Bos and Jasper Krijn for allowing me to use the Green Lab throughout my research period.

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8.Appendix

A) For [H_2O_2]=500µM=500*10^(-6)mol/L=500*10^(-6)*34.0147mol/L*g/mol

=>[H_2O_2]=0.017g/L=W= amount of H_2O_2 generated(mg/L);

Now, (1)=>W= qM/nF=>q=WnF/M=0.017*2*96485/(34.0147)g/L*C/mol*mol/g

=>q=96.5C/L=CD

For CDR= 5 C/L/min;

Time,t=CD/CDR=96.5/5min=18.7min=18min52sec or 1122sec

Also, (2)=> dq/dt= CDR= 5=i/V

=>i= dq/dt*V=5*1 C*L/(L*min*C/min)=5*1/(60) C*L/(L*sec*C/sec)

=>i=0.083A= applied current

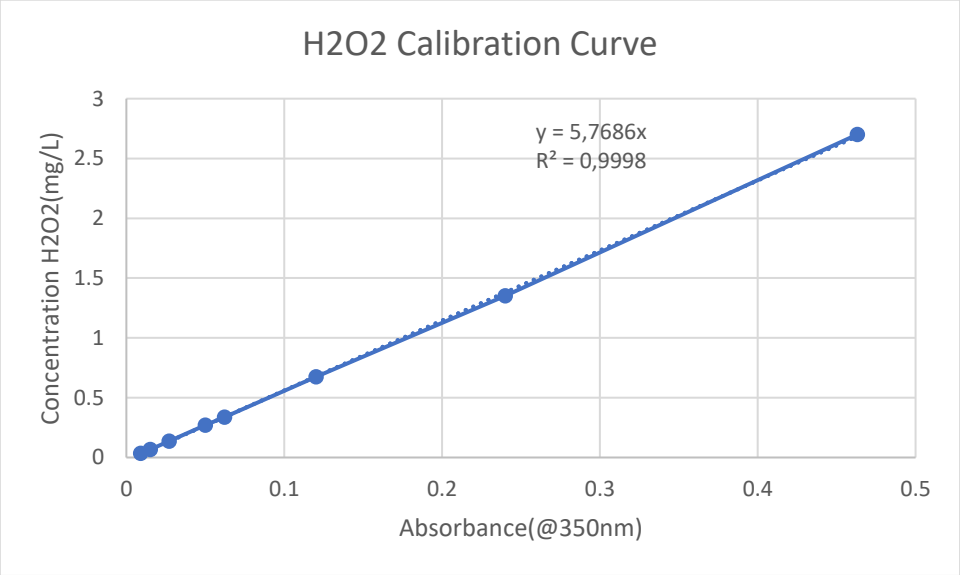

Figure 10: The H_2O_2 calibration curve obtained from the absorbance values measured in the spectrophotometer

Table 4:Faradaic efficiency of H_2O_2 and Fe for $[H_2O_2]$=500µM & CDR=5C/L/min

H2O2= 500µM CDR= 5C/L/min CD= 96.5C/L		i=0.083A	t=18min42sec		
H2O2					
Reading 1	Reading 2	Avg(mg/L)		µM	Faradaic efficiency
1.956	1.91	1.956		57.50	60.56
Fe					
Reading 1	Reading 2	Avg			
25.7	29.1	27.4		490.64	98.1

Table 4 shows that the faradaic efficiency of H_2O_2 is about 60.56% and that of Fe is 98.1% when it should have produced 500 µM of H_2O_2 concentration, at a CDR of 5C/L/min and CD=96.5C/L/min. The manner in which these efficiencies were calculated in each of the cases is described below:

We have now; produced Fe=27.4mg/L=$(26*10^3)$ /55.845µM=490.64 µM
But theoretically should have produced 500µM.
Hence, the faradaic efficiency of Fe=(490.64/500)*100%= 98.1%

Now, as 1 mole of H_2O_2 oxidizes 2 moles of Fe(II).

Hence; H_2O_2 used=490.64/2=245.32µM

Also dissolved sample contains=1.956mg/L=$1.956*10^3$ /(34.0147)=57.50 µM

Hence, total H_2O_2 generated= (245.32+57.50) µM=302.82µM

But theoretically should have produced 500µM.

Hence, the faradaic efficiency of H_2O_2 = (302.82/500)*100%=60.56%

Table 5 :Faradaic efficiency of H_2O_2 and Fe for [H_2O_2]=500µM & CDR=40C/L/min

H2O2= 500µM CDR= 40C/L/min CD= 96.5C/L		i=0.67A	t=2min25sec		
H2O2					
Reading 1	Reading 2	Avg(mg/L)		µM	Faradaic efficiency
2.11	3.33	2.72		79.96	67.26
Fe					
Reading 1	Reading 2				
28.6	28.67	28.635		512.75	102.5

Table 5 shows that the faradaic efficiency of H_2O_2 which is about 67.26% and that of Fe is 102.5% when it should have produced 500 µM of H_2O_2 concentration, at a CDR of 40C/L/min and CD=96.5C/L/min. It has been observed that the faradaic efficiencies of both the Fe and H_2O_2 have increased slightly by 4.4% and 6.7% respectively.

Table 6 :Faradaic efficiency of H_2O_2 and Fe for $[H_2O_2]$=500µM & CDR=80C/L/min

H2O2= 500µM CDR= 80C/L/min CD= 96.5C/L		i=1.33A	t=1min13sec		
H2O2					
Reading 1	Reading 2	Avg(mg/L)		µM	Faradaic efficiency
4.367	5.34	4.853		142.67	76.32
Fe					
Reading 1	Reading 2				
25.6	27.78	26.69		477.92	95.58

Table 6 shows that the faradaic efficiency of H_2O_2 which is about 76.32% and that of Fe is 95.58% when it should have produced 500 µM of H_2O_2 concentration, at a CDR of 80C/L/min and CD=96.5C/L/min. It has been observed that the faradaic efficiencies of both the H_2O_2 have increased by 9.06% respectively with respect to the case with same H_2O_2 concentration and CDR=5C/L/min, although there is a slight reduction of the faradaic efficiency of Fe, which is a little deviating from the ideal case where it should have increased based on the increased CDR. This might be due to some deviations in maintaining a stable pH between 7-7.5 range, throughout the experimental period, which might have had a considerable interference in the Fe oxidation processes.

Table 7 :Faradaic efficiency of H_2O_2 and Fe for $[H_2O_2]$=250µM & CDR=5C/L/min

H2O2= 250µM CDR= 5C/L/min CD= 48.22C/L		i=0.083A	t=9min39sec		
H2O2					
Reading 1	Reading 2	Avg(mg/L)		µM	Faradaic efficiency
0.9	1.02	0.96		28.22	55.75
Fe					
Reading 1	Reading 2	Avg			
12.43	12.4	12.415		222.31	88.94

Table 7 shows that the faradaic efficiency of H_2O_2 which is about 55.75% and that of Fe is 88.94% when it should have produced 250 µM of H_2O_2 concentration, at a CDR of 5C/L/min and CD=48.22C/L/min. These efficiencies seem to be a little lower than that of the case with 250 µM of H_2O_2 concentration and at a CDR of 5C/L/min. The CD is also reduced from 96.5C/L/min to 48.22C/L/min. For Fe, the faradaic efficiency reduced by 9.16% and for H_2O_2, the faradaic efficiency reduced by 4.81%.

Table 8 :Faradaic efficiency of H_2O_2 and Fe for $[H_2O_2]$=250µM & CDR=40C/L/min

H2O2= 250µM CDR= 40C/L/min CD= 48.22C/L		i=0.67A	t=1min12sec		
H2O2					
Reading 1	Reading 2	Avg(mg/L)		µM	Faradaic efficiency
3.044	3.857	3.45		101.42	88.79
Fe					
Reading 1	Reading 2	Avg			
14	12.93	13.465		241.11	96.44

Table 8 shows that the faradaic efficiency of H_2O_2 which is about 88.79% and that of Fe is 96.44% when it should have produced 250 µM of H_2O_2 concentration, at a CDR of 40C/L/min and CD=48.22C/L/min. It has been observed that the faradaic efficiencies of both the Fe and H_2O_2 have increased by 7.5% and 33.04% respectively. The increase in the faradaic efficiency of H_2O_2 is significant, and the increased CDR from 5C/L/min to 40C/L/min must have an influential implication to it.

Table 9 :Faradaic efficiency of H_2O_2 and Fe for $[H_2O_2]$=250µM & CDR=80C/L/min

H2O2= 250µM CDR= 80C/L/min CD= 48.22C/L		i=1.33A	t=36sec		
H2O2					
Reading 1	Reading 2	Avg(mg/L)		µM	Faradaic efficiency
3.33	3.54	3.435		100.98	94.28
Fe					
Reading 1	Reading 2	Avg			
14.9	15.2	15.05		269.49	107.78

Table 9 shows that the faradaic efficiency of H_2O_2 which is about 94.28% and that of Fe is 107.78% when it should have produced 250 µM of H_2O_2 concentration, at a CDR of 80C/L/min and CD=48.22C/L/min. It important to note that there has been an observed increase in the faradaic efficiencies of both the Fe and H_2O_2 by 18.04% and 38.53% respectively, with respect to the case with same H_2O_2 concentration and CDR=5C/L/min. The increase in the faradaic efficiency of H_2O_2 is significant, and the increased CDR from 5C/L/min to 40C/L/min must have an influential implication to it.

Table 10 :Faradaic efficiency of H_2O_2 and Fe for [H_2O_2]=100µM & CDR=5C/L/min

H2O2= 100µM CDR= 5C/L/min CD= 19.28C/L		i=0.083A	T=3min52sec		
H2O2					
Reading 1	Reading 2	Avg(mg/L)		µM	Faradaic efficiency
1	0.948	0.974		28.634	78.19
Fe					
Reading 1	Reading 2	Avg			
5.4	5.67	5.535		99.11	99.11

Table 10 shows that the faradaic efficiency of H_2O_2 which is about 78.19% and that of Fe is 99.11% when it should have produced 100 µM of H_2O_2 concentration, at a CDR of 5C/L/min and CD=5C/L/min. The CD is reduced from 48.22C/L/min to 19.28C/L/min and in ideal condition, the efficiency should reduce from that of table 5, instead there is a little increase in both the efficiencies of both Fe and H_2O_2.

Table 11 :Faradaic efficiency of H_2O_2 and Fe for $[H_2O_2]$=100µM & CDR=40C/L/min

H2O2= 100µM CDR= 40C/L/min CD= 19.28C/L		i=0.67A	T=29sec		
H2O2					
Reading 1	Reading 2	Avg(mg/L)		µM	Faradaic efficiency
1.124	1.103	1.113		32.72	79.99
Fe					
Reading 1	Reading 2	Avg			
4.89	5.67	5.28		94.547	94.55

Table 11 shows that the faradaic efficiency of H_2O_2 which is about 79.99% and that of Fe is 94.55% when it should have produced 100 µM of H_2O_2 concentration, at a CDR of 40C/L/min and CD=19.28C/L/min. It has been observed that the faradaic efficiencies of H_2O_2 has slightly increased by 1.8%, however for Fe it has decreased a bit by 4.56% respectively. Ideally both should increase, but again due to human error of maintenance of the circumneutral pH range, must have created such anomaly in case of Fe.

Table 12 :Faradaic efficiency of H_2O_2 and Fe for $[H_2O_2]$=100µM & CDR=80C/L/min

H2O2= 100µM CDR= 80C/L/min CD= 19.28C/L		i=1.33A	T=15sec		
H2O2					
Reading 1	Reading 2	Avg(mg/L)		µM	Faradaic efficiency
1.23	1.257	1.2435		36.56	92.07
Fe					
Reading 1	Reading 2	Avg			
6.6	5.8	6.2		111.02	111.02

Table 12 shows that the faradaic efficiency of H_2O_2 which is about 92.07% and that of Fe is 111.02% when it should have produced 100 µM of H_2O_2 concentration, at a CDR of 80C/L/min and CD=19.28C/L/min. It has been observed that the faradaic efficiencies of both Fe and H_2O_2 has increased by 11.91% and 13.88% respectively, when compared to table 8.

Table 13a) :First reading of the measured concentration of H_2O_2 in mg/L for $[H_2O_2]$=500µM and CDR=5C/L/min

H2O2= 500µM					
CDR= 5C/L/min					
CD= 96.5C/L	i=0.083A	t=18min42sec			
Reading 1					
H2O2 conc. Measurement	(in A)		Average	Final avg	(in mg/L)
Blank	0.000				
Initial unfiltered sample 1	0.015				
Initial unfiltered sample 2	0.015				
Initial unfiltered sample 3	0.002				
Final filtered sample 1	0.323	0.341	0.332		
Final filtered sample 2	0.330	0.346	0.338		
Final filtered sample 3	0.343	0.357	0.3475	0.3391	2

Table 13(b) :Second reading of the measured concentration of H_2O_2 in mg/L for $[H_2O_2]$=500µM and CDR=5C/L/min

Reading 2					
H2O2 conc. Measurement	(in A)		Average	Final avg	(in mg/L)
Blank	0.000				
Initial unfiltered sample 1	0.032				
Initial unfiltered sample 2	0.052	0.062			
Initial unfiltered sample 3	0.090	0.099			
Final filtered sample 1	0.310	0.320	0.315		
Final filtered sample 2	0.290	0.295	0.2925		
Final filtered sample 3	0.333	0.340	0.3365	0.315	1.91

Table 13(c) :First reading of the measured concentration of Fe in mg/L for $[H_2O_2]$=500µM and CDR=5C/L/min

Reading 1				
Iron concentration	(in mg/L)			Avg
Initial Sample Fe(T)	0	0	0	
Initial Sample Fe(II)	0	0	0	
Final filtered Fe(T)	0	0	0	
Final filtered Fe(II)	0	0	0	
Final unfiltered Fe(T)	25.7	25.7	25.7	25.7
Final unfiltered Fe(II)	0.2	0.2	0.2	

Table 13(d) :Second reading of the measured concentration of Fe in mg/L for [H_2O_2]=500µM and CDR=5C/L/min

Reading 2				
Iron concentration	(in mg/L)			Avg
Initial Sample Fe(T)	0.5	0.5	0.5	
Initial Sample Fe(II)	0.2	0.5	0.5	
Final filtered Fe(T)	0.1	0.1	0.1	
Final filtered Fe(II)	0	0	0	
Final unfiltered Fe(T)	29.2	29	29.1	29.1
Final unfiltered Fe(II)	0.8	0.7	0.8	

Table 14(a) :First reading of the measured concentration of H_2O_2 in mg/L for [H_2O_2]=500µM and CDR=40C/L/min

H2O2= 500µM						
CDR= 40C/L/min						
CD= 96.5C/L		i=0.67A	t=2min25sec			
	Reading 1					
	H2O2 conc. Measurement	(in A)		Average	Final avg	(in mg/L)
	Blank	0.000				
	Initial unfiltered sample 1	0.009				
	Initial unfiltered sample 2	0.010				
	Initial unfiltered sample 3	0.010				
	Final filtered sample 1	0.308	0.420	0.364		
	Final filtered sample 2	0.303	0.428	0.3655		
	Final filtered sample 3	0.314	0.425	0.3695	0.366	2.11

Table 14(b) :Second reading of the measured concentration of H_2O_2 in mg/L for [H_2O_2]=500µM and CDR=40C/L/min

Reading 2					
H2O2 conc. Measurement	(in A)		Average	Final avg	(in mg/L)
Blank	0.000				
Initial unfiltered sample 1	0.015				
Initial unfiltered sample 2	0.020	0.022			
Initial unfiltered sample 3	0.017	0.022			
Final filtered sample 1	0.488	0.491	0.4895		
Final filtered sample 2	0.666	0.670	0.668		
Final filtered sample 3	0.575	0.580	0.5775	0.578	3.33

Table 14(c) :First reading of the measured concentration of Fe in mg/L for [H_2O_2]=500µM and CDR=40C/L/min

Reading 1	(in mg/L)			Avg
Iron concentration				
Initial Sample Fe(T)	0	0	0	
Initial Sample Fe(II)	0.1	0.1	0.1	
Final filtered Fe(T)	0	0	0	
Final filtered Fe(II)	0	0	0	
Final unfiltered Fe(T)	28.6	28.6	28.6	28.6
Final unfiltered Fe(II)	0.3	0.3	0.3	

Table 14(d) :Second reading of the measured concentration of Fe in mg/L for [H_2O_2]=500µM and CDR=40C/L/min

Reading 2				
Iron concentration	(in mg/L)			Avg
Initial Sample Fe(T)	0.8	0.8	0.6	
Initial Sample Fe(II)	0.1	0.1	0.1	
Final filtered Fe(T)	0.2	0.2	0.2	
Final filtered Fe(II)	0.2	0.2	0.4	
Final unfiltered Fe(T)	28.6	28.7	28.7	28.67
Final unfiltered Fe(II)	0.7	0.5	0.7	

Table 15(a) :First reading of the measured concentration of H_2O_2 in mg/L for [H_2O_2]=500µM and CDR=80C/L/min

H2O2= 500µM					
CDR= 80C/L/min					
CD= 96.5C/L	i=1.33A	t=1min13sec			
Reading 1					
H2O2 conc. Measurement	(in A)		Average	Final avg	(in mg/L)
Blank	0.000				
Initial unfiltered sample 1	0.051	0.065			
Initial unfiltered sample 2	0.071	0.090			
Initial unfiltered sample 3	0.099	0.102			
Final filtered sample 1	0.606	0.655	0.63		
Final filtered sample 2	0.880	0.909	0.894		
Final filtered sample 3	0.746	0.752	0.749	0.757	4.367

Table 15(b) :Second reading of the measured concentration of H_2O_2 in mg/L for $[H_2O_2]$=500µM and CDR=80C/L/min

Reading 2					
H2O2 conc. Measurement	(in A)		Average	Final avg	(in mg/L)
Blank	0.000				
Initial unfiltered sample 1	0.055				
Initial unfiltered sample 2	0.080	0.089			
Initial unfiltered sample 3	0.077	0.078			
Final filtered sample 1	0.888	0.890	0.889		
Final filtered sample 2	0.998	0.999	0.9985		
Final filtered sample 3	0.890	0.898	0.894	0.927	5.34

Table 15(c) :First reading of the measured concentration of Fe in mg/L for $[H_2O_2]$=500µM and CDR=80C/L/min

Reading 1				
Iron concentration	(in mg/L)			Avg
Initial Sample Fe(T)	0.5	0.5	0.5	
Initial Sample Fe(II)	0.1	0.1	0.1	
Final filtered Fe(T)	0	0	0	
Final filtered Fe(II)	0	0	0	
Final unfiltered Fe(T)	25.6	25.6	25.6	25.6
Final unfiltered Fe(II)	0.2	0.2	0.2	

Table 15(d) :Second reading of the measured concentration of Fe in mg/L for $[H_2O_2]$=500µM and CDR=80C/L/min

Reading 2	(in mg/L)			Avg
Iron concentration				
Initial Sample Fe(T)	0.5	0.5	0.5	
Initial Sample Fe(II)	0.2	0.3	0.2	
Final filtered Fe(T)	0	0	0	
Final filtered Fe(II)	0	0	0	
Final unfiltered Fe(T)	27.8	27.7	27.8	27.78
Final unfiltered Fe(II)	0.9	0.9	0.9	

Table 16(a) :First reading of the measured concentration of H_2O_2 in mg/L for $[H_2O_2]$=250µM and CDR=5C/L/min

H2O2= 250µM					
CDR= 5C/L/min					
CD= 48.22C/L	i=0.083A	t=9min39sec			
Reading 1					
H2O2 conc. Measurement	(in A)		Average	Final avg	(in mg/L)
Blank	0.000				
Initial unfiltered sample 1	0.03	0.090			
Initial unfiltered sample 2	0.031	0.048			
Initial unfiltered sample 3	0.059	0.064			
Final filtered sample 1	0.155	0.159	0.157		
Final filtered sample 2	0.140	0.145	0.1425		
Final filtered sample 3	0.168	0.170	0.169	0.156	0.9

Table 16(b) :Second reading of the measured concentration of H_2O_2 in mg/L for $[H_2O_2]$=250µM and CDR=5C/L/min

Reading 2					
H2O2 conc. Measurement	(in A)		Average	Final avg	(in mg/L)
Blank	0.000				
Initial unfiltered sample 1	0.081	0.087			
Initial unfiltered sample 2	0.090	0.099			
Initial unfiltered sample 3	0.088	0.090			
Final filtered sample 1	0.199	0.202	0.2		
Final filtered sample 2	0.177	0.180	0.1785		
Final filtered sample 3	0.156	0.157	0.1565	0.178	1.02

Table 16(c) :First reading of the measured concentration of Fe in mg/L for $[H_2O_2]$=250µM and CDR=5C/L/min

Reading 1				
Iron concentration	(in mg/L)			Avg
Initial Sample Fe(T)	0.5	0.5	0.5	
Initial Sample Fe(II)	0.1	0.1	0.1	
Final filtered Fe(T)	0	0	0	
Final filtered Fe(II)	0	0	0	
Final unfiltered Fe(T)	12.4	12.5	12.4	12.43
Final unfiltered Fe(II)	0	0	0.1	

Table 16(d) :Second reading of the measured concentration of Fe in mg/L for [H_2O_2]=250µM and CDR=5C/L/min

Reading 2				
Iron concentration	(in mg/L)			Avg
Initial Sample Fe(T)	0.5	0.5	0.5	
Initial Sample Fe(II)	0.8	0.8	0.6	
Final filtered Fe(T)	0	0	0	
Final filtered Fe(II)	0.1	0.1	0.1	
Final unfiltered Fe(T)	12.3	12.4	12.5	12.4
Final unfiltered Fe(II)	0.3	0.3	0.3	

Table 17(a) :First reading of the measured concentration of H_2O_2 in mg/L for [H_2O_2]=250µM and CDR=40C/L/min

H2O2= 250µM						
CDR= 40C/L/min						
CD= 48.22C/L		i=0.67A	t=1min12sec			
	Reading 1					
	H2O2 conc. Measurement	(in A)		Average	Final avg	(in mg/L)
	Blank	0.000				
	Initial unfiltered sample 1	0.067	0.070			
	Initial unfiltered sample 2	0.078	0.080			
	Initial unfiltered sample 3	0.064	0.068			
	Final filtered sample 1	0.487	0.497	0.492		
	Final filtered sample 2	0.495	0.506	0.5		
	Final filtered sample 3	0.588	0.595	0.5915	0.527	3.044

Table 17(b) :Second reading of the measured concentration of H_2O_2 in mg/L for [H_2O_2]=250µM and CDR=40C/L/min

Reading 2					
H2O2 conc. Measurement	(in A)		Average	Final avg	(in mg/L)
Blank	0.000				
Initial unfiltered sample 1	0.080	0.082			
Initial unfiltered sample 2	0.088	0.090			
Initial unfiltered sample 3	0.066	0.070			
Final filtered sample 1	0.729	0.754	0.737		
Final filtered sample 2	0.666	0.670	0.668		
Final filtered sample 3	0.600	0.602	0.601	0.668	3.857

Table 17(c) :First reading of the measured concentration of Fe in mg/L for [H_2O_2]=250µM and CDR=40C/L/min

Reading 1				
Iron concentration	(in mg/L)			Avg
Initial Sample Fe(T)	0.4	0.4	0.5	
Initial Sample Fe(II)	0.2	0.2	0.1	
Final filtered Fe(T)	0	0	0	
Final filtered Fe(II)	0.4	0.3	0.3	
Final unfiltered Fe(T)	14	14	14	14
Final unfiltered Fe(II)	0.1	0.1	0.1	

Table 17(d) :Second reading of the measured concentration of Fe in mg/L for [H_2O_2]=250µM and CDR=40C/L/min

Reading 2				
Iron concentration	(in mg/L)			Avg
Initial Sample Fe(T)	0.7	0.7	0.6	
Initial Sample Fe(II)	0.1	0.2	0.1	
Final filtered Fe(T)	0	0	0	
Final filtered Fe(II)	0	0	0	
Final unfiltered Fe(T)	13	12.9	12.9	12.93
Final unfiltered Fe(II)	0.5	0.6	0.6	

Table 18(a) :First reading of the measured concentration of H_2O_2 in mg/L for [H_2O_2]=250µM and CDR=80C/L/min

H2O2= 250µM					
CDR= 80C/L/min					
CD= 48.22C/L	i=1.33A	t=36sec			
Reading 1					
H2O2 conc. Measurement	(in A)		Average	Final avg	(in mg/L)
Blank	0.000				
Initial unfiltered sample 1	0.090	0.099			
Initial unfiltered sample 2	0.080	0.085			
Initial unfiltered sample 3	0.086	0.088			
Final filtered sample 1	0.526	0.527	0.5265		
Final filtered sample 2	0.418	0.425	0.4215		
Final filtered sample 3	0.780	0.793	0.786	0.578	3.33

Table 18(b) :Second reading of the measured concentration of H_2O_2 in mg/L for $[H_2O_2]$=250µM and CDR=80C/L/min

Reading 2					
H2O2 conc. Measurement	(in A)		Average	Final avg	(in mg/L)
Blank	0.000				
Initial unfiltered sample 1	0.088	0.089			
Initial unfiltered sample 2	0.072	0.077			
Initial unfiltered sample 3	0.078	0.080			
Final filtered sample 1	0.555	0.566	0.5605		
Final filtered sample 2	0.777	0.778	0.777		
Final filtered sample 3	0.505	0.510	0.5075	0.615	3.54

Table 18(c) :First reading of the measured concentration of Fe in mg/L for $[H_2O_2]$=250µM and CDR=80C/L/min

Reading 1				
Iron concentration	(in mg/L)			Avg
Initial Sample Fe(T)	0.3	0.3	0.3	
Initial Sample Fe(II)	0	0	0	
Final filtered Fe(T)	0	0	0	
Final filtered Fe(II)	0	0	0	
Final unfiltered Fe(T)	14.9	14.9	14.9	14.9
Final unfiltered Fe(II)	0.3	0.3	0.3	

Table 18(d) :Second reading of the measured concentration of Fe in mg/L for $[H_2O_2]$=250µM and CDR=80C/L/min

Reading 2				
Iron concentration	(in mg/L)			Avg
Initial Sample Fe(T)	0.8	0.8	0.8	
Initial Sample Fe(II)	0.5	0.5	0.5	
Final filtered Fe(T)	0	0	0	
Final filtered Fe(II)	0	0	0	
Final unfiltered Fe(T)	15	15.3	15.3	15.2
Final unfiltered Fe(II)	0.8	0.8	0.8	

Table 19(a) :First reading of the measured concentration of H_2O_2 in mg/L for $[H_2O_2]$=100µM and CDR=5C/L/min

H2O2= 100µM					
CDR= 5C/L/min					
CD= 19.28C/L	i=0.083A	t=3min52sec			
Reading 1					
H2O2 conc. Measurement	(in A)		Average	Final avg	(in mg/L)
Blank	0.000				
Initial unfiltered sample 1	0.058	0.060			
Initial unfiltered sample 2	0.052	0.054			
Initial unfiltered sample 3	0.053	0.055			
Final filtered sample 1	0.160	0.163	0.1615		
Final filtered sample 2	0.181	0.185	0.183		
Final filtered sample 3	0.175	0.177	0.176	0.1735	1

Table 19(b) :Second reading of the measured concentration of H_2O_2 in mg/L for $[H_2O_2]$=100µM and CDR=5C/L/min

Reading 2					
H2O2 conc. Measurement	(in A)		Average	Final avg	(in mg/L)
Blank	0.000				
Initial unfiltered sample 1	0.050	0.050			
Initial unfiltered sample 2	0.058	0.060			
Initial unfiltered sample 3	0.056	0.058			
Final filtered sample 1	0.156	0.158	0.157		
Final filtered sample 2	0.163	0.165	0.164		
Final filtered sample 3	0.171	0.173	0.172	0.164	0.948

Table 19(c) :First reading of the measured concentration of Fe in mg/L for $[H_2O_2]$=100µM and CDR=5C/L/min

Reading 1				
Iron concentration	(in mg/L)			Avg
Initial Sample Fe(T)	0.5	0.5	0.5	
Initial Sample Fe(II)	0	0	0	
Final filtered Fe(T)	0.4	0.4	0.4	
Final filtered Fe(II)	0.5	0.3	0.2	
Final unfiltered Fe(T)	5.5	5.5	5.5	5.5
Final unfiltered Fe(II)	0.3	0.3	0.3	

Table 19(d) :Second reading of the measured concentration of Fe in mg/L for [H_2O_2]=100µM and CDR=5C/L/min

Reading 2				
Iron concentration	(in mg/L)			Avg
Initial Sample Fe(T)	0.6	0.5	0.7	
Initial Sample Fe(II)	0	0	0	
Final filtered Fe(T)	0	0	0	
Final filtered Fe(II)	0	0	0	
Final unfiltered Fe(T)	5.7	5.7	5.6	5.67
Final unfiltered Fe(II)	0.4	0.4	0.5	

Table 20(a) :First reading of the measured concentration of H_2O_2 in mg/L for [H_2O_2]=100µM and CDR=40C/L/min

H2O2= 100µM						
CDR= 40C/L/min						
CD= 19.28C/L		i=0.67A	t=29sec			
	Reading 1					
	H2O2 conc. Measurement	(in A)		Average	Final avg	(in mg/L)
	Blank	0.000				
	Initial unfiltered sample 1	0.038	0.039			
	Initial unfiltered sample 2	0.055	0.057			
	Initial unfiltered sample 3	0.055	0.058			
	Final filtered sample 1	0.190	0.192	0.191		
	Final filtered sample 2	0.198	0.200	0.199		
	Final filtered sample 3	0.194	0.196	0.195	0.195	1.124

Table 20(b) :Second reading of the measured concentration of H_2O_2 in mg/L for [H_2O_2]=100µM and CDR=40C/L/min

Reading 2					
H2O2 conc. Measurement	(in A)		Average	Final avg	(in mg/L)
Blank	0.000				
Initial unfiltered sample 1	0.033	0.035			
Initial unfiltered sample 2	0.056	0.058			
Initial unfiltered sample 3	0.080	0.082			
Final filtered sample 1	0.186	0.188	0.187		
Final filtered sample 2	0.197	0.199	0.198		
Final filtered sample 3	0.188	0.190	0.189	0.191	1.103

Table 20(c) :First reading of the measured concentration of Fe in mg/L for [H_2O_2]=100µM and CDR=40C/L/min

Reading 1				
Iron concentration	(in mg/L)			Avg
Initial Sample Fe(T)	0.5	0.5	0.5	
Initial Sample Fe(II)	0	0	0	
Final filtered Fe(T)	0.2	0.1	0.1	
Final filtered Fe(II)	0	0	0	
Final unfiltered Fe(T)	4.8	4.9	4.9	4.89
Final unfiltered Fe(II)	0.5	0.6	0.6	

Table 20(d) :Second reading of the measured concentration of Fe in mg/L for [H_2O_2]=100µM and CDR=40C/L/min

Reading 2				
Iron concentration	(in mg/L)			Avg
Initial Sample Fe(T)	0.4	0.4	0.4	
Initial Sample Fe(II)	0	0	0	
Final filtered Fe(T)	0.3	0.3	0.1	
Final filtered Fe(II)	0	0	0	
Final unfiltered Fe(T)	5.6	5.7	5.7	5.67
Final unfiltered Fe(II)	0.1	0	0.1	

Table 21(a) :First reading of the measured concentration of H_2O_2 in mg/L for [H_2O_2]=100µM and CDR=80C/L/min

H2O2= 100µM					
CDR= 80C/L/min					
CD= 19.28C/L	i=1.33A	t=15sec			
Reading 1					
H2O2 conc. Measurement	(in A)		Average	Final avg	(in mg/L)
Blank	0.000				
Initial unfiltered sample 1	0.057	0.060			
Initial unfiltered sample 2	0.057	0.060			
Initial unfiltered sample 3	0.060	0.062			
Final filtered sample 1	0.201	0.203	0.202		
Final filtered sample 2	0.207	0.209	0.208		
Final filtered sample 3	0.233	0.235	0.234	0.214	1.23

Table 21(b) :Second reading of the measured concentration of H_2O_2 in mg/L for $[H_2O_2]$=100µM and CDR=80C/L/min

Reading 2					
H2O2 conc. Measurement	(in A)		Average	Final avg	(in mg/L)
Blank	0.000				
Initial unfiltered sample 1	0.066	0.082			
Initial unfiltered sample 2	0.087	0.89			
Initial unfiltered sample 3	0.078	0.081			
Final filtered sample 1	0.233	0.235	0.234		
Final filtered sample 2	0.216	0.222	0.219		
Final filtered sample 3	0.200	0.202	0.201	0.218	1.257

Table 21(c) :First reading of the measured concentration of Fe in mg/L for $[H_2O_2]$=100µM and CDR=80C/L/min

Reading 1				
Iron concentration	(in mg/L)			Avg
Initial Sample Fe(T)	0.8	0.6	0.8	
Initial Sample Fe(II)	0	0	0	
Final filtered Fe(T)	0	0	0	
Final filtered Fe(II)	0	0	0	
Final unfiltered Fe(T)	6.6	6.6	6.6	6.6
Final unfiltered Fe(II)	0.2	0.2	0.2	

Table 21(d) :Second reading of the measured concentration of Fe in mg/L for $[H_2O_2]$=100µM and CDR=80C/L/min

Reading 2				
Iron concentration	(in mg/L)			Avg
Initial Sample Fe(T)	0.6	0.6	0.7	
Initial Sample Fe(II)	0.4	0.4	0.4	
Final filtered Fe(T)	0.8	0.5	0.8	
Final filtered Fe(II)	0.2	0.2	0.1	
Final unfiltered Fe(T)	5.8	5.8	5.8	5.8
Final unfiltered Fe(II)	0.2	0.2	0.3	

Table 22 :Parameters considered with same follow up experiments but adding 500µg/L As(III) and 100µM of Fe(II) as a stock solution for CDR=5C/L/min and CDR=80C/L/min for both anoxic and aerobic situations

As(III) in µg/L	Fe(II) in µM	CDR (C/L/min)	Time (min & sec)	Current i (Ampere)
500	100	5	3min52sec	0.083
500	100	80	15sec	1.33