



DEPARTAMENTO DE INGENIERÍA QUÍMICA
FACULTAD DE CIENCIAS Y TECNOLOGÍAS QUÍMICAS
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DEVELOPMENT OF CLEANING TECHNOLOGIES FOR SAFE WATER SUPPLY FROM HIGHLY-POLLUTED SOURCES

MEMORIA

que para optar al grado de Doctor en Ingeniería Química por la Universidad de
Castilla-La Mancha presenta

JULIA ISIDRO ELVIRA

Directores:

Dra. Cristina Sáez Jiménez

Dr. Javier Llanos López

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Dña. Cristina Sáez Jiménez, Catedrática de Ingeniería Química de la Universidad de Castilla-La Mancha, y

D. Javier Llanos López, Profesor Titular de Ingeniería Química de la Universidad de Castilla-La Mancha

CERTIFICAN

Que el presente trabajo de investigación titulado: “DEVELOPMENT OF CLEANING TECHNOLOGIES FOR SAFE WATER SUPPLY FROM HIGHLY-POLLUTED SOURCES”, constituye la memoria que presenta **Dña. Julia Isidro Elvira** para aspirar al grado de Doctor por la Universidad de Castilla-La Mancha en el programa de doctorado de Ingeniería Química y Ambiental, y que ha sido realizado en los laboratorios del Departamento de Ingeniería Química de la Universidad de Castilla-La Mancha bajo su dirección.

Y para que conste a los efectos oportunos, firman el presente certificado en Ciudad Real a 30 de Enero de 2020.

Dña. Cristina Sáez Jiménez

D. Javier Llanos López

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C. Sáez, J. Isidro, E. Mena, J. Llanos, J. Lobato, P. Cañizares, M.A. Rodrigo. *Disinfection of highly fecal-polluted surface waters through the CabECO process.* 10th World Congress of Chemical Engineering. Barcelona. Octubre 2017. Oral.

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J. Isidro, C. Sáez, J. Llanos, P. Cañizares, M.A. Rodrigo. *Testing and comparing different commercial electrochemical cells for water supply disinfection.* XXXIX Meeting GE-RSEQ & 3rd E3 Mediterranean Symposium. Madrid. Julio 2018. Poster.

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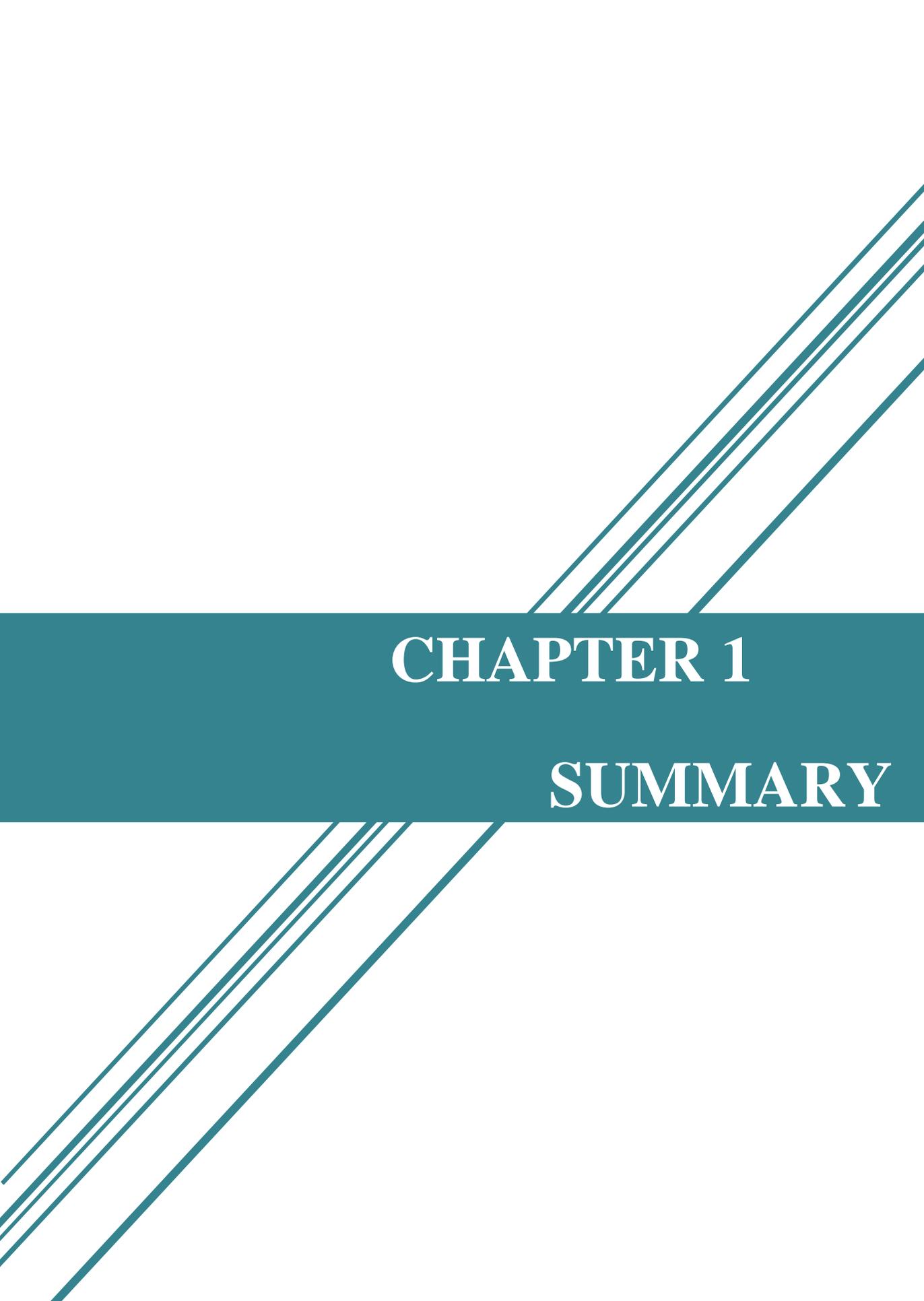
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CHAPTER 1

SUMMARY

Provide safe water is one of the main challenges faced by Humankind nowadays. Even more important than energy or food, water is the key element for life. Human beings need for water and because of climate change and of anthropogenic activity (industry, farming, etc.) it is getting more and more difficult to find reservoirs with high quality. This situation is becoming dramatic in regions with periodic droughts and, because of that, currently reclaiming of wastewater is becoming a key topic in search of a robust supply of water in developed countries. Likewise, this situation is also important in many rural areas in which the lack of high-quality water causes important health and social problems and, unfortunately, prevents the economic growth. Thus, the search for high-quality reservoirs of water and/or the development of technologies that can improve the quality of water is a topic of major interest.

In this context, SafeWaterAfrica H2020 project focuses on a major challenge in African countries: In the 15 sub-Saharan African countries 108 million people have limited or even no access to clean water. In this sense, the project aims to develop a low-cost solution, easy to handle and operate for rural and peri-urban areas of South Africa and Mozambique, at the same time highly efficient in the degradation of harmful pollutants and very effective in killing microbiological contaminants. The project includes capacity building and business development so that system ownership and responsibility are in the hands of the local rural communities. The joint European-African development results in a low-cost solution easy to handle and operate. To do this, ten transdisciplinary partners from Europe and Africa, assisted by eight enterprises and organisations in the Advisory Board, have worked jointly over a project duration of 42 months to *provide high-quality water to rural population in African countries by the development of the complete chain value of a new process based on the electrolytic treatment of water with anodes of doped diamond.*

Within this H2020 project, the role of the Electrochemical and Environmental Engineering Laboratory and, therefore, of this PhD thesis, was to *evaluate if the electrochemical technology developed by CONDIAS GmbH (German partner) is efficient in the treatment of low-quality surface water (fecal-polluted) and to design, if there is a necessity, auxiliary treatment system with the premises of being compact and low cost (made with cheap materials), easy to manipulate and easy to be*

connected to clean energy sources. This global objective has been divided into five partial objectives that have been assessed in Chapter 5.

Initially, in section 5.1, three different commercial cells of the same manufacturer (CONDIAS GmbH): ECWP[®], CabECO[®] and MIKROZON[®], were tested in order to determine which of them have the best prospected for water disinfection. The cells are equipped with the same diamond anodes, but their mechanical design is completely different, varying not only by geometry but also by flow conditions. The first one is an undivided cell (ECWP[®]) meanwhile the other two are PEM-electrolyzers in which the electrolyte that separates the anode and cathode is a proton exchange membrane. Design and sizing parameters give an advantage to these last cells (CabECO[®] and MIKROZON[®]): the production of chlorates and perchlorates can be minimized when operating in a single-pass mode, which becomes a really remarkable point. In addition, the short hydraulic residence time (0.008 s for 90 L h⁻¹, which is the maximum allowable flowrate) in MIKROZON[®] cell allows to avoid the production of perchlorate and to enhance its behaviour. Nevertheless, CabECO[®] cell was chosen as the most suitable for South African applications regarding its robustness and long durability.

Consequently, in section 5.2 CabECO[®] cell was evaluated in more detail for the disinfection of highly fecal-polluted surface water. Firstly, disinfection tests were carried out in a discontinuous mode to evaluate the influence of the electrode current charge passed. The effect of the current density was also studied in order to optimize the disinfection conditions and to simultaneously prevent the formation of undesirable by-products (chlorates and perchlorates) during the electrolysis. Results demonstrated that this technology is robust and efficient, and it can suitably disinfect water. During electrolysis, the chloride contained in the water was oxidized to hypochlorite, and this compound was combined with ammonia to form chloramines. Both hypochlorite and chloramines (formed by the well-known break point reaction) promoted persistent disinfection and seemed to be mainly responsible for the disinfection attained during the electrochemical process. Chlorate and perchlorate could also be produced, although the low concentrations of chloride in the tested water made them irrelevant. The removal of the total organic carbon under the applied operating conditions was not very efficient (although it reached 50% in two hours) and the production of trihalomethanes was very low, below 100 ppb for all tests. Secondly, CabECO[®]

electrochemical cell was evaluated in continuous mode. Results showed that this cell is very efficient in the removal of Total Coliforms and *Pseudomonas Aeruginosa* and it can achieve decays up to 4-log units when treating 90 L h⁻¹ with a single cell (only 24 cm² of diamond electrode). Efficiency of the disinfection depends on the current charge applied and neither organo-chlorinated species nor perchlorates are formed at the conditions evaluated. A two-log unit sterilization can be attained with the technology, which shows worse prospects for this application than for disinfection. However, electrode fouling caused by strongly polluted water may diminish the disinfection efficiency and it can even prevent the use of this technology in those cases.

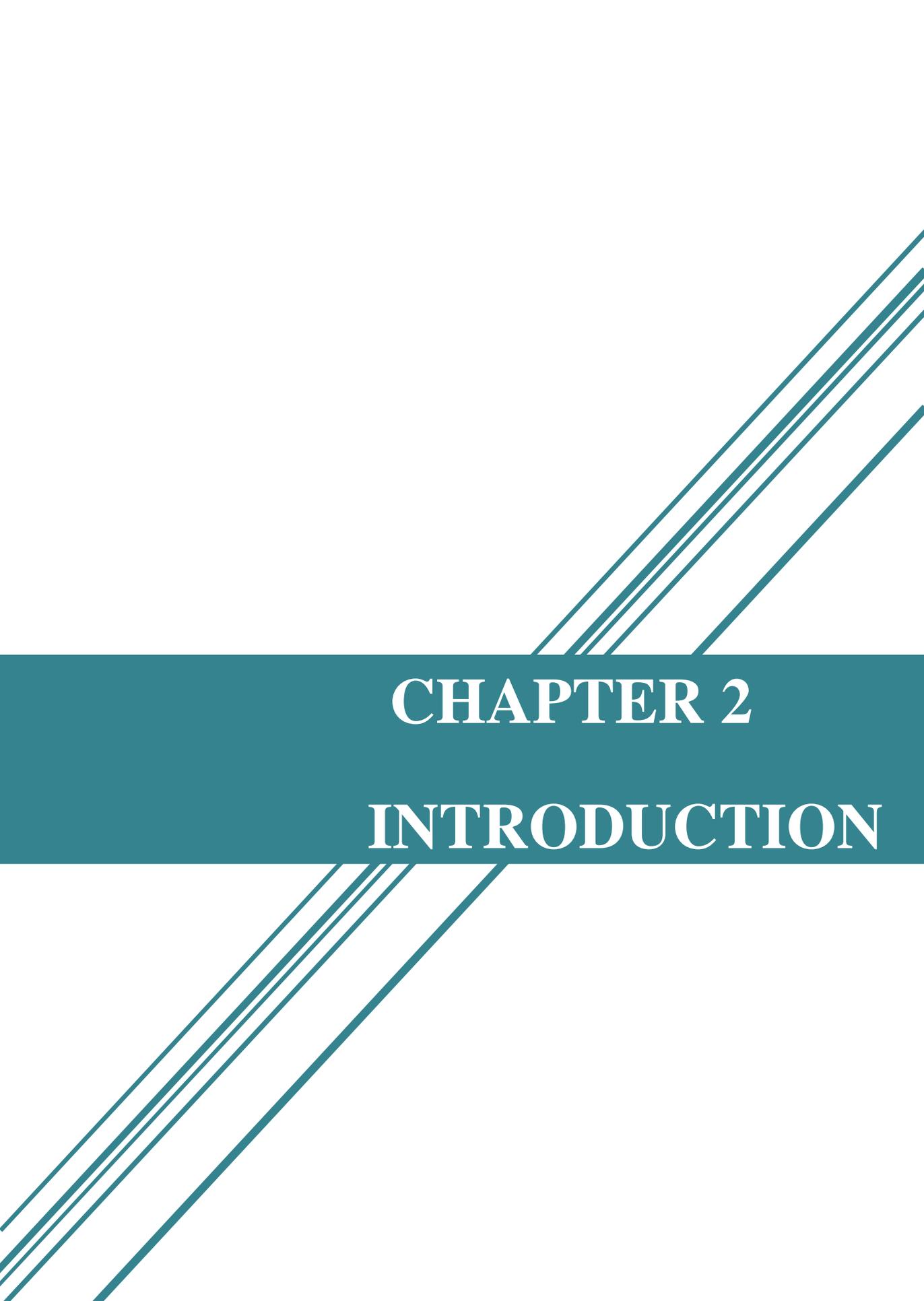
In view of the previous arguments, in section 5.3 a pre-disinfection treatment was developed in order to guarantee the efficiency and durability of the electrochemical disinfection process. That is especially suited for highly polluted surface water and is based on the combination of coagulation-flocculation, lamellar sedimentation and filtration into a single-column unit, in which the interconnection between treatments is an important part of the overall process. The new system, the so-called PREDICO (PRE-DIinfection Column) system, was built with low-cost consumables from hardware stores (in order to promote in-house construction of the system in poor countries) and was tested with a mixture of 20% raw wastewater and 80% surface water (in order to simulate an extremely fecal-polluted stream, typical from South-African countries). Results confirmed that PREDICO system helps to avoid fouling in later electro-disinfection processes and attains a remarkable degree of disinfection (3-4 log units), which supplements the removal of pathogens attained by the electrolytic cell (more than 4 log units). The most important sizing parameters for the PREDICO system are the surface loading rate (SLR) and the hydraulic residence time (HRT); SLR values under 20 cm min⁻¹ and HRT values over 13.6 min in the PREDICO system are suitable to warrant efficient performance of the system.

At that point, it was addressed the design of new electrocoagulation approaches to dose iron coagulants and, thus to avoid the need for the storage and dosing of iron-based chemicals. Two different reactors were constructed following the same principles: low cost materials, easy to handle and operate. The first of them, named as Electrochemically-Assisted Coagulant - Production & Dosing Unit (ECU)

exhibited an efficient performance in the dosing of coagulants regardless of the ionic conductivity of the water matrixes tested (within the range $100 \mu\text{S cm}^{-1}$ to $1000 \mu\text{S cm}^{-1}$), covering a wide range of potential real surface waters. The behaviour of the ECU device was compared to that of a conventional chemical dosing of iron, showing a better pH (pH around 8 for ECU but lower than 4 for equivalent chemical dosing) and conductivity (decrease for ECU but increase up to 60% for equivalent chemical dosing) control. Moreover, the ECU unit produced a noticeable amount of Fe^{2+} ions, due to the limited access of atmospheric oxygen inside the device. The ECU system was sized so that it can provide the typical amount of coagulant required for the treatment of a typical surface water. Thus, after being developed, and delivered the first test carried out in the SafeWaterAfrica prototype demonstrated that because of the special characteristic of the South African water sources, an upscaling was required. Then, a different design was proposed and called the improved ECU (i-ECU). It integrates an easy to manipulate iron dissolving (in order to allow an easy replacement of iron sheets), capable of producing iron (II), a venturi device to oxidize iron (II) to iron (III) just at the inlet of the coagulation chamber of the PREDICO.

Finally, in section 5.4 PREDICO system was re-adapted for the treatment of matrix of water completely different of those that had been designed. In this case, groundwater was selected in order to check the flexibility of the system and its capability to face the treatment not only of highly-polluted surface-water but also of a typical groundwater. A pre-treatment focused on the softening of the water was applied and, thus, the high concentrations of calcium and magnesium, and nitrates (related to farm activities) were the most relevant parameters to be adjusted. At that point, two ion exchange resins beds were introduced, one cationic for removal calcium and magnesium and one anionic for replacing nitrates by chlorides. These beds substituted the sand & GAC filters of the original PREDICO. In addition, the coagulation chamber was transformed into a reaction chamber by changing the coagulant dosing by lime dosing, contributing to a better performance of the softening of the water treated. Moreover, it was done another set of experiments in which the performance of CabECO[®] and MIKROZON[®] cells for the disinfection of the pre-treatment effluents were studied, in order to determine if the pre-treatment was enough enough. Results obtained were satisfactory and allowed to confirm that the PREDICO technology can be easily transformed in order to face successfully the pre-

treatment of groundwater, obtaining water with good quality to be disinfected with the technology developed in the SafeWaterAfrica project.



CHAPTER 2

INTRODUCTION

Historically, water has been regarded as an infinity resource. Even more important than energy or food, water is the key element for life. In contrast, the natural water reservoirs have been massively exploited without taking into account the devastating consequences that this fact could cause. Thus, since a few years ago the availability of good quality water has become a problem of a major significance. This problem is associated with pollution caused by human activities related to the development of modern society, as well as abruptly changing rain patterns and more extreme drought periods in many regions due to climate change.

In addition, water use and consumption has increased at twice the rate of population growth, highlighting the large gap between population development and water demand, so that water has gone from being an infinitely available resource to a scarce one in many countries. In this way, the Food and Agriculture Organization of the United Nations (FAO) established “Clean Water and Sanitation” one of the Sustainable Development Goals (SDG) due to the increasing water stress worldwide. The water stress (showing in the Figure 2.1), determined as the ratio of total fresh water withdrawn to the total renewable freshwater resources country or region, after considering the water needed for sustaining the natural environment, affects countries on every continent.

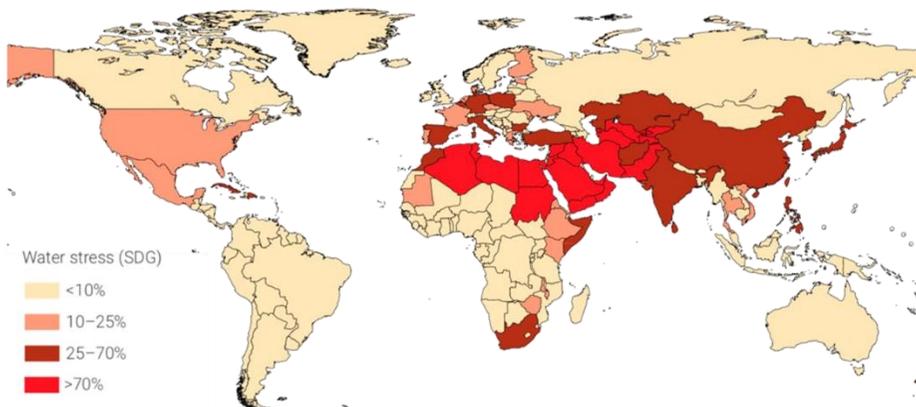


Figure 2.1. World Water Stress map (FAO, 2019).

As shown in Figure 2.1, water stress is over 60% in Western Asia, Central Asia and North Africa, which means that these regions face severe water stress, at least during some parts of the year. These difficulties are typically addressed by making use

of non-conventional water resources, such as wastewater reuse, desalinated water and direct use of agricultural drainage water. In these regions, and particularly in the most affected subregions, efforts must be made to reduce water withdrawal by increasing productivity and efficiency in the use of water resources.

However, most other regions are below this threshold and most remain well below the 25 per cent threshold of initial water stress, up to which there is potential to increase water use by people and the economy in a sustainable manner. Further analysis at the country level reveals that 23 countries experience water stress of more than 70 per cent, while 15 countries extract more than 100 per cent of their renewable freshwater resources.

From 2000-2017, the global population using at least basic drinking water services increased by 1.7 billion people, or 0.48 percentage points per year (WHO, 2019). In 2017, 71 per cent of the global population (5.3 billion people) used a safely managed drinking water service; that is, an improved drinking water source located on premises, available when needed and free from contamination. On the other hand, 785 million people still lacked even a basic drinking water service, defined as drinking water from an improved source, provided collection time is not more than 30 minutes for a round trip. This includes 144 million people who collect untreated surface water for drinking. This data corresponded in the majority of cases with rural areas in which the lack of high-quality water causes important health and social problems and, unfortunately, prevents the economic growth. The most of this people lived in rural areas of developing countries (WHO, 2019). In the Figure 2.2 is shown a map of the rural population which use at least basic sanitation services.

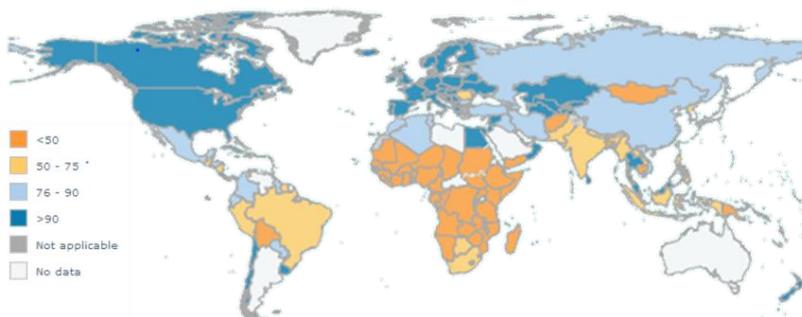


Figure 2.2. Rural population using at least basic sanitation services (%),2017. (WHO, 2019).

According to the WHO/UNICEF Joint Monitoring Programme for Water Supply and Sanitation, at least 1.2 billion people worldwide are estimated to drink water that is not protected against contamination from faeces. Thereby, unclean water join with a poor sanitation services are leading cases of child mortality. Only the diarrhoea is estimated to cause 1.5 million child deaths per yerar, mostly among childer under five living in developing countries.

In addition to the health problems, the issue of rural water supply has a strong gender dimension, as it is women and girls who take primary responsibility for water collection in more than 75% of rural households in developing countries (WHO, 2010). They also bear the disproportionate burden of care when children or family members become ill from unsafe water. This has a negative impact on the time that women and girls can devote to education and economic activities, which has a substantial impact on their human rights, as well as on local economic development.

The search for high-quality reservoirs of water and/or the development of technologies that can improve the quality of water is a topic of major interest.

2.1 Drinking Water Treatment Plants (DWTP)

In order to be used safely, water should be properly treated before being consumed. Currently, surface water and groundwater are the two major sources of drinking water. The treatment depends on the source of water because the characteristics of water obtained from surface water reservoirs has nothing to do with those of groundwater reservoirs.

Surface water, originating from lakes, artificial reservoirs, rivers or wetlands, naturally contains sediments and organic species, such as humic and fulvic acids. The concentrations of each of these pollutants strongly depend on the level of the eutrophication of the source and the hydrodynamic characteristics of the water catchment area. Consequently, surface water may be turbid. In addition, in rural areas, farming may cause fecal pollution of the water sources. In several countries farming is seriously affecting the quality of fresh water reservoirs used for human supply, thus necessitating the oversizing of the typical technologies used to obtain the drinking water or even designing new types of treatment technologies capable of addressing fecal pollution.

Groundwater refers to all the water occupying the voids, pores and fissures within geological formations, which originated from atmospheric precipitation either directly by rainfall infiltration or indirectly from rivers, lakes or canals. Thus, its composition is determined by the geological nature of the soil. This water is constantly in contact with the ground in which it stagnates or circulated, so equilibrium develops between the composition of the soil and that of the water: i.e. water that circulates in a sandy or granitic substratum is acidic and has a few minerals. Water that circulates in limestone contains bicarbonates alkalinity. Even so, regardless of the source of groundwater is often high in mineral content such as magnesium and calcium salts, iron and manganese depending on the chemical composition of the stratum through which the rock flows.

Then, it is common to find treatment schemes consisting of the sequence coagulation-flocculation-sedimentation-filtration in the first case of the treatment of Surface water and aeration-ion exchange in the case of ground water. Figure 2.3 shows a typical scheme of a Drinking Water Treatment Plant (DWTP)

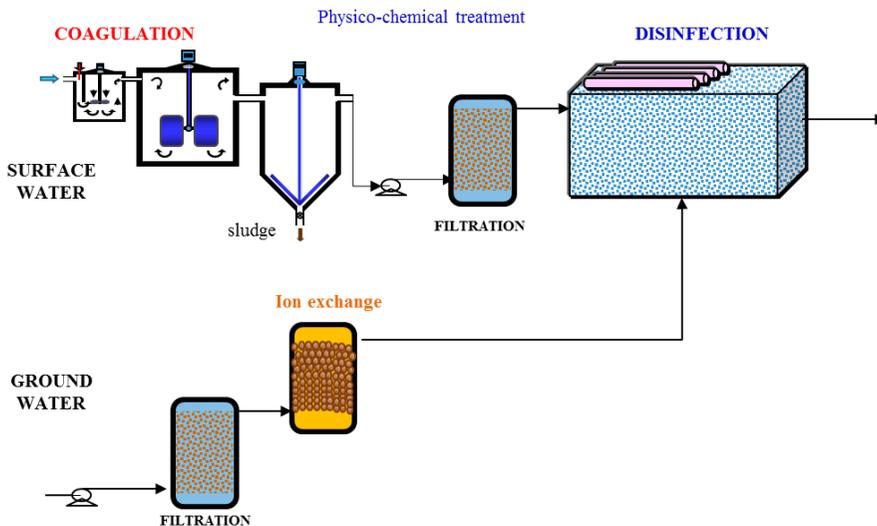


Figure 2.3. Typical scheme of drinking water treatment plant.

The operating mode of a DWTP, shown in Figure 2.3., can have different configurations depending on the quality of the water of origin and the desired final quality: However, they are all governed by common principles, which are described below:

a) **Roughing:** aims to remove the coarse solids in the source water. This operation protects the station from possible obstructions or difficulties in treatment due to coarse solids. This elimination is done by means of roughing grids, in which the solids will be trapped. The grids can have different configurations of size, disposition or inclination.

b) **Coagulation:** removes dirt and other particles suspended in water. Alum and other chemicals are added to water to form tiny sticky particles called “floc” which attract the dirt particles. The combined weight of the dirt and the alum (floc) become heavy enough to sink to the bottom during sedimentation.

Drinking water, in different quantities, contains suspended material, solids that can settle at rest, or dispersed solids that do not settle easily. A considerable part of these non-settling solids may be colloids. In colloids, particles are stabilized by a series of charges of the same sign on their surface, causing two neighboring particles to be repelled as two magnetic poles are repelled. Since this prevents the particles from colliding and thus forming larger masses, called flocs, the particles do not settle. Coagulation is the process by which suspended colloidal particles are destabilized to promote agglomeration by the addition of chemical coagulants and mixing energy. The chemicals cancel out the electrical charges on the surface of the colloid allowing the colloidal particles to agglomerate forming flocs. The coagulation not only removes turbidity, but also the concentration of organic matter and some of the microorganisms. The coagulant dose is an important parameter to calculate since an inadequate dose can interfere negatively on the functioning of the flocculation, coagulation and sedimentation or clarification units.

Similar effects can be achieved by electrocoagulation, when a current is applied to dissolve iron (or steel) or aluminium anodes immersed in contaminated water. Therefore, the electrocoagulation technique (or electrochemically assisted coagulation) can be defined as an electrochemical process in which, from compounds coming from the dissolution of an anode, the colloidal matter existing in a waste water is grouped, making it possible to separate it by conventional solid-liquid separation techniques (decantation, flotation). Hence, it can be said that it differs from conventional coagulation in the way the reagent is added, since in conventional

coagulation it is added in the form of salts while in electrocoagulation (Figure 2.4) it is generated from a metal.

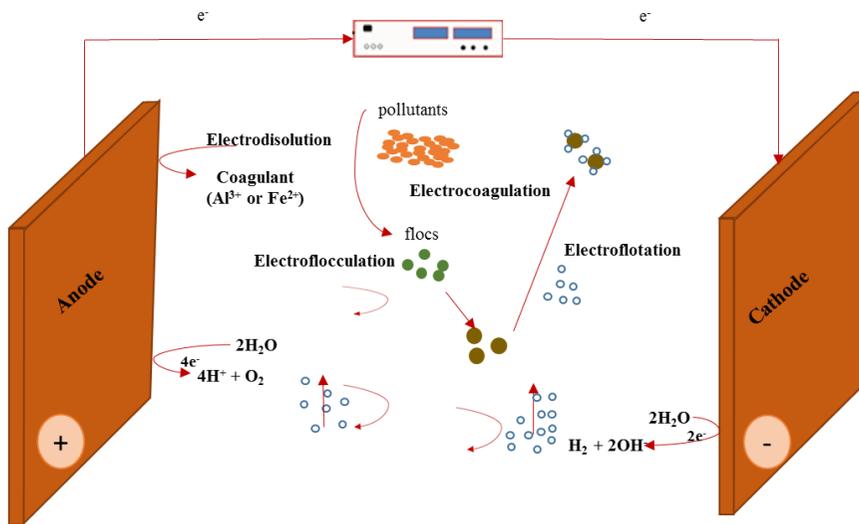


Figure 2.4. Process involved in an electrocoagulation reactor (Martínez, 2007).

c) **Flocculation:** is the agglomeration of destabilized particles into micro-flocs and then into flocs. Two types are distinguished; pericinetic flocculation and orthokinetic flocculation. In the first one the agglomeration is produced by the natural movement of the water molecules, known as Brownian movement. The second is based on the collisions of particles due to the movement of water induced by an external energy, and can be of mechanical or hydraulic origin. Flocculants are polymers or polyelectrolytes with very high molecular weights that can be of various natures; mineral, organic or synthetic.

d) **Sedimentation:** consists of the separation through gravity of suspended particles of greater density than water. One could speak of clarification instead of sedimentation, since the product required is water, and not the solids that are deposited at the bottom.

e) **Filtration:** in this stage the small particles that have not been extracted in the previous processes are retained. It is therefore a refining process. Once the water has been decanted, it will go through a filtration stage to finish the clarification process, eliminating the particles, which are retained in the filtering medium, forming a porous

bed, through which the fluid circulates, called the filtering medium. The filter is usually made up of silica or anthracite sand of different granulometries. Expanded shale or activated carbon can be used as a refining material, so that, in addition to retaining the suspended matter, it will adsorb particles capable of producing odour and taste in the water.

f) Disinfection: as seen in Figure 2.3, regardless the different treatment technologies, there is a common final post treatment in all cases, the disinfection, which becomes the key process for a safe use of water (Bebelis et al., 2013). This treatment consists of killing pathogens and warrant that they will not be present in water during its consumption. Currently, there are many technologies in-use such as chlorination (with hypochlorite, chlorine, chlorine dioxide or chloramines), UV disinfection and ozonation. Among them, electrolysis can be considered as emerging technology with very promising results and very different processes, which range from the electrocoagulation to the electrochemical oxidation of chlorides to yield chlorine, passing through the production of different oxidant such as ozone or ferrates.

Currently there are multiple methodologies to detect microbial contamination of water. However, the high costs that they represent, the analysis times and isolation in culture of microorganisms, have been an obstacle to establish the microbial quality of water for human consumption. The use of microorganisms that are bioindicators of water quality reduces costs and facilitates the implementation of efficient measures for the treatment and control of water and diseases associated with its transmission. Drinking water, defined as "suitable for human consumption and for all normal domestic uses, including personal hygiene", must be free from disease-causing microorganisms.

Microbiological indicators of water quality are organisms that behave similarly to pathogenic microorganisms whose origin, concentration, habitat and reaction to external factors are the same as most other organisms. Their presence determines the existence of pathogens and makes it possible to compare their reactions to changes in pH and temperature or the application of physical or chemical means of disinfection, with the advantage of being more easily cultivated or identified, and economically feasible (Rios-Tobon et al., 2017).

The main bioindicators established throughout the world include fecal coliforms, *Escherichia Coli*, and *Enterococcus*, although the abundance of *Escherichia Coli* has been more associated with health risk compared to the rest of the coliforms (Larrea- Murrell et al, 2013). However, with the new technologies and different studies around the world, it has been possible to show that other microorganisms such as *Pseudomonas Aeruginosas*, *Fecal Streptococci*, *Norovirus* and *Cryptosporidium*. have a better behavior as bioindicators and could optimize the diagnosis of drinking water treatment plants and systems.

Escherichia Coli is the main indicator of fecal matter in water. It is a type of bacteria that lives in the intestine of both people and warm-blooded animals. It is one of the most common causes of several common bacterial infections in humans and animals such as enteritis, urinary tract infection, septicaemia, and other clinical infections such as neonatal meningitis (Allocati et al, 2013).

Pseudomonas Aeruginosa, an opportunistic pathogen naturally present in the environment, is not classified as a pathogen in its own right, although it can cause disease in people with impaired defence mechanisms. Consumption of water containing large numbers of this microorganism can lead to a variety of infections. The importance of *Pseudomonas* became greater when its capacity to inhibit coliforms, being the most used water contamination indicators in the world, was proven. There is a great risk of consuming water with a zero coliform index, which could be inhibited by *Pseudomonas* (Soares et al., 1996).

2.1.1 Disinfection technologies

The disinfection technique using chlorine and/or chlorinated products is the most widely used method for the disinfection of drinking water. It is based on the addition of chlorine, or one of its derivatives (hypochlorite or chlorine dioxide) to the water. After a time of contact, the inactivation of the pathogenic microorganisms takes place. But this technique has a number of disadvantages:

- Unpleasant smell and taste in the drinking water.
- Ineffectiveness against certain types of resistant microorganisms.
- Chlorinated trihalomethanes are produced in the presence of organic matter.

In recent years, there has been an accumulation of data showing that exposure to

trihalomethanes is associated with an increased risk of cancer, especially of the bladder, and reproductive disorders (Villanueva et al., 2001 and Koivusalo et al., 1999). Among trihalo methanes, chloroform generation is the most common by-product of disinfection (Komulainen et al., 1997 and Driedger et al., 2000).

These disadvantages have prompted the search for alternative methods of disinfection. The most important of these are shown below:

-Ozonization (O_3) is one of the strongest oxidants available in drinking water treatment. Although it has been applied principally for disinfection, it has been also used for the removal of suspended solids, the oxidation of organic materials, odor control and sludge processing (Robson et al., 1985). Ozone is generated on-site because it has a comparatively short half-life in either its normal gaseous form or when dissolved in water. Ozone for full scale applications is generated by passing a filtered, dried, oxygen-bearing gas (ambient air, high-purity oxygen, or oxygen-enriched air) through a gap between two electrodes across which a high-voltage electrical current is maintained. The rate of ozone generation is controlled by varying either the voltage or frequency of the applied power. Due to its short half-life in water, it can not be considered as a persistent disinfectant.

-Ultraviolet disinfection is a physical process in which ultraviolet energy is absorbed in the DNA of microorganisms, causing structural changes in it that prevent microorganism from propagating. The peak absorption wavelength for DNA is between 250 and 265 nm. Low-pressure mercury lamps, which emit approximately 85% of their output energy at 253.7 nm, are the most efficient and effective source of ultraviolet radiation for disinfection systems. The use of ultraviolet radiation is an effective method of disinfecting drinking water. One of its principal advantages is that it leaves no residual in the treated water. The economics of the process depend on site-specific conditions. The effectiveness of ultraviolet disinfection is directly related to the dose (quantity of energy) absorbed by microorganism. The dose is the product of the rate at which energy is delivered (intensity) and the time of exposure to this intensity. Required doses (equally reported in units of $uW\text{-s}/cm^2$) are quite variable, depending on the water characteristics and the disinfection goal. Contact time are typically short (1 minute or less). As it is the case for ozone, it is not a persistent disinfectant as it does not leave any residual dose in water.

Chemical disinfection technologies, such as chlorination or ozonation, present different drawbacks that limit their application. The formation of disinfection by-products and the loss of disinfection efficiency through the presence of organic matter are crucial when considering chemical disinfection technologies (Arapoglou et al., 2003; Kinani et al., 2016; Pan et al., 2016; Li et al., 2017b). Physical disinfection processes, such as UV irradiation, membrane separation and thermal disinfection, are associated with high costs and maintenance efforts and do not fulfil the requirements for primary and residual water disinfection. For this reason, the electrochemical generation of desinfectants species is becoming more important in the recent decades.

2.2 Electrochemical generation of desinfectants species for disinfection processes

Electrochemical disinfection, also called “Electrodisinfection”, consists of the direct electrolysis of the water to be disinfected without the addition of chemicals. It is based on the production of oxidants from the oxidation of anions directly contained in the raw water or wastewater, such as chloride, sulphate, phosphate or carbonate (Canizares et al., 2009). These powerful oxidants can attack microorganisms and remove them from the stream. The energy is introduced by applying, by means of a direct current power supply, a potential difference between two conductive elements called electrodes, which are inserted in the liquid, as shown in Figure 2.5. The two electrodes are connected to a DC power supply, which causes a transport of electrons from the anode to the cathode. The electrode connected to the negative pole of the power supply is called the cathode, and the reduction (electronic transfer from the electrode) takes place there. The electrode connected to the positive pole is called the anode, where oxidation (electronic transfer to the electrode) takes place.

Figure 2.5. shows a diagram of an electrochemical cell, where the direction of the electron current can be seen, as well as the cathode and the anode and the reduction and oxidation reactions:

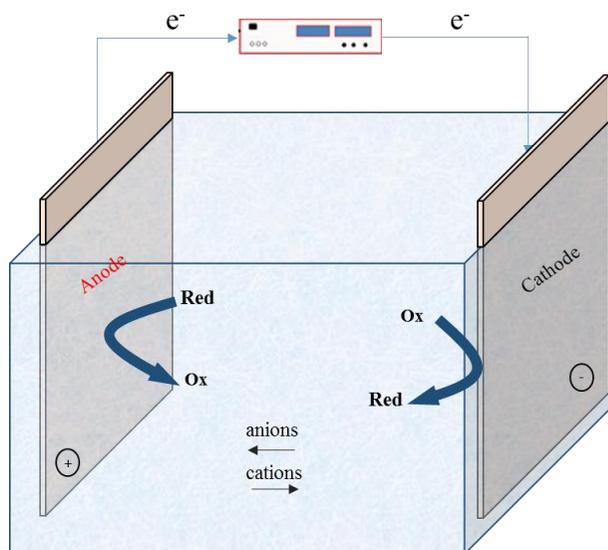
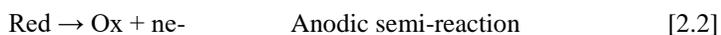
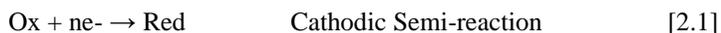


Figure 2.5. Electrochemical cell scheme.

To maintain the charge balance, it is necessary that inside the cell there is charge transport, this implies the existence of ions: anions, which transport the negative charges towards the anode, and cations, which transport the positive ones towards the cathode, originating the following semi-reactions that take place inside the cell (Eq. 2.1-2.2):



Depending on the oxidizing / reducing agent that causes the redox reaction, the electrolytic reactions are classified into the following types:

- Direct reactions: the electronic transfer to the product of interest takes place directly on the electrode surface (Figure 2.6. a).

- Indirect reactions: the electronic transfer takes place to an oxidising or reducing agent, usually inorganic, which subsequently reacts chemically with the compound of interest. These reactions can in turn be classified as reversible or

irreversible, depending on whether or not the oxidising or reducing agent can be returned to its initial state. (Figure 2.6.b).

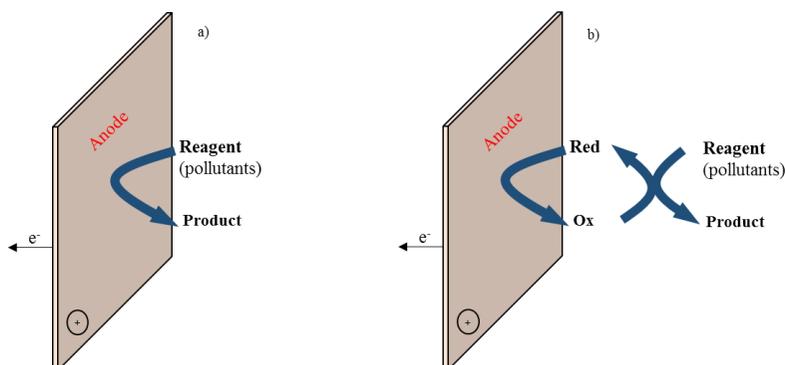


Figure 2.6. a) Direct electrochemical reaction. b) Indirect electrochemical reaction.

In recent years, disinfection systems have been developed for conventional water treatment, as the advantages of this procedure make it more attractive than other methods. Disinfection using electrochemical technology is environmentally friendly, low cost, easy to operate and capable of inactivating a wide range of microorganisms, bacteria, viruses or algae (Rajeshwar et al., 1997). In addition, it has a number of operational advantages over other traditional technologies:

- The main element needed to carry out the reactions is the electron. For this reason, the addition of chemical reagents is limited, which means minimising the cost of these and the production of waste, as well as reducing the costs of transport and storage of the same.

- The experimental equipment is simple and allows the process to be easily automated because the variables handled by the electrochemical reactors are easily measured and manipulated (current intensity and potential difference).

- These are highly energy-efficient processes, which means they have lower energy requirements than other processes.

- Electrochemical processes generally take place at atmospheric pressure and ambient temperature.

In this context, electrodesinfection or electrochemical disinfection is defined as an electrolysis that aims to eliminate pathogenic microorganisms contained in the

water. The microorganisms can be inactivated either directly or by generating active chemical species, such as free radicals or other ions. Direct inactivation involves the electro-adsorption of the microorganism on the surface of the electrode and its consequent destruction (Matsunaga et al, 1994).

The direct and indirect processes that occur are not always identifiable, and it is possible that, in many of the studies carried out at present, both play a significant role. That is why, given the complexity of the process, several hypotheses are developed regarding the mechanisms of elimination of microorganisms, some of which are (Patermarakis et al., 1990):

- If low voltages are used (5 - 15 V) the elimination of microorganisms is achieved by the formation of species such as chlorine, hypochlorite, hypochlorous acid, chlorine dioxide or bromide species (if Cl^- or Br^- are present in the water to be treated).
- The electric field directly causes the destruction of the microorganisms, what is due to the electrochemical oxidation of the intracellular coenzyme A (CoA), which decreases the breathing of the microorganism and generates the consequent cell death.
- The formation of radicals (active oxygen atoms produced on the anode, as well as HO_2^- ; OH^- and Ozone) can be responsible for disinfection if high voltages are used. These agents are highly active, but very unstable and short-lived.
- The carbonate and sulfate ions present in water can be oxidized on the anode to form percarbonates or persulphates which are excellent oxidizing agents for bacteria.
- The dissolution of the electrode material into solution can also be responsible for disinfection (especially metal ions in transition such as copper and silver).

Figure 2.7. shows an outline of the processes that can occur simultaneously in an electrodesinfection reactor: A crucial factor in this electrochemical process is the choice of the anodic material, which can be of various materials such as: DDB (Boron-Doped Diamond), AI (stainless steel), iron and aluminum, MMO (Metal Mixed Oxide electrodes) or carbon felt.

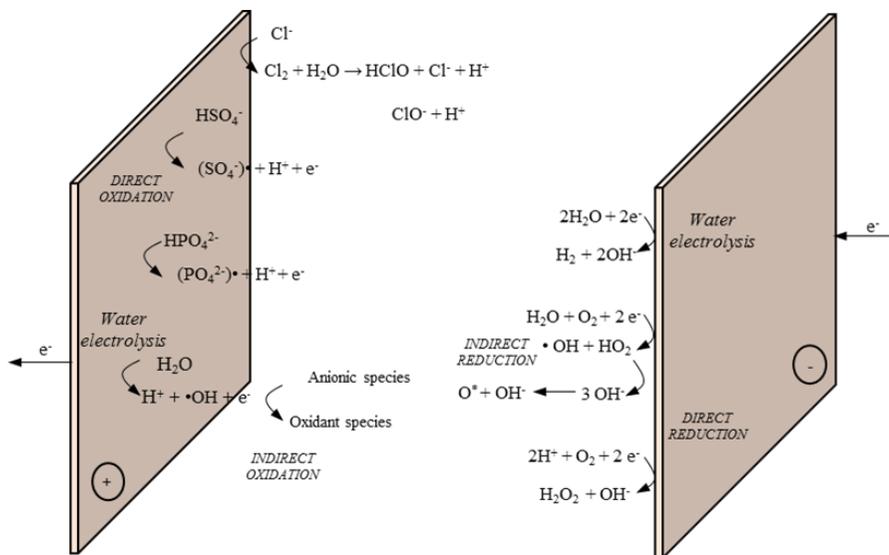


Figure 2.7. Electrochemical generation of microorganism deactivating agents.

2.2.1 Bored Doped Diamond Electrodes

The appearance of conductive diamond as an anodic material meant an important advance in the Advanced Oxidation Processes (AOP's), due to the high activity that it presents in the oxidation of contaminating organic compounds, which means a great advance in water treatment. In addition to the production of oxidants in the anode from anions contained in the water, some also produce oxidants in the cathode (Velazquez-Pena et al., 2013). In this way, reactions occur at the cathode such as the production of hydrogen peroxide by reducing the oxygen produced at the anode, which normally saturates the water during electrolysis (Valero et al., 2017) and the formation of other oxidants such as ozone (Heim et al., 2015; Rajab et al., 2015), must be included in the compounds that contribute to the disinfection action of the system.

Diamond electrodes are prepared by depositing a layer of diamond on a substrate, which is usually silicon, whose function is to favour the flow of current to the deposited electrode and serve as a mechanical support. The electrode materials must have good chemical and electrochemical stability, high mechanical resistance, a low coefficient of thermal expansion and good thermal and electrical conductivities (Carey et al., 1995). Diamond has all these properties, except that of electrical conductivity, so

it must be subjected to a doping treatment so that it can be used for electrochemical purposes. This treatment is usually done by adding B_2H_6 (Fujimori et al., 1990) or $B(CH_3O)$ (Ran et al., 1993 and Fryda et al., 1999), thus making the diamond an electrically conductive material, which makes it suitable for electrochemical processes. After the doping process, the diamond retains most of the physical-chemical properties it initially possessed and three other electrochemically interesting properties are added (Hupert et al., 2003):

- High thermal conductivity. It makes the diamond an almost perfect conductor of heat, facilitating the processes of dissipation of thermal energy generated by the Joule effect and, in turn, protecting the electrode from possible structural changes.

- High electrochemical stability. DDB does not suffer chemical attacks by water components, unlike other materials used in electrooxidation that compete with it, such as lead and tin oxides.

- Wide electrochemical window: these electrodes make it possible both to achieve high yields and to develop processes that would be masked by water oxidation with other electrodes.

Unfortunately, electrochemical disinfection using DDB electrodes can lead to the appearance of highly oxidized chlorine species, chlorates and perchlorates (Bergmann et al., 2009), under certain operating conditions, which have a possible carcinogenic effect on humans. In addition, the reaction of halogenated species with organic molecules produces the reaction of formation of organically adsorbable halogens (AOX) and trihalomethanes.

Nowadays, commercial electrochemical cells are being studied, being objective to find a water disinfection technology that does not generate harmful compounds for health, making it suitable for human consumption. In order to study the disinfection efficiency of these cells, two pathogen indicators can be quantified: Total Coliforms and *Pseudomonas Aeruginosa*. In addition, total aerobic microorganisms can also be studied in order to evaluate, in addition to the disinfection efficiency, the sterilisation efficiency.

2.2.2 Electrochemical cells

The electrochemical reactor should be considered as the heart of any electrochemical process and flow cell design has been the focus of much electrochemical engineering effort over the last forty years (Walsh and Ponce de Leon, 2018). Due to the requirement of a uniform current and potential distribution in most electrolysis reactors, the use of a cell geometry with a constant inter-electrode gap between anode and cathode, is a characteristic alternative employed in parallel plate electrochemical reactors. Decreasing the inter-electrode gap distance between anode and cathode can, however, create problems with hold up of gaseous or two-phase solid-liquid electrode products. For a particular application, differences in design arise from the desire to minimise energy consumption, increase reactor productivity, and maintain high selectivity. In processes in which the electroactive species is diluted or the conductivity of the solution is low, different measures such as refurbishment of the electrolyte or the use of three-dimensional electrodes have to be considered. The reactor designs are, however, a consequence of a number of earlier academic approaches seasoned by practical experience in academia and industry. The essential components of an electrochemical cell are the electrodes (number and type), the anodic and cathodic compartment separators (porous spacers, diaphragms or membranes) and the turbulence promoters (elements that favour the transport of products to and from the electrodes). Different reactor designs are illustrated in Figure 2.8.

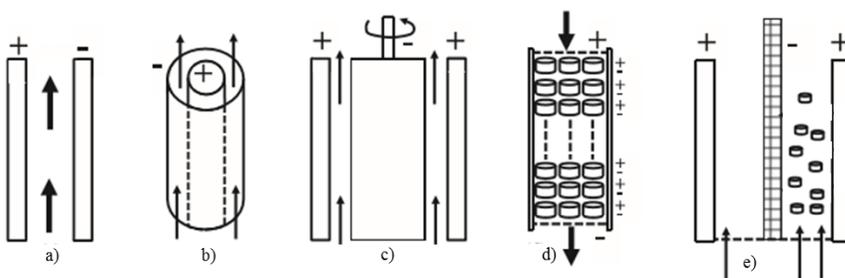


Figure 2.8. Principal types of undivided reactor design. a) parallel plate electrodes in a rectangular flow channel, b) concentric cylindrical electrodes, c) rotating cylinder. d) trickle tower containing 3-D electrode layers and e) active fluidised bed electrode. Adapted from

Walsh and Ponce de Leon, 2018.

The versatile parallel plate geometry (filter-press) is one of the most widely used for wastewater treatment (Cornejo et al., 2020). Nevertheless, it should be able to generate suitable turbulence conditions to promote mass-transfer processes from the bulk solution to the electrode surface, where electrochemical reaction takes place. Therefore, the simple parallel plate geometry is frequently enhanced by inclusion of porous, 3-dimensional electrodes, structured electrode surfaces and bipolar electrical connections, with necessary consideration of the reaction environment, especially potential and current distributions, uniformity of flow and mass transport rates, electrode activity, side reactions and current leakage.

In the recent years several commercial electrochemical cell designs have been developed following the filter press structure (e.g. ElectroCell ABTM, ICITM, DiaCell[®]) that allow minimizing the distance between the electrodes and improving the electrolyte turbulence, and thus the transport of matter to the electrode. Additionally, within the general design philosophy of filter press cells, new reactors with different electrode configuration have been developed. They are based on: concentric and rotating cylindrical electrodes, bipolar trickle towers containing 3-D electrode layers and active fluidised bed electrodes. These types of reactors are reported to enhance the performance of the traditional technologies in some cases (Walsh and Ponce de Leon, 2018). In addition, recently new electrochemical cells based on polymer exchange membrane (PEM) technology has been developed to be specially used in disinfection processes. In these cells the electrolyte that allows to close the ionic circuit is not the water but a PEM, which is directly connecting the anode and the cathode.

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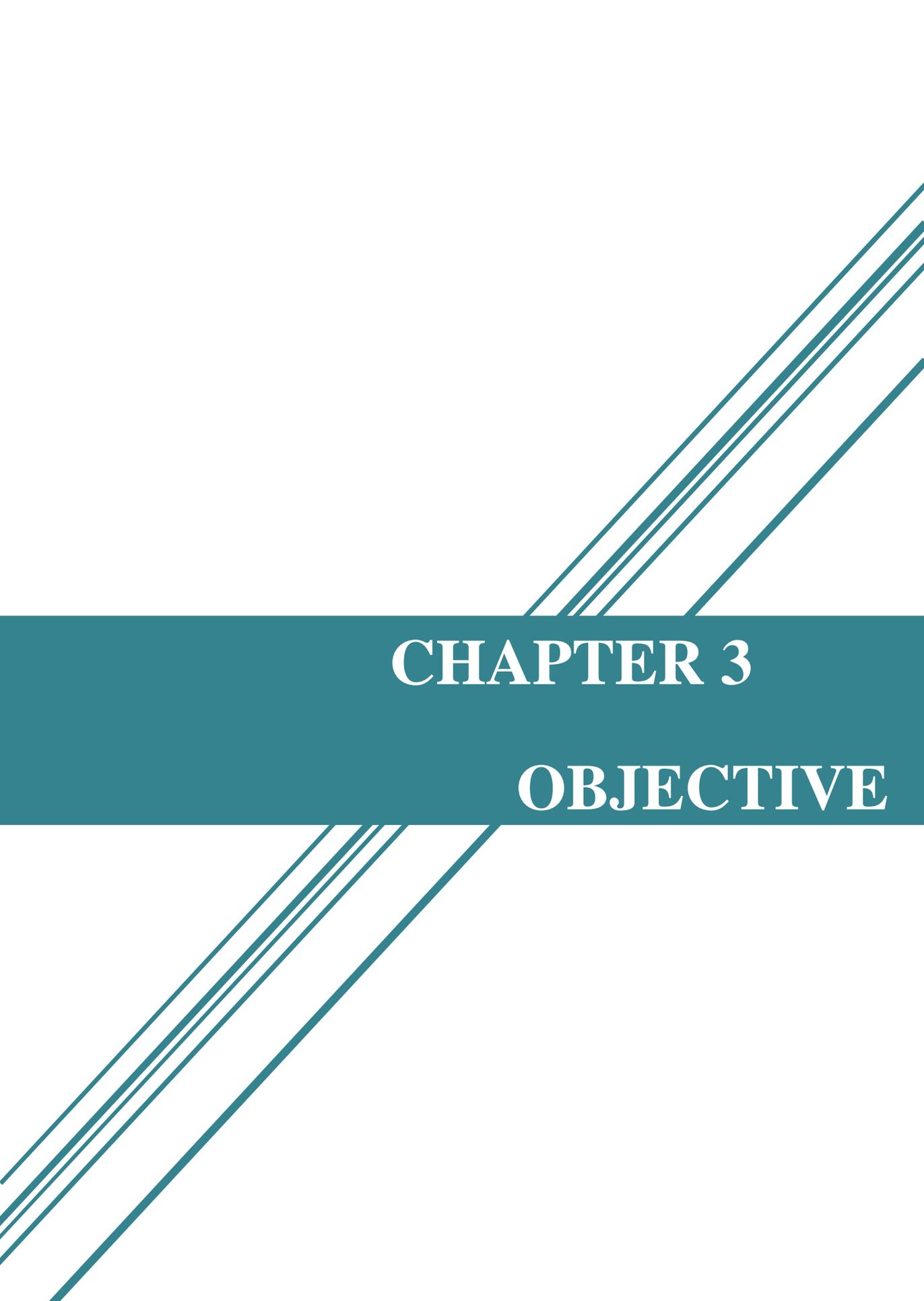
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CHAPTER 3

OBJECTIVE

Since 1999, the Electrochemical and Environmental Engineering Laboratory (E3L) of the Chemical Department of the University of Castilla-La Mancha has been working in the development of electrochemical processes for wastewater treatment. In this topic, ten doctoral theses have been carried out to evaluate the applicability of electro-oxidation, electrocoagulation/electroflotation and electro-irradiated technologies for the treatment of both real and synthetic wastewater. Additionally, taking advantage of the knowledge gained during these years and the need to contribute to the development of new treatment technologies in the field of urban and industrial wastewater to solve environmental concerns, the E3L has also participated in numerous projects with private companies in the search of technological solutions for the management of liquid wastes. In many cases, electrochemical technologies have aroused a great deal of interest for both wastewater treatment and reclamation of water due to their versatility, which allow the development of processes with high efficiency and low waste generation.

With this background, in 2016 a H2020 European Project (SafeWaterAfrica, grant agreement No 689925) was initiated with the ultimate goal of *providing high-quality water to rural population in African countries* (South Africa and Mozambique). The container-based water purification systems should provide 900 l/h (which is the typical flow rate of tap water) of purified water. Assuming, that 25 litres of purified water should be the right of every citizen, 36 people could be served every hour. For an average operation time of 9 hours per day, the system will supply purified water to more than 300 people. To meet this goal, it was proposed to fully develop, in cooperation with a total of ten African, German and Italian partners, the *complete chain value of a new process based on the electrolytic treatment of water with anodes of doped diamond*, which in turn is founded on novel electrochemical cells developed and manufactured by the partners Fraunhofer and CONDIAS GmbH (from Germany) and based on the use of an electrochemical cell capable of producing high amounts of ozone (among other disinfectants), even in low-conductivity water. However, the low quality of water sources found in the target countries led to the rethinking of the project, due to the presence of solids in water may represent a handicap for direct electrochemical disinfection, because they can obstruct the water flow in the interelectrode gap or even contribute to the fouling of the electrode surface, preventing electrochemical reactions. This problem is very important in many

rural areas of Africa where there is an additional problem not typically found in the EU nowadays: the fecal pollution of the water sources caused, for example, by the farms activity, which affects seriously the quality of fresh water reservoirs used for human supply. For this reason, the aim of the project was extended to the *design of a pre-disinfection system capable of producing high-quality water for disinfection*. Additionally, in the first stages of the process, the very different characteristics of water sources available in those countries was detected, and, therefore, the goal had to cover all possible scenarios. To do this, it was decided to evaluate the treatment of two types of water separately: surface water and groundwater.

Within this H2020 project, *the role of UCLM researchers (and of this PhD thesis) was to evaluate if the electrochemical technology developed by CONDIAS GmbH is efficient in the treatment of low-quality surface water and to design, if there is a necessity, auxiliary treatment system with the premises of being compact and low cost (made with cheap materials), easy to manipulate and easy to be connected to clean energy sources*. Due to the dual nature of this technical and research work, the initial stages were primarily oriented to check the feasibility of electrochemical electrodisinfection system to disinfect fecal polluted surface water. In the second stage, the efforts were focused on the development of technological approaches for the pretreatment of low-quality surface water. Therefore, the global objective may be divided into five partial objectives:

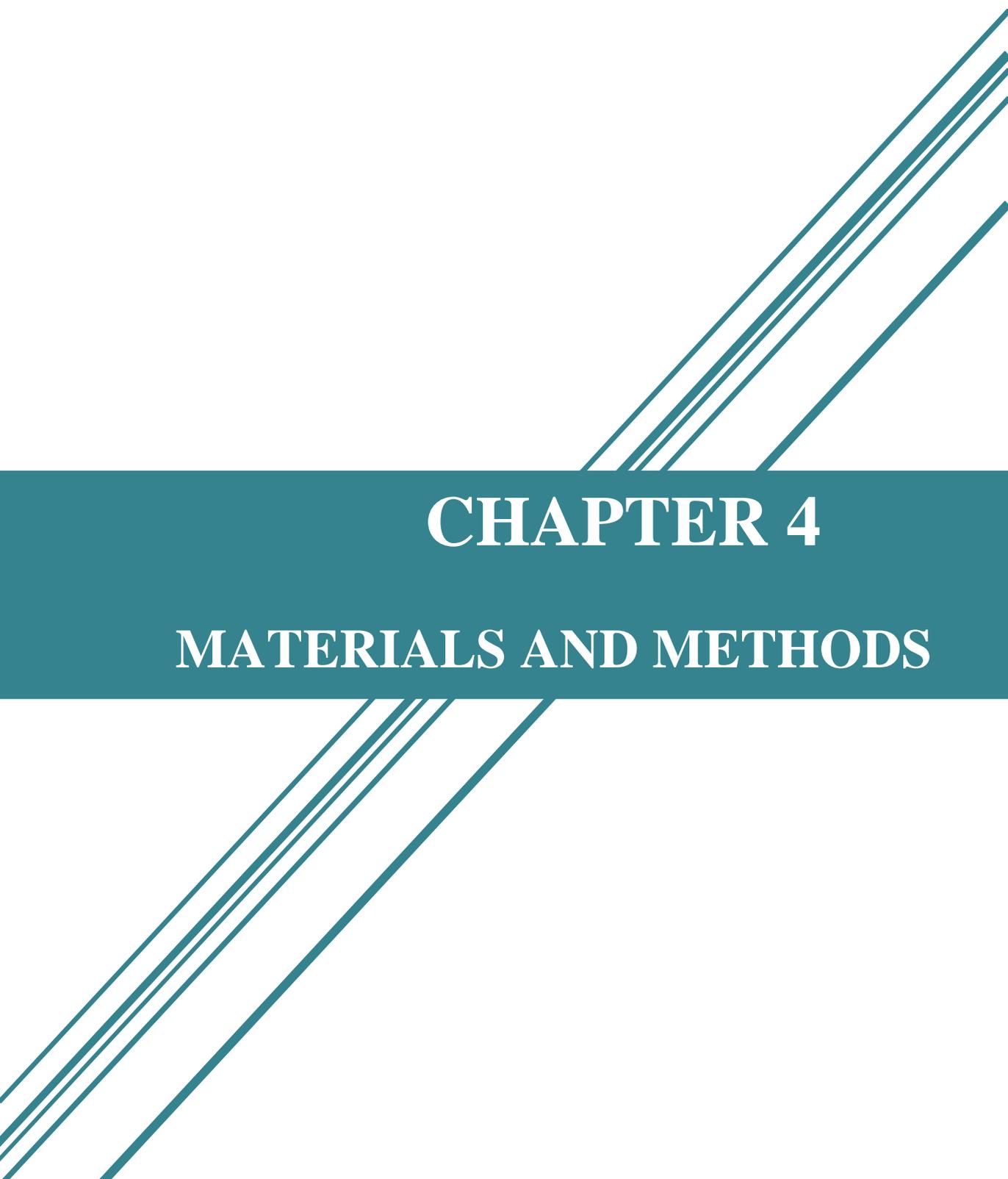
- To evaluate different commercial cells manufactured by CONDIAS GmbH and equipped with diamond electrodes and to determine which of them have the best prospects for application in disinfection of drinking water avoiding the main problem typically associated to the use of diamond electrodes: the formation of chlorates and perchlorates.

- To establish if selected electrochemical technology is efficient in the direct disinfection of surface water with fecal pollution (simulating that found in many rural sites in South Africa and Mozambique) and to determine the influence of the main operation parameters (current density, flowrates and operation mode).

- To design a pre-disinfection system (consisting of coagulation-flocculation, sedimentation and filtration units) to pre-treat highly polluted surface water, in order to obtain sufficiently high-quality water to be connected to an electrochemical cell, protecting electrode surface and preventing the blocking of the electrochemical cell.

- To design electrochemical dosing reactors to supply coagulant to the coagulation tank included in the pretreatment system, with the premises of providing long-operation time, easy operation, easy for replacing electrodes and low cost.

- To check the robustness and flexibility of the treatment process for the treatment of other type of source of water, implementing the changes required (re-design stage) to attain safe water.

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CHAPTER 4

MATERIALS AND METHODS

This section describes the analytical methods, as well as the experimental setups and reagents used in this research work.

4.1 Chemical reagents

Table 4.1 shows the chemical reagents used in this work, as well as their supplier, purity and use.

Table 4.1. Reagents used.

Reagent	Supplier	Purity / %	Use
Sodium chloride	Panreac	PA	Supporting electrolyte
Sodium sulphate	Panreac	99	Supporting electrolyte
Sodium hydroxide	Sigma Aldrich	99	pH modifier
Sulfuric Acid	Panreac	95	pH modifier
Arsenic(III) oxide	Fluka	99.5	Determination of Hypochlorite
Hydrochloric acid	Panreac	37	Fabrication of MMO electrodes
Citric acid	Sigma Aldrich	99	Fabrication of MMO electrodes
Ethylene glycol	Sigma Aldrich	99	Fabrication of MMO electrodes
Ruthenium(III) chloride hydrate	Alfa Aesar	99.9	Fabrication of MMO electrodes
Titanium(IV) butoxide	Sigma Aldrich	97	Fabrication of MMO electrodes
<i>P. Aeruginosa</i> (ATCC® 9027™)	Scharlab	pure culture	Simulation of polluted water
<i>Escherichia Coli</i> (ATCC® 25922™)	Scharlab	pure culture	Simulation of polluted water

4.1.1 Raw water

In this work, two main water sources were selected to simulate different samples composition: surface water and groundwater. Surface water was collected at the inlet of the municipal Water Treatment Plant of Ciudad Real (which received directly, by pumping, surface water from Gasset Reservoir). Typically, quality of surface water is very high (absence of significant anthropogenic pollution) because of the absence of industrial pollution sites or farm sites upstream or within the nearby of the Gasset reservoir. However, quality of supplied water in Ciudad Real largely depends on the season because of the very important span of temperatures through the year (minimum monthly average is 5.5°C and maximum monthly average is 25.6°C) and the scarcity and randomness of rains.

To simulate fecal polluted water, with similar characteristics of potential application sites in South Africa and Mozambique, surface “polluted” water was: 1) intensified with pure cultures of *E. Coli* and *Pseudonoma Aeruginosa* (intensified water), 2) mixed with the effluent of the secondary clarifier of the Wastewater Treatment Plant (WWTP) of Ciudad Real in a ratio of 95/5 v/v (surface water/effluent of WWTP) and 3) mixed with the outlet of primary decanter of WWTP in a ratio of 80/20 (surface water/effluent of WWTP). Table 4.2 shows the characterization of the surface water used in this work.

Table 4.2 Surface water composition.

Parameter	Intensified water	Fecal polluted water 95/5 v/v	Fecal polluted water 80/20 v/v	Units
<i>Total coliforms</i>	1.5E4 - 2.6E8	1355 – 18733	1.06E6	CFU 100 mL ⁻¹
<i>P. Aeruginosa</i>	5.4E4 - 5.3E8	3 – 45	5.8E5	CFU 100 mL ⁻¹
<i>Total aerobic microorganisms</i>	1.4E4 - 4.9E8	4644 – 399978	1.7E6	CFU 100 mL ⁻¹
Ph	7.17 - 8.17	7.8 - 8.12	6.7-8.9	Units
Conductivity	302 – 450	374 – 502	442- 560	mS cm ⁻¹
NH₄⁺	0 - 4.28	0 - 0.677	14.7-18.1	mg L ⁻¹
NO₃⁻	0 - 7.58	1.11 - 2.29	0.47-6.53	mg L ⁻¹
Cl⁻	32 - 69.5	59.4 - 74.9	63.8-93.8	mg L ⁻¹
SO₄²⁻	21.8 - 40.3	38.9 - 41.2	62.1-77.1	mg L ⁻¹
F⁻	0.01 - 0.198	0.05 - 0.35	0.06-0.21	mg L ⁻¹
Na⁺	17.2 - 40.2	29.4 - 34.3	41.2-59.6	mg L ⁻¹
K⁺	3.12 - 9.66	5.11 - 5.35	8.75-13.9	mg L ⁻¹
Ca²⁺	36.87 - 46.6	46.8 - 52.6	43.2-51	mg L ⁻¹
Mg²⁺	11.41 - 24.35	14.8 - 17.9	20.6-30.9	mg L ⁻¹

Groundwater was collected from a private irrigation well placed in the surroundings of Ciudad Real and which takes groundwater from aquifer 23 of Guadiana Basin. It was intensified with *E. Coli* and *Pseudomona Aeruginosa* as shown in Table 4.3.

Table 4.3. Characterization of groundwater intensified with microorganisms.

Parameter	Value	Units
<i>E. Coli</i>	1.48E6	CFU 100 mL ⁻¹
<i>P. Aureginosa</i>	5.88E6	CFU 100 mL ⁻¹
pH	7.01	Units
Conductivity	1414	μS cm ⁻¹
Cl⁻	85.71	mg L ⁻¹
NO₃⁻	40.02	mg L ⁻¹
SO₄⁻²	352.92	mg L ⁻¹
Na⁺	72.72	mg L ⁻¹
K⁺	3.67	mg L ⁻¹
Ca²⁺	171.62	mg L ⁻¹
Mg²⁺	110.63	mg L ⁻¹

4.2 Experimental set-ups and procedures

4.2.1 Electrochemical cells

Electrochemical cells used in this work were manufactured by CONDIAS GmbH (Germany): ECWP[®], CabECO[®] and MIKROZON[®] were tested whose main characteristic are described below. The experimental set-up used integrates electrochemical cell, power supply, pump, reservoir tank and heat exchanger and it can operate in continuous and discontinuous mode, as it is schematized in Figure 4.1. In discontinuous mode (Figure 4.1 a), water is continuously recirculated through electrochemical cell. In continuous mode (Figure 4.1 b) water only passes one time through the cell during the experiment (no recycling). This means that after a transient response, each experiment of this second series gives only one steady state value for each parameter. Regarding the current applied, the cells worked in galvanostatic mode by fixing a constant intensity either in discontinuous or continuous mode.

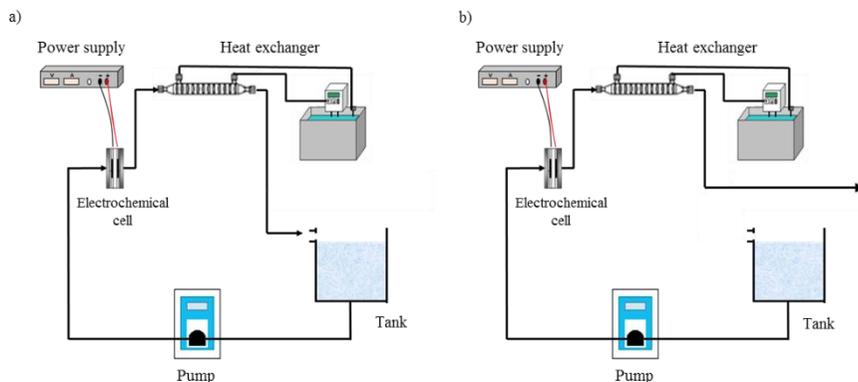


Figure 4.1. Experimental set-up scheme: a) discontinuous mode b) continuous mode.

At the beginning of the experiment, the reservoir tank is filled with the volume according to the type of test. For the test carried out at discontinuous mode, 5 L of water was introduced in the tank, meanwhile when the cells operated in continuous mode a tank of 100 L was used. Once the tank is filled, the pump and the power supply are switched on and the electrolysis starts. The cells were connected to the water reservoir by a peristaltic pump and powered by a Promax DC FA-376 power supply. A Keithley 2000 multimeter was used to monitor current and cell voltage. In all cases, a heat exchanger with a thermostated bath (Digiterm 100 JP Selecta, Barcelona, Spain) was used to maintain the temperature at the desired set point (25 °C).

a) ECWP®

The CONDIACEL® type ECWP system is specially designed for wastewater treatments. It is an undivided cell and consists of five perforated electrode packages. Each package has one anode (DIACHEM® electrode) of 4.2 cm² and two stainless steel cathodes. Table 4.4 shows the specifications data sheet supplied by the manufactures. Besides, the number of packages can be easily adjusted, depending on the final application. In this case, cathodes are made of stainless steel but it can be replaced by DIACHEM® cathodes, in order to be able to reverse the polarity to prevent fouling.

Table 4.4. Specification data sheet of ECWP® cell.

Technical information	
Temperature of the medium (recommended)	60°C (up 90°C, a touch protection is needed)
Pressure (max.)	4 bar
Flow rate	Up to 25 L min ⁻¹
Current per package (max.)	2 A
Voltage (max.)	18 V
Wetted materials	Stainless steal, Tealon TF 1590
Stack properties	
Anodes	5 x DIACHEM® electrodes
Cathodes	10 x Stainless steel electrodes
Electrode Dimension	Ø 20 x 1.5 mm
Electrode type	Perforated electrode
Anode/cathode gap	0.5 mm
Active anodic area per package	≈ 420 mm ²
Cell dimension (height)	≈158 mm
Weigh	0.6 Kg

DIACHEM® electrodes, placed in ECWP® cell, are very suitable for Electrochemical Advanced Oxidation Processes (EAOP), as it promotes the generation of hydroxyl radicals, directly from water molecules at the anode surface. In particular, CONDIACELL® ECWP is recommended for an EAOP system aiming to eliminate trace organics from wastewater stream or where the COD level is lower than 500 mg L⁻¹. Figure 4.2 shows a picture of the ECWP® cell used in this work.

**Figure 4.2.** ECWP® cell with a detail of its perforated diamond anodes.

b) CabECO®

CabECO® cell (50x24x1.3 mm³) is specially designed to produce ozone in low-conductivity water. It consists in one gap cell equipped with four DIACHEM® meshes electrodes (diamond coating on a structured silicon substrate). The electrodes are assembled in two stacks with a NAFION® cation exchange membrane separating the anode and cathode. Thus, the membrane acts as an electrolyte instead of the water (as in conventional cells). This fact allows the generation of disinfection species from low-salt waters as it is the case of the surface water.

CabECO® cell has two diamond anodes with a total area of 24 cm² (Figure 4.3). They are placed in the external part of the stack. In this way, it is maximized the volume of water that pass through the anodic compartment in order to favor the anodic reactions which produce the disinfectants. Table 4.5 shows the specification data sheet given by the manufacturer.

Table 4.5. Specification data sheet of CabECO® cell.

Technical information	
Temperature range medium	60°C
Pressure (max.)	2 bar
Pressure drop	0.1 bar 300 L h ⁻¹
Current (Continuous operation)	2 A
Max. current (short term)	4.8 A
Voltage (max.)	48 V
Wetted materials	PVDF, Titan, Nafion® Membrane
Stack properties	
Anodes	2 x DIACHEM® electrodes
Cathodes	2 x DIACHEM® electrodes
Electrode Dimension	50x24x1.3 mm
Electrode type	Mesh
Distance from anode/cathode	Membrane
Active anodic area	≈ 24 cm ²
Cell dimension	≈45 mm x 35 mm x 160 mm
Weigh	0.3 Kg



Figure 4.3. CabECO[®] unit. Left side: electrode stack; right side: CabECO[®] reactor.

c) MIKROZON[®]

The MIKROZON[®] cell, as well as the CabECO[®] cell, is especially designed to produce ozone in low-conductivity water. The cell can be used to produce ozonized water. It is equipped with two DIACHEM[®] electrodes (diamond coating on a structured silicon substrate), which are arranged in a membrane electrode assembly with a fumasep[®] cation exchange membrane. Although MIKROZON[®] cell follows the same principles than CabECO[®], two diamonds electrodes separated by a membrane, it is so much smaller than the previous one. Thus, the main characteristic of this cell is its reduced size and of course the smaller electrodes dimension (15x7.5x0.725 mm³). Table 4.7 shows the specification data sheet of MIKROZON[®] cell and Figure 4.4 shows a picture of MIKROZON[®] cell.



Figure 4.4. MIKROZON[®] cell.

Table 4.7. Specification data sheet of MIKROZON® cell.

Technical information	
Temperature limits of medium	40°C
Pressure (max.)	10 bar
Flow rate	0.5 up to 1.5 L min ⁻¹
Current (Continuous operation)	1.2 A
Voltage (max.)	24 V
Wetted materials	PVDF, PSU, Titanium, EPDM, Silicone
Stack properties	
Anodes	DIACHEM® electrode
Cathodes	DIACHEM® electrode
Electrode Dimension	15 mm x 7.5 mm x 0.725 mm
Membrane	Fumasep®
Active anodic area	112.5 mm ²
Cell dimension	≈61 mm x 31 mm x 36 mm
Weigh	70 g

4.2.2 PRE-Disinfection Column (PREDICO)

The PRE-Disinfection Column (PREDICO) is designed as a low cost and easy to operate system, made with PVC hardware consumables and capable to removed coarse pollution. It follows the typical sequence implemented in the most municipal water treatment facilities, that consists of a sequence of coagulation-flocculation, sedimentation and filtration units. Thus, the experimental set-up designed combines the three operation units required to pre-treat surface water before disinfection into a column. This PREDICO system makes use of the connection to increase the performance of each unit. That is, the coagulation tank (sized for a hydraulic retention time of 6 minutes) sited at the bottom of PREDICO also acts as the concentration zone of the tubular decanter (sized for a hydraulic retention time of 10.3 minutes and a superficial load of 12m h⁻¹, while the top of the tubular decanter acts as a reservoir for the granulated activated carbon (GAC) filtering (sized for 2 minutes). Two PREDICO units were constructed with PVC consumables and with a capacity of 20L h⁻¹ (bench scale plant) and 300 L h⁻¹ (pilot plant).

In the last stage of this work, PREDICO is re-designed to face the pre-treatment of groundwater (characterized by its high conductivity and hardness). Thus, coagulation chamber is replaced by a lime bed and filtration unit is replaced by an ion exchange unit equipped with cationic and anionic resins.

Figure 4.5 shows a picture of the two systems designed, bench scale and pilot plant, as well as the sequence of units to treat surface water or groundwater.

The experimental procedure is simple. At the beginning of the experiment, reservoir tank (1 m³ of capacity) is filled with target water. Then, the pump is switched on and the treatment starts. Water is introduced from the bottom to the top of PREDICO. Firstly the water come across to the reaction chamber, in which coagulant or lime is added, depending on types of water (surface or groundwater). Secondly, water goes through the tubular decanter and the solids formed in the earlier step precipitate and are accumulated in the reaction chamber, which from they are purged. Finally, water passed through the carbon filter or ion exchange resins (depend on water sources) and it is stored in an intermediate tank. Afterwards, the pretreated water is subjected to an electrodisinfection process as it was described in the section 4.2.1.

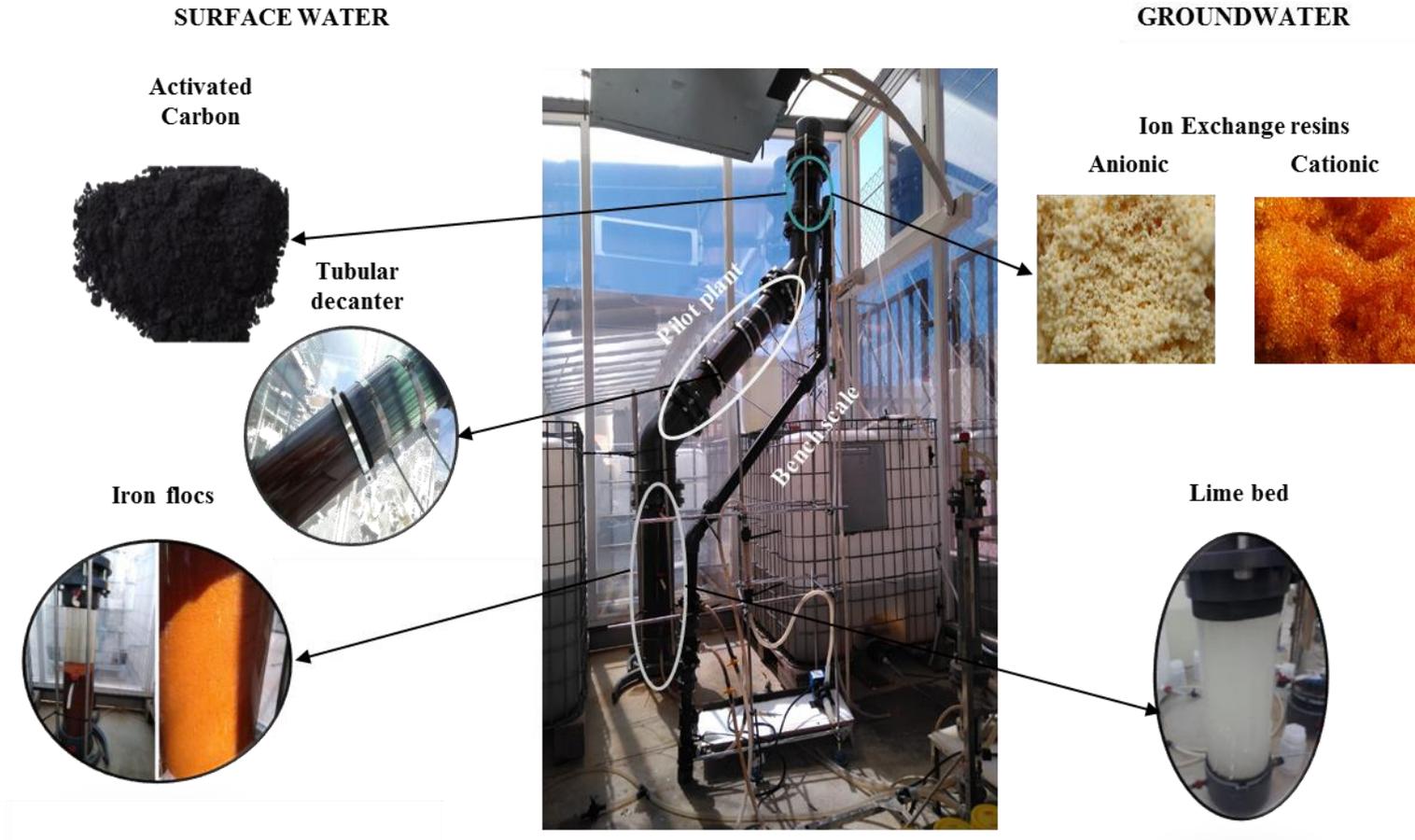


Figure 4.5. PREDICO system at bench scale and pilot plant with a detail of the units implemented to treat surface water and groundwater.

4.2.3. Electrochemically-Assisted coagulant - Production & Dosing Unit

a) ECU

A novel Electrochemically-assisted Coagulant – production & dosing Unit (ECU) was developed to be used as a low-cost and easy-to-use electrochemical device to provide the required dosing of coagulants at the PREDICO coagulation chamber, to replace the conventional chemical dosing of coagulants. Thus, it was designed to provide long-term operation and an easy system for replacing the iron bed that is being dissolved, trying to reduce the operating costs and to enhance the real applicability of the device. Figure 4.6 shows a picture and a schematic plot of the cell designed for the improved production and dosing of coagulant.

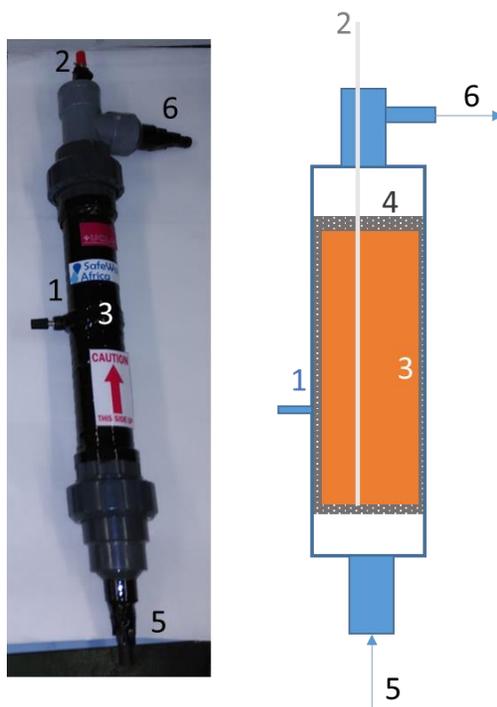


Figure 4.6. Picture and schematic plot of the ECU. 1: external stainless steel cathode; 2: stainless steel anode feeder; 3) internal bed of iron particles; 4) internal plastic mesh; 5) reactor inlet; 6) reactor outlet.

It consists in an internal bed of 1 kg of iron particles (3) placed inside an internal plastic mesh (4) that allows the pass of the fluid but avoids short-circuit of anode and cathode. The reactor has an internal stainless steel rod (2) immersed inside the bed of iron particles. This internal rod behaves as anode feeder, allowing the anodic dissolution of the iron bed. The cathode is an external stainless steel tube (1), electrically isolated from the anode by the internal plastic mesh. The cell behaves as a flow-through reactor, in which the fluid enters through the bottom (5) and exits the cell through an overflow (6) at the top. The top of the cell can be easily separated from the body of the cell by a threaded joint in order to allow an easy replacement of the iron bed once it has been completely dissolved.

The experimental procedure consisted in once the tank is filled with the target water, the pump and the power supply are switched on successively. The experiments are carried out in continuous mode with a flowrate of 15 L h^{-1} and under galvanostatic conditions. Each experiment spends 45 min. The current was progressively from 0.00 to 0.40 A in steps of 0.10 A, giving results for four increasing values of applied electric charge (ratio of intensity and flow rate). In order to achieve the stabilization of the system, the samples were taken 5 minutes after each intensity variation

To carry out studies on conventional chemical coagulation, a laboratory-scale installation was used, consisting of a 15-point magnetic stirring multipoint plate model MIX 15 ECO supplied by the company 2 mag in borosilicate glass reactors with a capacity of 250 mL. To simulate a real treatment process, the pH of the samples was adjusted to 8.0 by adding NaOH. The experiments of conventional chemical coagulation were carried out in a simple sep up as the schematized in the Figure 4.7.



Figure 4.7. Laboratory-scale multiple stirring unit used in conventional chemical coagulation.

b) Improved-ECU (i-ECU)

To face higher coagulant dosages an improved-ECU (i-ECU) was developed following the same premises: easy to manipulate, easy replacement of iron sheets and cheap materials. It consists in two outer Metal Mixed Oxide (MMO) electrodes connected to the power supply and sacrificial iron electrodes placed in the central point. The development of this reactor will be described step by step in the section 5.3.3. Figure 4.8 shows a picture of the i-ECU experimental set up.

The experimental procedure follows the same steps than the ECU. In this case it was performed different electrode configurations and operation mode, in order to find the best operations conditions that manages to dissolve the maximum amount of iron. Then, it was combined continuous and discontinuous process with galvanostatic and potentiostatic modes.



Figure 4.8. Bench scale i-ECU the set-up picture.

All materials needed, except for the MMO electrodes can be purchased in a hardware store. The bend MMO were synthesized following the Pechini method (Figure 4.9). Thus, after mechanized a titanium sheet to form the two semi-cylinders, the electrodes were pretreated. The pre-treatment involved: 1) sanding; 2) rinsing with isopropyl alcohol; 3) immersing in 20% hydrochloric acid solution and 4) immersing in 10% oxalic acid solution for each electrode.

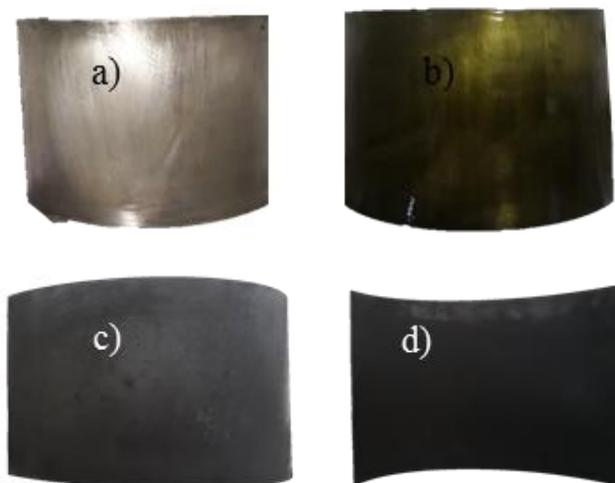


Figure 4.9. MMO electrodes synthesizing steps a) titanium support pretreated; b) first precursor layer before be introduced in a furnace; c) intermediated and d) final electrode.

After that, they were recovered with the precursor solution prepared by the dissolution under agitation at 90 °C of a citric acid (CA) in ethylene glycol (EG), with a molar ratio EG/CA/metallic precursors of 10:3:1. The CA was previously dissolved in EG heated up to 60 °C. The obtained precursor solution is brushed over the titanium bend plates and after that, they are heated at 130 °C for 30 min, 250 °C for 10 min and at 400 °C for 5 min (in furnace). This procedure is repeated until a mass loading of 1.2 mg cm⁻² (approximately 2 μm of thickness). Finally, anodes are calcined at 400 °C for 60 min (Santos, T.E.S et al., 2015; Santos, G.O.S et al., 2015; Pechini, M.P et al., 1967).

4.3 Analytical methods

4.3.1 Microbial characterization

The microbial characterization was done following strictly the experimental procedure described in the standard methods. Firstly, materials and glasswares are sterilized in an autoclave at 121 °C for at least 15 min. Additionally, samples are taken in clean, sterile, wide-mouth, nonreactive borosilicate glass in accordance with ISO 19458, and analyzed immediately to avoid unpredictable changes in the microbial population.



Figure 4.10. Filtration system inside fume hood.

Microorganisms were measured following the ISO 8199 regulation by the membrane filtration technique. The test portion was passed through a membrane filter of 45 mm of diameter and a pore size diameter of 45 μm , certified according to the standard ISO 7704:1985, which retained the microorganisms sought. The membrane was placed facing up in a specific culture medium (supplied by Scharlab) for each microorganism. Formation of bubbles and wrinkles must be avoided. Then, the culture plates were incubated for a certain time and temperature depending on each microorganism. Then, the bacterial growth was determined by and result was expressed as a number of colony-forming units (CFU) in a 100 ml of sample.

a) Total Coliforms

A prepared selective medium called CCA COLIFORMS CHROMOGENIC AGAR was used for the detection of Total coliforms and *E. Coli* according to ISO 9308-1. The plate was incubated with the membrane for 18-24 h at $36\pm 2^\circ\text{C}$. Then, colonies colored from salmon-pink to red were considered as Coliforms different to *E. Coli* and those colored from blue to violet as *E. Coli*.

b) *Pseudomona Aureginosa*

The solid selective medium CN SELECTIVE AGAR was used for the detection of *Pseudomonas aeruginosa* in accordance with ISO 16266 and EN 12780-2002. In this case the incubation time is 48 hours at $30\text{-}35^\circ\text{C}$.

c) Total aerobic microorganism

A commercially prepared culture medium Trytone Yeast Extract Agar was used, according to ISO 6222:1999. In this case, it was incubated at 37°C for 24-48 hours.

4.3.2 Ion Chromatography (IC)

Ions concentration was measured by ion chromatography using a Metrohm 930 Compact IC Flex coupled to a conductivity detector. A Metrosep A Supp 7 column was used to determine anions, by passing through it a mobile phase consisting of 85:15 v/v 3.6 Mm Na₂CO₃/acetone with a flow rate of 0.8 cm³ min⁻¹. In addition, a Metrosep A Supp 4 column was used to analyze cations, by passing through it a mobile phase consisting of 1.7 Mm HNO₃ and 1.7 Mm 2,6-pyridinedicarboxylic acid with a flow rate of 0.9 cm³ min⁻¹. The temperature of the oven was 45 and 30 °C for the determination of anions and cations, respectively. The volume injection was 20 µL.

4.3.3 Total Organic Carbon (TOC) and Inorganic Carbon (IC)

TOC concentration was monitored using a Multi N/C 3100 Analytik Jena analyzer. This equipment uses the complete combustion of the sample with a pure oxygen stream at 680 °C. The oven contains a platinum catalyst supported in alumina. The carbon dioxide generated is measured by infrared spectrometry and is directly related with the Total Carbon (TC) of the sample.

In the case of the Inorganic Carbon (IC), the sample is acidified by the addition of phosphoric acid at 10%, in order to get the displacement of the chemical equilibrium from carbonates and bicarbonates to carbonic acid. Once again, the carbon dioxide released is measured by infrared spectrometry and is related with the value of IC of the sample analyzed.

Once the TC and IC measurements are known, the value of Total Organic Carbon is obtained by difference from the previous ones. The analyzer carries out a minimum of three measurements per sample. The result will be valid only if the variation between them is less than 2%.

4.3.4 Hypochlorite

In the case of the hypochlorite, the peak of chromatogram interferes with the chloride peak. Therefore, it is used an automatic titrator Methrom 702 SM Titrino for the redox determination that allows to quantify in a differentiated way the hypochlorite concentration. The analytic method employed it is based in the redox reaction between the arsenite and the hypochlorite (Ec. 4.1)



The hypochlorite is reduced to chloride by the continuous addition of arsenite, which in turns is oxidized to arsenate. The excess added arsenite results in a significant decrease in the electrolyte potential (with reference to a platinum electrode) is reading by the automatic titrator.

Arsenic trioxide and sodium hydroxide are used as reagent solution with a concentration of 0.001 M and 2 M, respectively. As a pre-treatment, the 10 ml sample are basified by the addition of 2 ml of 2 M NaOH in order to determine the hypochlorite concentration. Thus, the hypochlorite generated is calculated by equivalents as follow (Ecs. 4.2-4.3).

$$\text{Eq} (\text{As}^{3+}) = \text{Eq} (\text{ClO}^-) \quad [4.2]$$

$$M (\text{As}^{3+}) \cdot V (\text{As}^{3+}) \cdot n^{\circ} e^- = M (\text{ClO}^-) \cdot V (\text{ClO}^-) \cdot n^{\circ} e^- \quad [4.3]$$

4.3.5 pH and conductivity

The pH measurement is based in the use of a selective electrode. It is employed a pH-meter GLP 22 (CRISON). The pH-meter is previously calibrated with standard solutions before each set of measures.

The ionic conductivity is determined by a conductivity meter GLP 31 EC (CRISON).

4.3.6 Turbidity

The turbidity is determined using a turbidimeter 115 VELP scientific. It employs a nephelometric method according to 2130 B (Standard Methods for the Examination of Water and Wastewater). It consists in the comparison of the intensity of light scattered by the sample under defined conditions with the intensity of light scattered by a standard reference suspension under the same conditions. This equipment measures the intensity of the light scattered at 90° from the incident light path.

4.3.7 Inorganic chloramines: colorimetric method based in N,N-diethyl-p-phenylenediamine (DPD)

The inorganic chloramines are quantified following a colorimetric method according to 4500 Cl-G (Standard Methods for the Examination of Water and Wastewater). It is based on the addition of N,N-diethyl-p-phenylenediamine (DPD) since the pink color that is generated in the solution when reacting with chlorine species. It allows determining the free chlorine and, at the same time, is able to distinguish quantitatively between monochloramine (NH₂Cl), dichloramine (NHCl₂), trichloramine (NCl₃). For the determination of the measures it is used a spectrophotometer Agilent Cary 300 UV-Vis. The minimum concentration of chlorine perceptible is 10 µg dm⁻³ and the maximum 4 mg dm⁻³. The previous calibration of the spectrophotometer is required. The calibration is carried out with a stock solution containing 891 mg dm⁻³ of KMnO₄ (sol. 1).

For the determination of the concentration of inorganic chloramines the sample is divided in two parts (10 ml each one). To the first one, 0.5 ml of DPD indicator (8.1 mM de DPD, 37.8 mM de H₂SO₄ and 0.5 mM of EDTA) and 0.5 ml of KH₂PO₄/Na₂HPO₄ buffer solution (338.1 mM of KH₂PO₄, 169 mM of Na₂HPO₄ and 21.5 mM of EDTA), are added. After that, the resulting solution is mixed and measured (value A). The color obtained will be related with the free chlorine. Subsequently, KI (0.1mg) is added and mixed to the solution (value B). The KI allows the activation of the monochloramine, so that the color is the result of the appearance of the monochloramine and free chlorine. Then, 0.1g of KI are added and after 2 minutes standing the measure is taken (Reading C). The addition of iodide ion in excess results in the colorimetric response of dichloramine.

Secondly, to estimate the proportion of trichloramine a small crystal of KI (0.1 mg) is mixed with 10 ml of sample in a beaker. In another beaker, 0.5 ml of $\text{KH}_2\text{HPO}_4/\text{Na}_2\text{HPO}_3$ buffer solution (338.1 mM of KH_2HPO_4 , 169 Mm of Na_2HPO_3 and 21.5 Mm of EDTA) and 0.5 ml of DPD indicator (8.1 mM de DPD, 37.8 mM de H_2SO_4 and 0.5 mM of EDTA) are added. After that, the content of the second beaker is added in the first one and it is measured instantaneously (Reading N). Once the readings are calibrated, the combination of the readings performed in the spectrophotometer at 515 nm allows to obtain the amount of inorganic chloramines following Table 4.8.

Table 4.8. Determination of the different chlorine species based on photometric readings.

Reading	NCl_3 Absent	NCl_3 Present
A	Free Cl	Free Cl
B – A	NH_2Cl	NH_2Cl
C – B	NHCl_2	$\text{NHCl}_2 + \frac{1}{2} \text{NCl}_3$
N	-	Free Cl + $\frac{1}{2}\text{NCl}_3$
2(N - A)	-	NCl_3
C – N	-	NHCl_2

4.3.8 Total Suspended Solids

Total suspended solids (TSS) is the dry-weight of suspended particles, that are not dissolved in a sample of water and that can be trapped by a filter. Previously, 45 μm filters are washed with 20-30 mL of de-ionized water to remove any solids left over from the manufacturing process. Then the filters are placed in an aluminum container and weight (a). Then they are dried for 30 minutes in a 104 °C oven. Finally, the filter and container are cooled in a desiccator and they are weighed (B). The value of TSS is calculated followed the equation 4.4

$$TSS(\text{mg } L^{-1}) = \frac{B(\text{mg}) - A(\text{mg})}{\text{Sample filtered volume (L)}} \quad [4.4]$$

4.3.9 Organo-chlorinated intermediates (Trihalomethanes)

The organo-chlorinated intermediates were analyzed by GC-MS using a Thermo Scientific DSQ II Series Single Quadrupole GC-MS with a NIST05-MS library. The column was a polar TR-WAXMS (30m x 0.25mm x 0.25 μ m). The temperature ramp was 70°C for 1 min, 30 °C min⁻¹ up to 300 °C and hold time 5 min. The inlet, source and transfer line temperatures were 250, 200 and 300°C, respectively.

4.3.10 Redox potential

The redox potential was measured with a waterproof tester ORP HI 98120 electrode provided by HANNA instruments.

4.3.11 Iron concentration

Total iron concentration was measured off-line using an inductively coupled plasma spectrometer (Liberty Sequential, Varian) with a detection limit < 1.55 ppb by diluting the samples to 50:50 (v/v) using NH₄NO₃ to ensure the total solubility of the metal.

4.4 Electrochemical parameters calculations

4.4.1 Current density

Current density is defined as the amount of electric current flowing through a unit of electrodic area. It is calculated following the Eq. 4.5, where j is the current density (A m⁻²), I the intensity applied (A) and A is the electrodic area.

$$j = \frac{I}{A} \quad [4.5]$$

4.4.2 Electric charge

The electric charge is a parameter used in electrochemical process, instead of the time, to express the evolution of the different variables. Thus, the electric charge can be used as a parameter of change of scale as it is directly related with the operation conditions in continuous (Eq. 4.6) and discontinuous mode (Eq. 4.7)

$$Q = \frac{j \cdot S}{q} \quad [4.6]$$

$$Q = \frac{j \cdot S \cdot t}{V} \quad [4.7]$$

Where Q is the electric charge applied (Ah L⁻¹), j is the current density (A m⁻²), S is the anodic surface (m²), t is the time (h), q is the flowrate (L h⁻¹) and V is the volume of electrolysis dissolution (L).

4.4.3 Amount of coagulant dosed electrochemically

The Faraday Law's stated that the amount of material liberated from an electrode during an electrochemical reaction is directly proportional to the total conducted charge or, equivalently, the average current multiplied by the total time. Thus, by the eq. 4.8 can be predicted the theoretical amount of coagulant generated in an electrocoagulation process.

$$m = \frac{I \cdot t \cdot M}{F \cdot z} \quad [4.8]$$

Where m is the mass of substance liberated at an electrode (g), I is the constant current passed through the substance (A), t is the total time the constant current was applied (s), M is the molar mass of the substance (g mol⁻¹), F is the Faraday constant (96485.33 C mol⁻¹), z is the valency number of ions of the substance (electrons transferred per ion).

4.4.4 Superficial Load Rate

The superficial load rate (SLR) is one of the guidelines for the design of settling tanks and clarifiers and clarifiers in treatment plants. It is used to determine if tanks and clarifiers are hydraulically (flow) over- or unloaded, as it the only parameter in the process of particles sedimentation. Thus, it is defined as the flowrate per the area of the sedimentation tank. (Eq. 4.9)

$$SLR = \frac{q}{A} \quad [4.9]$$

Where SLR is the Superficial Load Rate (m s⁻¹), q is the flowrate (m³ s⁻¹) and A is the area of the sedimentation tank (m²).

4.4.5 Hydraulic Retention Time

It is the average amount of time that a given volume of liquid stays in a reactor or tank. It is calculated by dividing the volume of a reactor (m^3) by the influent flow rate ($\text{m}^3 \text{h}^{-1}$). In wastewater treatment systems the HRT influences the treatment efficiency and is, therefore, an important design parameter.

4.5 References

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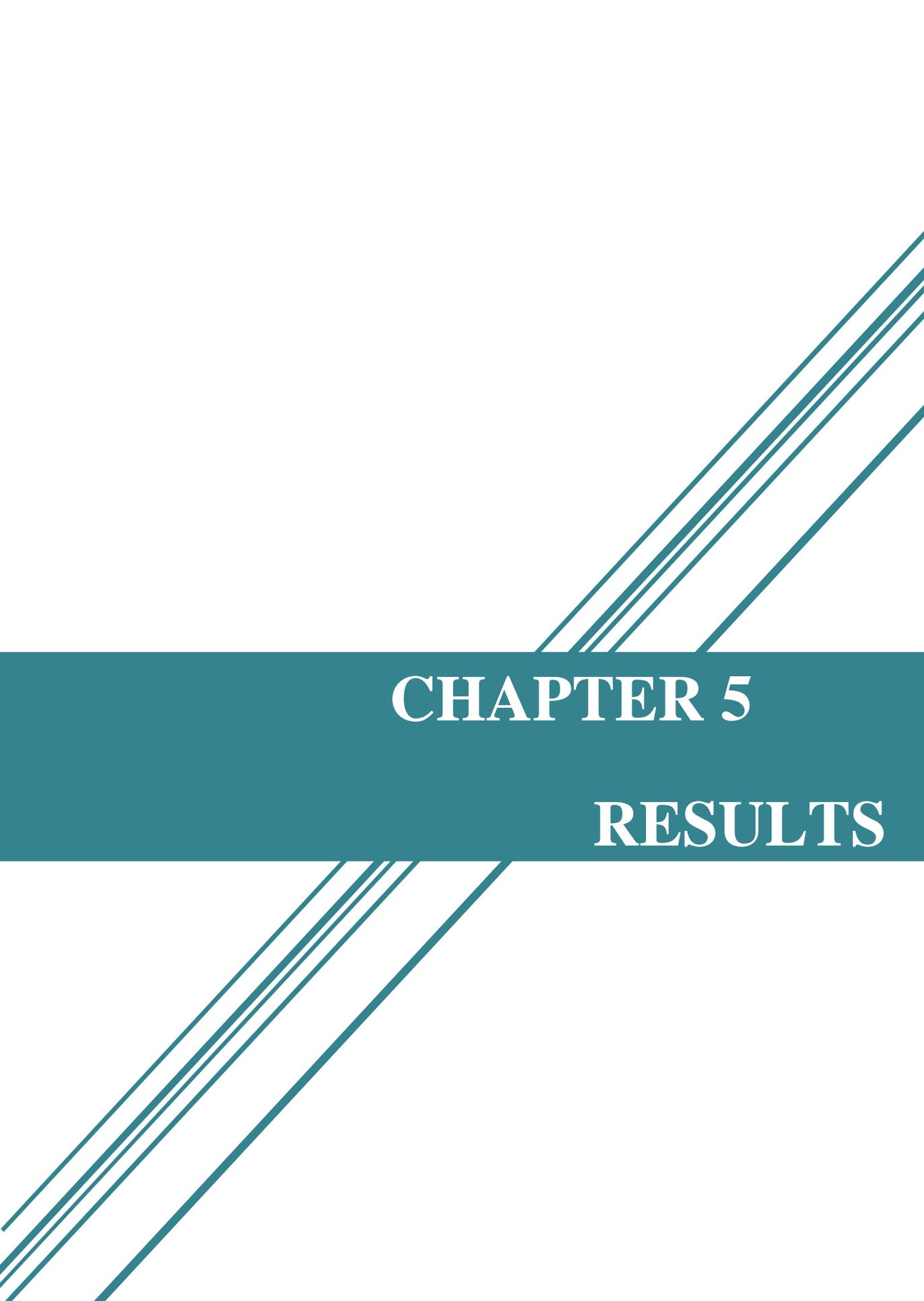
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CHAPTER 5

RESULTS

5.1 Electrochemical technology for the treatment of synthetic water intensified with microorganisms

In this chapter, it will be compared three commercial cells made by an European manufacturer (CONDIAS GmbH, Germany), trying to determine which of them have the best prospects for application in disinfection of drinking water. These cells are called: CONDIACELL® type ECWP, CabECO® and MIKROZON® cells and their main characteristics are shown in the chapter 4.2.1, The first cell is a non-divided cell specially designed for a very efficient mineralization of wastewater polluted with low amounts of organics (“wastewater polishing”), in which the treated liquid crosses through a sequence of five perforated diamond anodes. The second cell is a very new and special design made for the production of ozone in highly pure water (with low conductivity). In this latter case, electrodes are assembled in two stacks with a polymer exchange membrane (PEM) separating the anode and the cathode and acting as the electrolyte, which is directly connecting the anode and the cathode. In turn, both are in direct contact with the treated water expected to be disinfected. The third of them, the MIKROZON® cell is an evolution of the CabECO® cell, with the same configuration but a very low contact time between aqueous solution and the electrodes. It is worth to noting that these two last cells are designed to prevent the formation of chlorates and perchlorates.

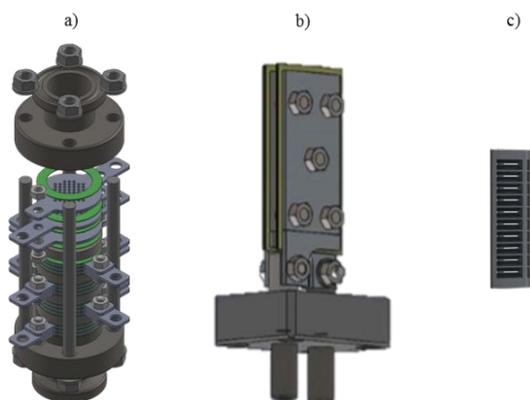


Figure 5.1. Scheme of the cell electrodes a) ECWP®; b) CabECO®; c) MIKROZON®.

Water used in these experiments was collected at the inlet of the municipal Water Treatment Plant of Ciudad Real and modified by the addition of strains of

Echerichia Coli and *Pseudomona Aureginosa*. Thus, the disinfection of the surface water sample tested here was evaluated by these two indicators of pathogenicity which were selected taking into account that: 1) they are the most common microbial contaminants in natural waters and wastewaters (Li et al., 2017a), and 2) the versatile metabolism of *Pseudomonas Aeruginosa* and its increasing resistance to antibiotics (Bruguera-Casamada et al., 2017). In addition, as already explained in the chapter 2.3 one of the drawbacks of using diamond coatings is the formation of undesirable chlorine species. The main aim of the chapter is determining which cell is the most appropriate for the disinfection of highly polluted water as well as the most suitable conditions to avoid the formation of undesirable by-products.

The measurement of pathogens and disinfectant species (free and combined chlorine compounds) were carried out immediately, and thus it was not necessary the addition of chemical reagents to stop the reaction between microorganisms and disinfectants. The experimental conditions studied in each of the electrodisinfection experiments carried out in this chapter with the cells ECWP[®], CabECO[®], MIKROZON[®] are detailed in the tables 5.1, 5.2 and 5.3, respectively.

Table 5.1. Planning of experiments of electrodisinfection of waters intensified in microorganisms with the ECWP[®] cell.

Test no.	Operation mode	Current density / A m ⁻²	Florate / L h ⁻¹	Volume of water treated / L	Maximun specific charge passed / Ah L ⁻¹
1	Continuous	476	90	90	0.011
2	Continuous	952	90	90	0.022
3	Continuous	1904	90	90	0.044
4	Continuous	1904	150	150	0.027
5	Continuous	1904	300	300	0.013
6	Discontinuous	9.52	-	5	0.004
7	Discontinuous	95.2	-	5	0.04
8	Discontinuous	952	-	5	0.4

Table 5.2. Planning of experiments of electrodisinfection of waters intensified in microorganisms with the CabECO® cell.

Test no.	Operation mode	Current density / $A\ m^{-2}$	Florate / $L\ h^{-1}$	Volume of water treated / L	Maximum specific charge passed / $Ah\ L^{-1}$
1	Continuous	416.7	90	90	0.011
2	Continuous	833.3	90	90	0.022
3	Continuous	1666.7	90	90	0.044
4	Continuous	1333.3	300	300	0.0106
5	Discontinuous	0	-	5	0
6	Discontinuous	8.33	-	5	0.0067
7	Discontinuous	83.33	-	5	0.067
8	Discontinuous	833.33	-	5	0.29

Table 5.3. Planning of experiments of electrodisinfection of waters intensified in microorganisms with the MIKROZON® cell.

Test no.	Operation mode	Conection	N° cells	Current density / $A\ m^{-2}$	Florate / $L\ h^{-1}$	Maximum specific charge passed / $Ah\ L^{-1}$
1	Continuous	-	1	10667	30	0.04
2	Continuous	-	1	10667	60	0.02
3	Continuous	-	1	10667	90	0.013
4	Discontinuous	-	1	2667	-	0.3
5	Discontinuous	-	1	5333	-	0.6
6	Discontinuous	-	1	8889	-	1
7	Continuous	Series	4	42668	30	0.16
8	Continuous	Series	4	42668	60	0.08
9	Continuous	Series	4	42668	90	0.04
10	Continuous	Parallel	4	10667	30	0.16
11	Continuous	Parallel	4	10667	60	0.08
12	Continuous	Parallel	4	10667	90	0.053

5.1.1 Study of the influence of the electrode configuration in water disinfection processes: ECWP[®] vs CabECO[®]

Several tests were carried out to characterize the influence of the electric current charge passed on the removal of Total Coliforms and *Pseudomonas Aeruginosa* obtained by the commercial electrochemical cells EWCP[®] and CabECO[®]. Thus, it is possible to compare two different configurations: a conventional set-up (ECWP[®]) vs a PEM cell (CabECO[®]).

Typically, for most surface water, the conductivity is high enough to attain an efficient process and no salt addition is needed. However, with direct electrochemical technology (ECWP[®]), conductivity is always a challenge and should be considered before the design of the disinfection process, because extremely low conductivities may prevent its use. Results shown in Figure 5.2 compare the performance of these two approaches. All the tests were run in continuous mode with a single pass of the water through the cell. Data reported at the outlet corresponds to the concentration measured at the steady state.

As it can be observed, disinfection results obtained by the ECWP[®] cell are good and rather similar to those obtained by other non-divided electrochemical cells already existing in the market. A 3-log decrease is attained in the concentration of both pathogens with charges as low as 0.02 Ah L⁻¹. In fact, in comparing them with other previous results published, they seem to be a little bit higher (at 0.01 Ah L⁻¹ this ECWP[®] cell attains 2-log decrease in the concentration, while in previous work with other cells pathogen reduction was found to be a little bit lower)(Cano et al., 2016). However, this is not a significant figure because this performance should not only depend on the cell but also on many other additional factors (Schaefer et al., 2015). Anyway, the improvement can be easily explained because of the special configuration of this cell that promotes high turbulence and, hence, a more efficient mass transport inside the cell. This confirms that electrolysis with diamond anodes is very efficient in the disinfection of water, allowing the removal of several log units of concentrations of both pathogens for very low electric current charges passed. This result also confirms the current charge applied as the key parameter to monitor the disinfection, because all results obtained lay over the same curve, despite each test was made at different current densities and flowrates.

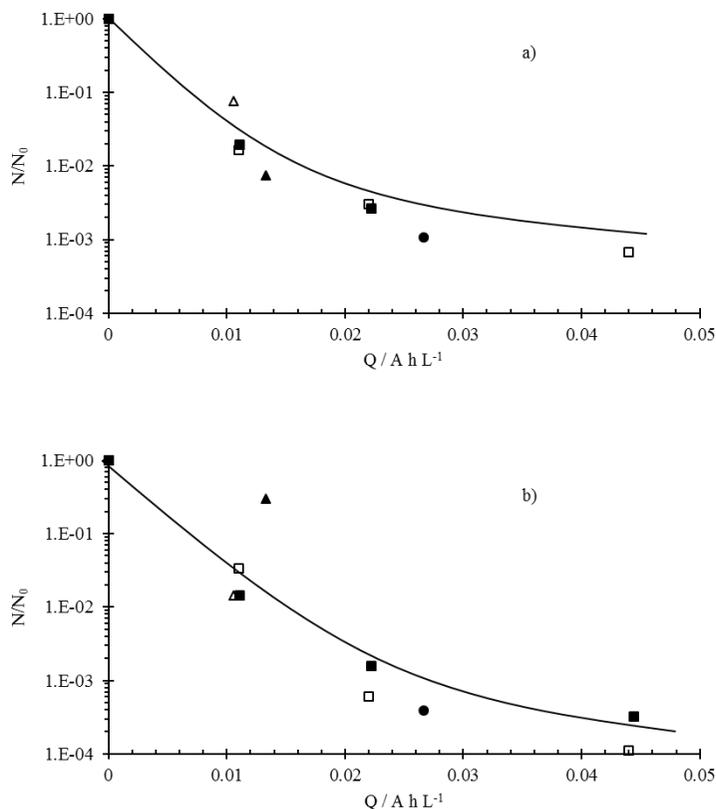


Figure 5.2. Disinfection attained by the ECWP® (filled symbols) and CabECO® (empty symbols) cells working in continuous mode a) Total coliforms; b) *Pseudomonas Aeruginosa*.

■ 90 L h⁻¹; ▲ 300 L h⁻¹; ● 150 L h⁻¹.

The technology of the CabECO® cell used is completely different and the electrolyte is not the treated water but a polymer electrolyte membrane (PEM), which connects directly the anode and the cathode of the cell. Thus, with this technology the conductivity of the water to be disinfected is no longer important and the electrochemical disinfection process can be used efficiently, even with water of very low conductivity. In fact, this cell has been proposed as efficient ozone generators in almost pure water by the reaction of the hydroxyl radical with oxygen (eq 5.1).



Figure 5.2 also shows the removal of total coliforms and *P. Aeruginosa* attained with CabECO® cell. Again, a clear exponential decrease in the concentration of surviving pathogens is observed, regardless of the flowrate treated and intensity applied, confirming that the specific current passed is the primary operating parameter of the electro-disinfection process. Charge values applied are not very high and this means that disinfection is very efficient.

In comparing the two cells evaluated in this work, important differences can be found in the efficiency of the electro-disinfection, being that the latter technology, with a PEM connecting the anode and the cathode, is more efficient than the technology that used undivided cells. In fact, in this case at 0.02 Ah L^{-1} , disinfection rates are almost or above 3-log units, which means at least 1-log more than the ECWP® cell.

Results about disinfection are not surprising, in particular taking into account the recent works shown in literature about electro-disinfection with diamond coatings. However, they bring up the significance of the cell design on the achievement of high efficiencies in the disinfection technology, especially because of the outstanding results obtained by the special cell concept. Besides, there is also a very important point regarding disinfection with diamond anodes, which should not be avoided in the discussion: the production of chlorates and perchlorates during the electrolysis. It is far away from controversy that efficiency in the generation of oxidants during the electrolysis with diamond anodes is over the values that can be attained with other electrodes such as the Mixed Metal Oxides (MMO) electrodes. Even so, the occurrence of hazardous species has been identified as a major drawback, which need to be addressed.

This can be clearly seen in Figure 5.3, in which the speciation of chlorine during the electrolysis carried out with the ECWP® cell is shown and where it can be seen that: 1) chlorate is formed in significant concentrations (even much higher than those of hypochlorite) as the main product and 2) perchlorate occurrence is observed. The data shown corresponds to steady state and the concentration of perchlorate was near the detection limit of the IC chromatograph used. This explains the singular detection of perchlorates at only an intermediate charge. Initially, the strategy used of continuous operation and single pass was implemented to minimize the production of the two hazardous species and results obtained demonstrate that it is partially successful

because concentrations are not high. However, results clearly point out that there is still room for improvement because the target is not simply the minimization but the total absence of both chlorinated products.

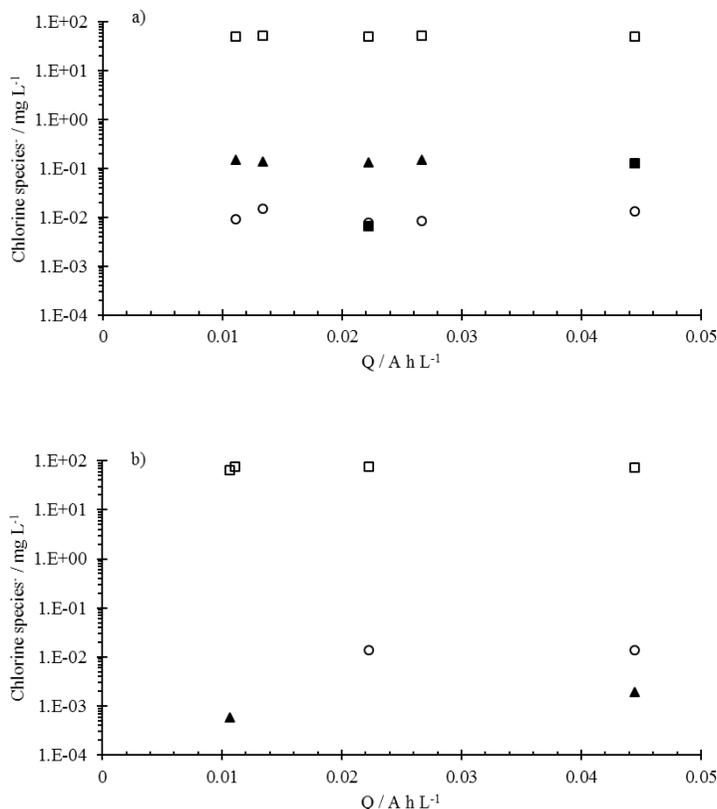


Figure 5.3. Chlorine speciation during the electrodisinfection test carried out with a) ECWP[®] and b) CabECO[®] cells working in continuous mode. □ chloride; ○ hypochlorite; ▲ chlorate; ■ perchlorate.

Originally, the different design concept used in the CabECO[®] cell is expected to have a positive influence on the prevention of the production of chlorates and perchlorates, because the most important electrolyte in the cell are not the salts contained but the proton exchange membrane that separates the anode and the cathode. This is confirmed in part b, which shows the results obtained in the CabECO[®] cell. As expected, the concentration of chlorates is much lower (more than one log difference). This means that the new configuration proposed for these cells minimize the risk of

production of hazardous byproducts with concentrations that are negligible in the case of chlorate ($< 2 \mu\text{g L}^{-1}$) and even below the detection limit of the IC in the case of perchlorates.

Continuous mode and single pass through the cell were pointed out to minimize the impact of the production of chlorate and perchlorate and results obtained in this work confirm this assumption. Formation of perchlorate is a sequential process in which the formation of chlorine and hypochlorite are the first steps (eqs. 5.2 and 5.3). It is important to maximize the yield of this low valent specie and trying to avoid its further oxidation. If contact time between the solution containing hypochlorite and the electrode is very short, this further oxidation can be expected to be avoided.

However, in order to know more about the mechanisms, it was decided to carry out additional treatments in discontinuous mode with both cells. In discontinuous mode, the water is recirculated through the reactor several times and it is expected that the oxidation of hypochlorite to chlorates and perchlorates will be more important, as compared to the results obtained in continuous mode and single pass. This is because the production of these two species is promoted by the interaction of the hydroxyl radicals formed on the surface of the diamond anodes and the hypochlorite according to eqs. 5.4- 5.6.

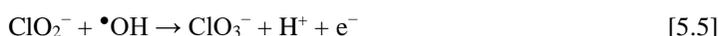


Figure 5.4 shows the performance of the electrodisinfection in discontinuous mode at current intensities within the range of 0.02-2.00 A carried out with the two cells. As seen, in general terms the same conclusions can be drawn from the results obtained by those cells. Both cells show similar capacities for disinfection also in discontinuous operation mode, being that the removal achieved is depending on the

electric current charge passed. Clearly, the discontinuous mode seems to be less efficient in disinfection than the continuous mode. Thus, for the same electric charges, the removals obtained in discontinuous mode are at least one-fold below those obtained in continuous mode and a much higher applied charge is required in order to attain the same removal percentage. The different speciation of chlorine can help to explain the differences observed.

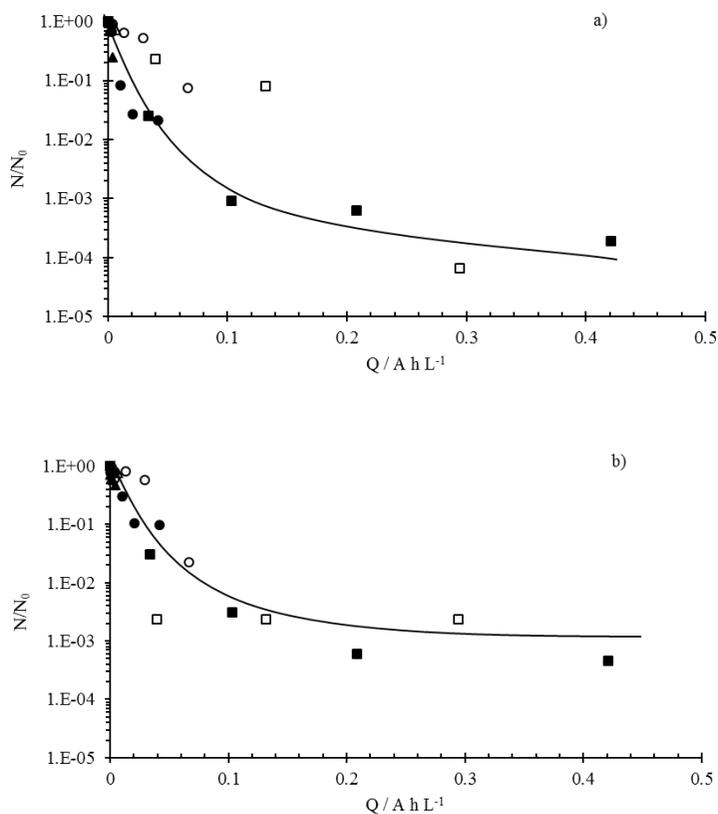


Figure 5.4. Disinfection attained by the ECWP[®] cell (full symbols) and CabECO[®] cell (empty symbols) cells working in discontinuous mode a) Total coliforms and b) *Pseudomonas*

Aeruginosa with: ▲ 0.02 A; ● 0.2 A; ■ 2.00 A.

However, what seems to be more important is not the reduction attained in the population of microorganism (which is very important and followed the trends expected) but the chlorine speciation attained by each of the cells (shown in Figure 5.5). Again, the speciation is rather different in the two cell concepts. The ECWP[®] cell

produces concentrations of hazardous byproducts that are 1-log higher than for the CabECO® cell. This confirms the outstanding performance of the use of a PEM as electrolyte instead of the treated water.

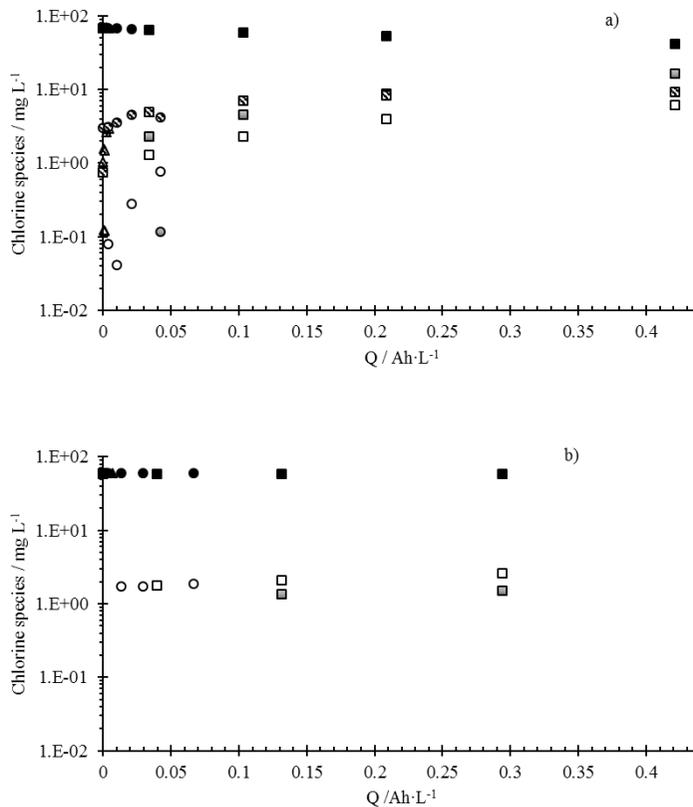


Figure 5.5. Chlorine speciation during the electrodisinfection test carried out with a) ECWP® and b) CabECO® cells in discontinuous mode. ▲ 0.02 A; ● 0.20 A; ■ 2.00 A. Chloride: full symbols; chlorate: empty symbols; perchlorate: degraded symbols; hypochlorite: dashed.

Anyhow, what it is more relevant from the data shown in this Figure, is the very high concentrations of chlorates and even perchlorate measured, especially when compared to those obtained in continuous operation mode with the same cells. They confirm that not only the cell, but more importantly, the operation mode can help to prevent the important problem of the occurrence of these hazardous species in electrochemical disinfection. Concentrations are much higher in the case of the ECWP® cell, confirming that the membrane-assembly concept used in the CabECO® technology

is suitable and advisable to prevent the formation of the chlorates and perchlorates but, in order to be efficient, these cells have to be operated in continuous mode, because the repeated pass of the treated water through the cells favors the undesired reactions shown in eqs 5.5 and 5.6.

5.1.2 Study of the influence of the cell size in water disinfection: CabECO® vs MIKROZON®

In the previous section, it was demonstrated that the design of a disinfection device following the concept of PEM cell may lead to a high efficiency in disinfection while reducing the occurrence of the hazardous species. For this reason, the following stage of this research consisted in comparing two cells with this non-conventional technology for disinfection of water. The CabECO® cell, that has already evaluated in the previous section, and the MIKROZON® cell, as in both of them the electrolyte is not the treated water but a polymer electrolyte membrane (PEM), which connects directly the anode and the cathode of the cell. Regarding the two cells used, differences are more in size than in configuration and residence times and contact time of the water with the electrodes are rather different. Figure 5.6 shows the removal of total coliforms attained with both cells and Figure 5.7 focuses on the removal of *P. Aeruginosa*.

A clear exponential decrease in the concentration of surviving pathogens is observed, regardless of the flowrate treated and intensity applied, confirming that the specific current passed is the primary operating parameter of the electro-disinfection process. Charge values applied are not very high and this means that disinfection is very efficient because even with power consumptions below 0.734 kWh m^{-3} , it can be attained up to a five-log decrease in the concentration. In comparing the CabECO® and the MIKROZON®, this second cell demonstrates a rather better behavior, being able to remove more than 5-log of Total coliforms and more than 4-log of removal of *P. Aeruginosa* for charges of only 0.04 Ah L^{-1} . Taking into account the lower cell voltages in this case the power consumption is as low as 0.522 kWh m^{-3} .

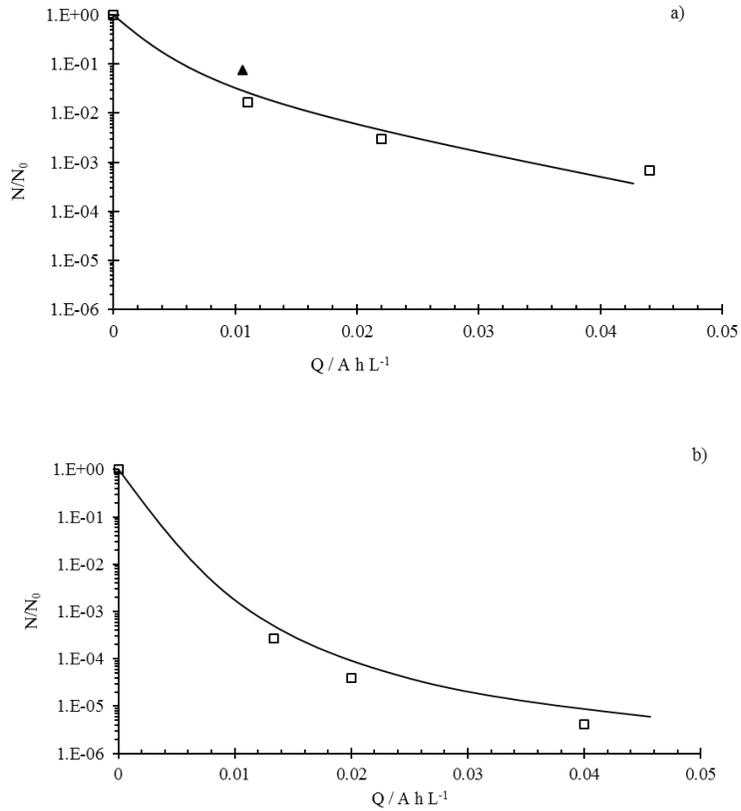


Figure 5.6. Removal of Total Coliforms attained by a) CabECO® (\square 90 L h⁻¹ at 1.0, 2.0 and 4.0 A; \blacktriangle 300 L h⁻¹ at 3.2 A) and b) MIKROZON® (\square 1.2 A and 30, 60 and 90 L h⁻¹) working in continuous mode at different flow rates and current densities as specified.

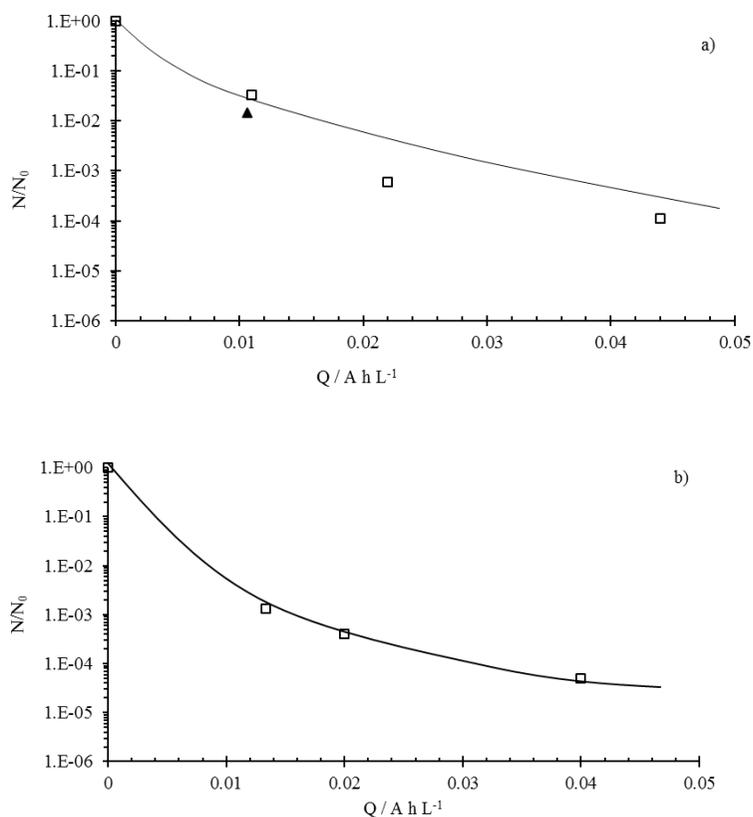


Figure 5.7. Removal of *Pseudomonas Aeruginosa* attained by a) CabECO® (□ 90 L h⁻¹ at 1.0, 2.0 and 4.0 A, ▲ 300 L h⁻¹ at 3.2 A) and b) MIKROZON® (□ 1.2 A and 30, 60 and 90 L h⁻¹) working in continuous mode at different flow rates and current densities as specified.

Again, the occurrence of chlorates and perchlorates during the electrolysis were evaluated in order to assure which cell was the most suitable for water disinfection. This can be clearly observed in Figure 5.8, which shows the speciation of chlorine during the electrolysis carried out with the two cells. Initially, the design concept used in the CabECO® and MIKROZON® cells is expected to have a positive influence on the prevention of the production of chlorates and perchlorates, because the most important electrolyte in the cell are not the salts contained but the proton exchange membrane that separates the anode and the cathode.

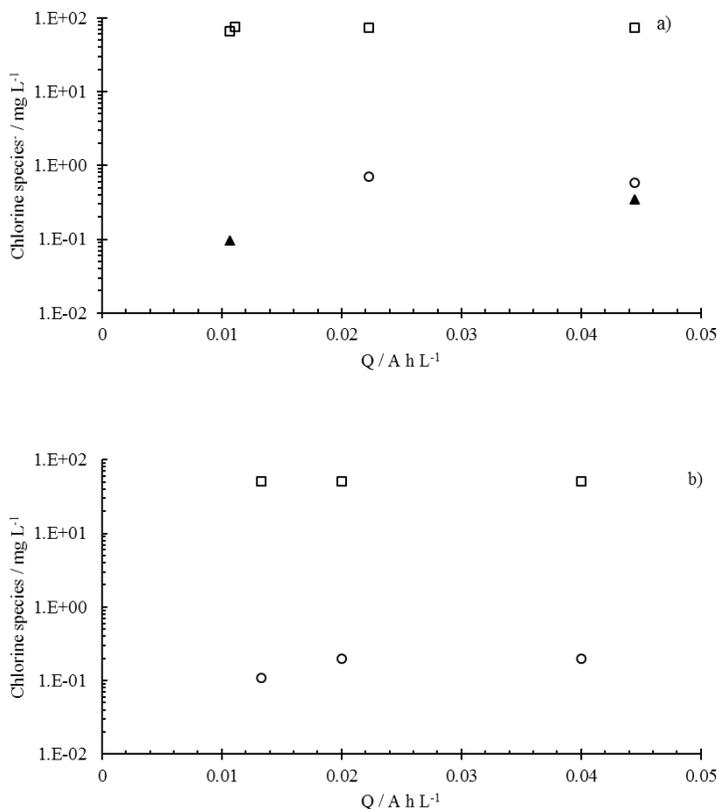


Figure 5.8. Chlorine speciation during the electrodisinfection tests carried out with a) CabECO® (90 L h⁻¹ at 1.0, 2.0 and 4.0 A and 300 L h⁻¹ at 3.2 A) and b) MIKROZON® (1.2 A at 30, 60 and 90 L h⁻¹) working in continuous mode. □ chloride; ○ hypochlorite; ▲ chlorate; ■ perchlorate.

As expected, the concentration of chlorates is very low in the CabECO® cell (more than one log difference in respect to other cells typically proposed for disinfection) and even undetectable in the case of the MIKROZON® (below 10 µg L⁻¹). In addition, in any case perchlorates were detected. This means that the novel configuration proposed for these cells minimize the risk of production of hazardous byproducts and it is particularly relevant in the case of the smallest MIKROZON® cell. In fact, this is an outstanding result, because it is the first time that it is reported that complete absence of these two hazardous species can be achieved. However, there is still one important question to be answered: why despite having the same internal

configuration, the MIKROZON[®] cell is capable to prevent the formation of chlorates and perchlorates?

Thus, it could be related with the hydraulic residence time (HRT) as it is the most relevant difference between the CabECO[®] and the MIKROZON[®] cells and most particularly, the contact time of the fluid with the electrode, which is close to 0.7 s in the case of the CabECO[®], (for the flowrate of 90 L h⁻¹) and only of 0.008-0.024 s for the MIKROZON[®] (for flowrates in the range 30- 90 L h⁻¹). Formation of perchlorate is a sequential process in which the formation of chlorine (and hypochlorite) is one intermediate step. If contact time between the solution containing hypochlorite and the electrode is very short, the further oxidation of hypochlorite is expected to be hindered. This is caused because further oxidation of hypochlorite to chlorates and perchlorates mainly occur by the direct action of hydroxyl radicals and the concentration of these radicals is much higher in the proximities of the electrodes (eqs. 5.4-5.6)

To study the influence of the HRT in the chlorine speciation and the disinfection efficiency, different operation modes and flux connections of the MIKROZON cell will be evaluated in the following section.

5.1.3 Role of the hydraulic residence time in the disinfection performance of a PEM electrochemical cell

In order to increase the Hydraulic Residence Time (HRT) of the fluid when came across the MIKROZON[®] cell, three different strategies were followed (Figure 5.9) :

- 1) 4 MIKROZON[®] connected in series (Figure 5.9 a) and operated in continuous mode.
- 2) 4 MIKROZON[®] connected in parallel (Figure 5.9 b) and operated in continuous mode
- 3) 1 MIKROZON[®] operated in discontinuous mode (Figure 5.9c)

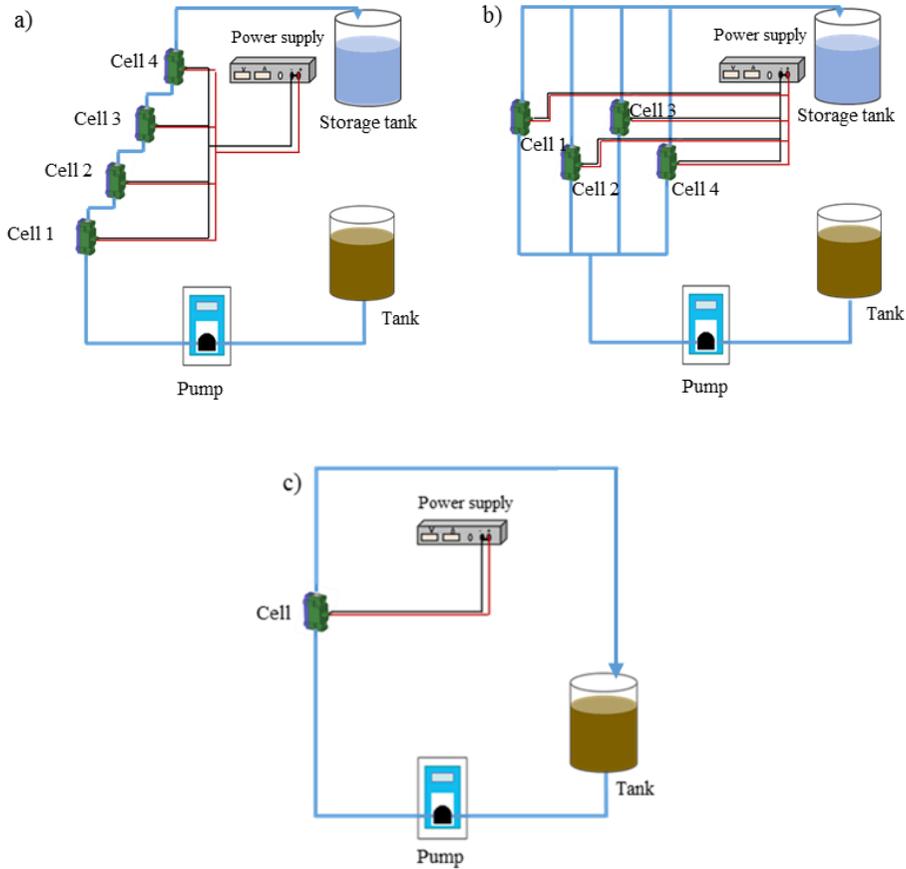


Figure 5.9. Scheme of the three strategies followed a) 4 MIKROZON[®] connected in series; b) 4 MIKROZON[®] connected in parallel; c) 1 MIKROZON[®] in discontinuous mode.

Firstly, in order to clarify the point of the low HRT of one MIKROZON[®] cell a series of tests was planned, consisting in a sequence of 4 MIKROZON[®] (Figure 5.9 a) fed with three different flowrates inside the recommended range according to the manufacturer (30-90 L h⁻¹ to promote good turbulence conditions inside the cell) and operating in continuous operation mode. Thus, the outlet of one MIKROZON[®] becomes the inlet of the following one. HRT in each cell varied from 0.008 up to 0.024 s and in the sequence of 4 cells from 0.032 to 0.096 s, still one-fold below of the HRT attained with the CabECO[®] cell. With this experiment, the current charge applied to water and the residence time increase from one cell to the following one. Results obtained are shown in Figure 5.10 regarding disinfection attained (Total Coliforms; *Pseudomonas Aeruginosa*) and in Figure 5.11 regarding hazardous species produced

(chlorates) for three different flowrates. Each point corresponds to the steady-state outlet of one single cell.

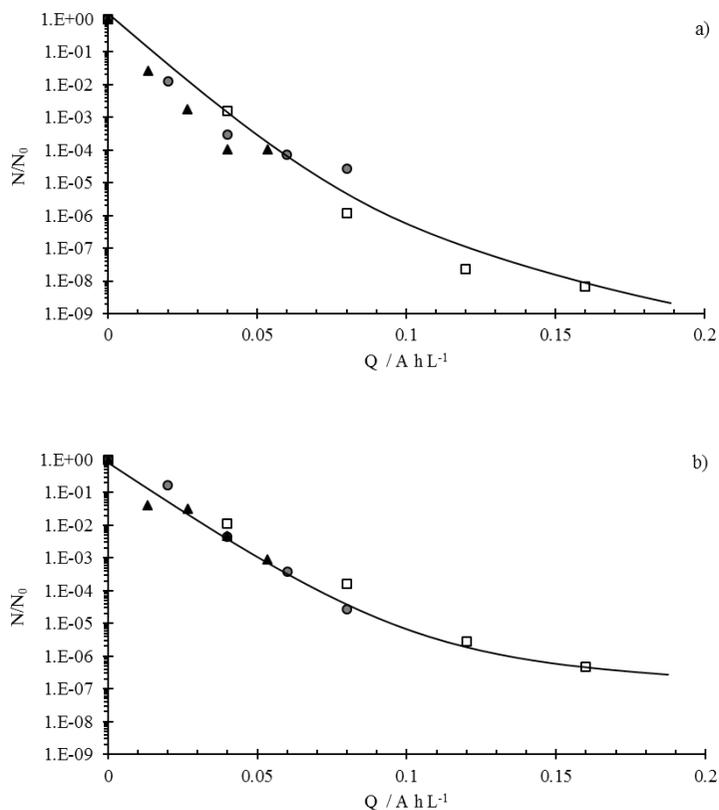


Figure 5.10. Disinfection attained by a sequence of 4 MIKROZON® a) Total Coliform and b) *Pseudomonas Aeruginosa* operated at \square 30; \bullet 60 and \blacktriangle 90 L h^{-1} working in continuous mode at the same current intensity of 1.2 A.

As expected, the higher the charge applied the higher the removal of pathogens attained. These small cells are capable to reduce more than 6-8 log units in water samples with a very high pathogen concentration. In addition, the low dispersion of the N/N_0 plots informs about the robustness of the technology, which is very important, in particular if taking into account that results are the consequence of the pass of water throughout a different number of cells.

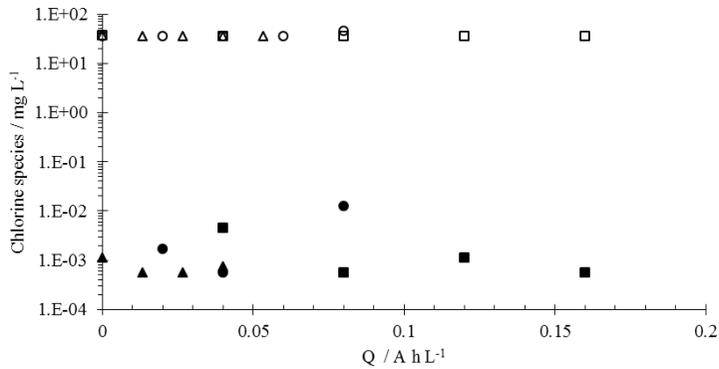


Figure 5.11. Chlorine speciation during the electrodisinfection tests carried out with a sequence of 4 MIKROZON[®] operated at ■ 30; ● 60 and ▲ 90 L h⁻¹ working in continuous mode at the same current intensity of 1.2 A. Empty symbols: chloride; full symbols: chlorate.

However, what it is more important is the very low concentration of chlorates which, in addition, were initially present in the water used at a level of 1 µg L⁻¹, close to the detection limit of the chromatographic technique used and that, with the use of the cells it does not overcome the limit of 5 µg L⁻¹ in any case. In addition, the very low concentrations of chlorate detected decreased from the tests made with 30 L h⁻¹ down to the tests fed with 90 L h⁻¹, although in all cases concentration is too negligible to draw any relevant conclusion except for the outstanding performance of the cells, which avoid chlorate and perchlorate formation, even when the residence time is increased up to four times from the recommended values by connecting them in series. Anyway, this trend supports the hypothesis of the great influence the HRT has on the prevention of the formation of chlorates and perchlorates during disinfection.

Secondly, in order to increase the HRT and check the capacity of disinfection and reproducibility another set of experiments were carried out for the treatment of surface water intensified with microorganisms by four different MIKROZON[®] cells operated in parallel (Figure 5.9 b). In every case the current applied was 1.2 A, the maximum value recommended by the manufacturer for a safe and optimized operation, and the flow rate was changed from 7.5 to 22.5 L h⁻¹, values lower than the recommended flowrate for these cells (30-90 L h⁻¹ in order to have an optimum turbulence). They were selected in order to operate in the worst possible conditions trying to see if the production of chlorates can be avoided as it was observed in previous

works even when increasing HRT from the recommended value of 0.008 s (90 L h^{-1}) up to almost 0.1 s (7.5 L h^{-1}). Thus, Figures 5.12-5.14 show the time course of the concentration of Total Coliforms and *Pseudomonas Aeruginosa* evaluated in continuous mode at 3 different flow rates.

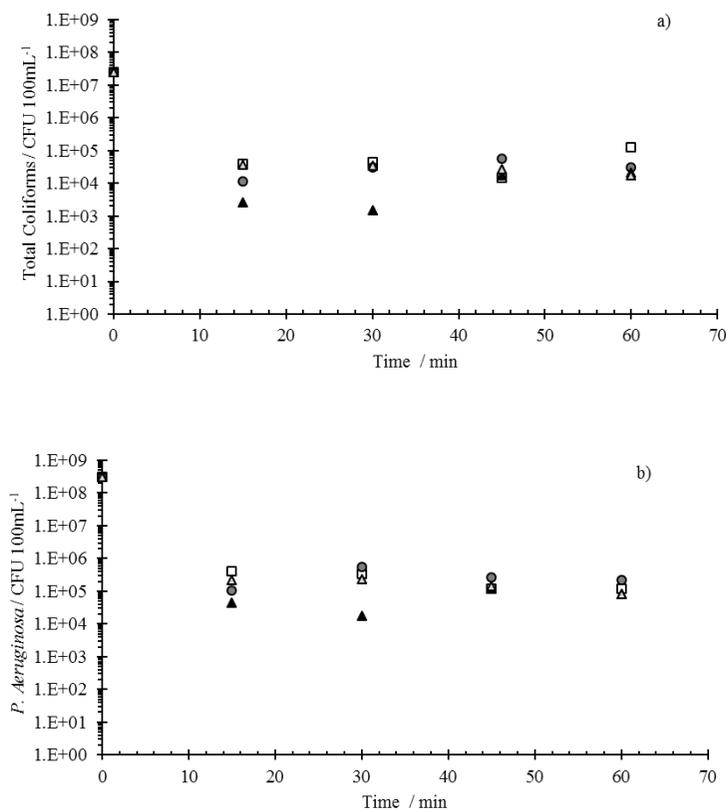


Figure 5.12. Disinfection attained by 4 MIKROZON® cells connected in parallel a) Total Coliforms and b) *Pseudomonas Aeruginosa* operated at 7.5 L h^{-1} working in continuous mode at the same current intensity of 1.2 A. □ Cell 1; ▲ Cell 2; △ Cell 3; ● Cell 4.

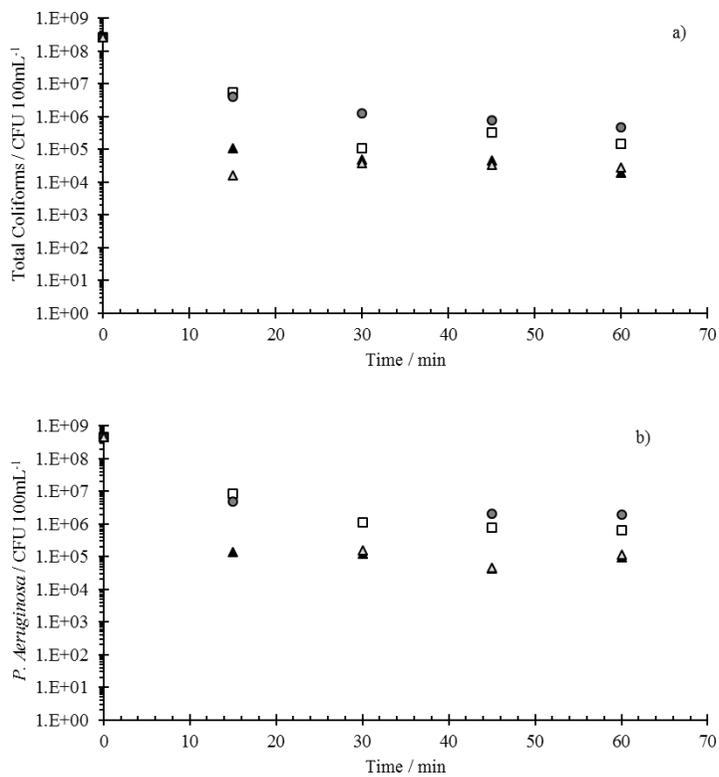


Figure 5.13. Disinfection attained by 4 MIKROZON[®] cells connected in parallel a) Total Coliforms and b) *Pseudomonas Aeruginosa* operated at 15 L h⁻¹ working in continuous mode at the same current intensity of 1.2 A. □ Cell 1; ▲ Cell 2; △ Cell 3; ● Cell 4.

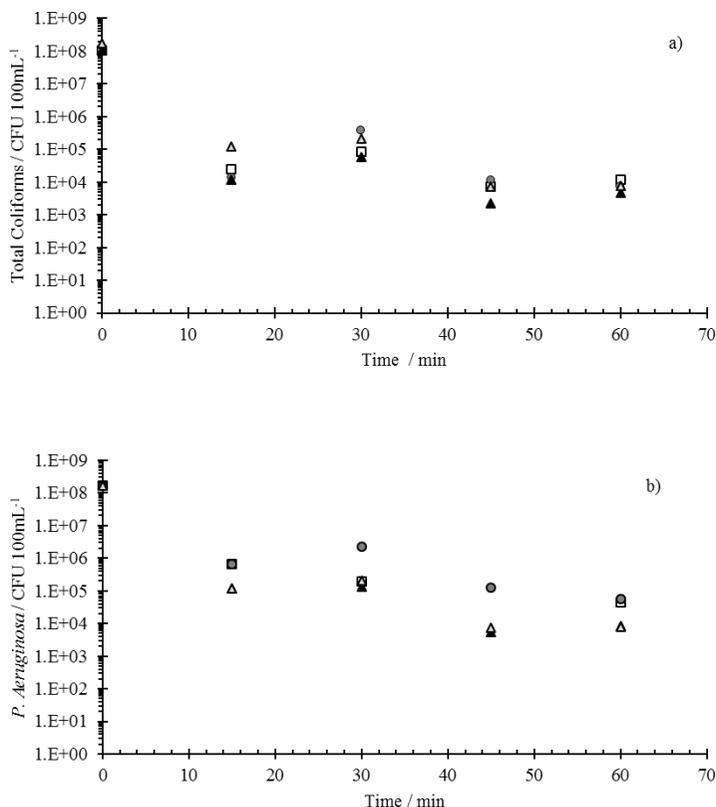


Figure 5.14. Disinfection attained by 4 MIKROZON[®] cells connected in parallel a) Total Coliforms and b) *Pseudomonas Aeruginosa* operated at 22.5 L h⁻¹ working in continuous mode at the same current intensity of 1.2 A. □ Cell 1; ▲ Cell 2; △ Cell 3; ● Cell 4.

As it can be observed, the stationary response is obtained very rapidly, regardless of the flow rate used and an important decrease in the concentration of both types of pathogens is obtained. In less than 10 minutes, there are no appreciable changes in the concentration although dispersion of data informs about the complexity of the processes happening inside the cell. Anyway, a remarkable removal of 4-5 logs is obtained in every case. This removal is in agreement with other tests previously made with the same electrolyzer. Thus, Figure 5.15 summarizes the effect of this current charge applied on the disinfection attained as well as the effect of the flowrate (using additional data obtained in 9 different tests run with the same cells). As seen, the removal attained with these cells depends on the flowrate and current charge passed and it can be even as high as 7-8 logs.

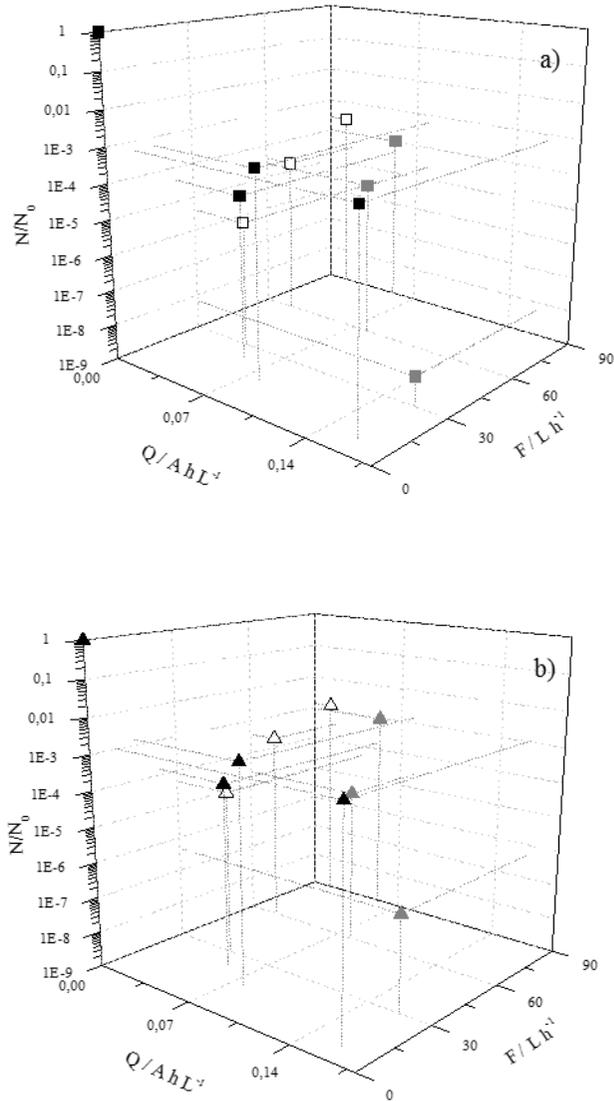


Figure 5.15. Disinfection attained following different strategies a) Total Coliforms and b) *Pseudomonas Aeruginosa* working in continuous mode. Empty symbols: 1 MIKROZON[®] operated at 30, 60 and 90 L h⁻¹ (section 5.1.2); Degraded symbols: 4 MIKROZON[®] connected in series operated at 30, 60 and 90 L h⁻¹; Full symbols: 4 MIKROZON[®] connected in parallel operated at 7.5, 15 and 22,5 L h⁻¹. Each cell was operated at the same current intensity of 1.2 A.

Regarding the production of chlorates and perchlorates during operation of the electrodisinfection, it is shown in Figure 5.16 for the three tests carried out with four cells each. It is important to point out that in previous works, concentration of chlorates in continuous disinfection at flowrates higher than 30 L h^{-1} never overpasses the level of $10 \mu\text{g L}^{-1}$. Nevertheless, in this case, no perchlorates were detected in any of the tests and, as seen the concentrations of chlorates measured are very low (in particular when increasing the flowrate up to values close to the ones recommended by the manufacturer) with values below $5.0 \mu\text{g L}^{-1}$ of limit in the case of operating at 22.5 L h^{-1} . Again, a high dispersion is obtained, being indicative of the many inputs that affect to the process performance.

Figure 5.17 shows, in a 3-D plot, the influence of the current charge passed and flowrate on the generation of chlorates with these cells. Again, it is important to keep in mind that perchlorates have never been detected and that in using low residence times, results clearly indicate that prevention of chlorates formation down to reasonable levels can be achieved, with large flowrates and low current charges being very important to use. Anyway, the maximum concentration reached is lower than $30 \mu\text{g L}^{-1}$ and in most cases the value is under $5 \mu\text{g L}^{-1}$ and even undetectable by IC. It is important to note that the process is operated in continuous mode and that the data shown are steady-state data. In addition, it is important to see that initial concentration of chloride is 50 mg L^{-1} , meaning that less than 0.1% is transformed into the hazardous species.

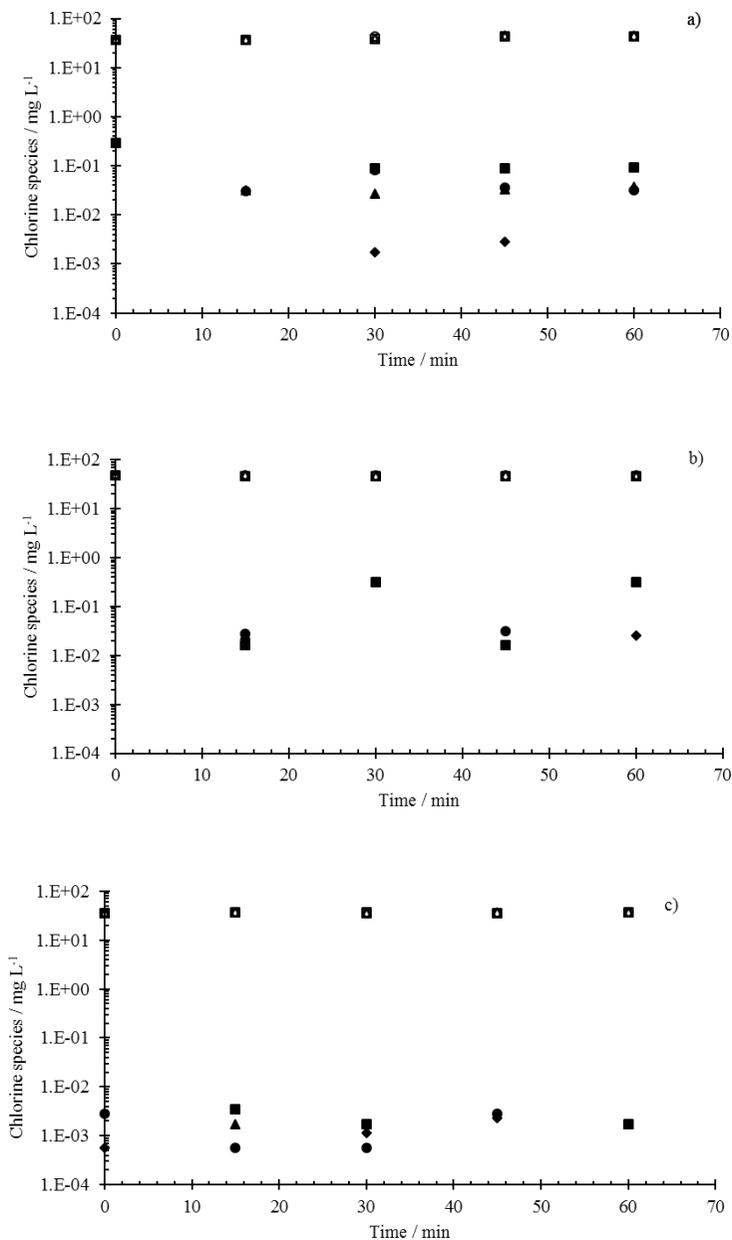


Figure 5.16. Chlorine speciation during the experiments carried out with 4 MIKOZON[®] cells connected in parallel operated at a) 7.5 L h⁻¹; b) 15.0 L h⁻¹; c) 22.5 L h⁻¹ working in discontinuous mode at the same current intensity of 1.2 A. chloride: empty symbols; chlorate: full symbols. ■ cell 1; ● cell 2; ◆ cell 3; ▲ cell 4.

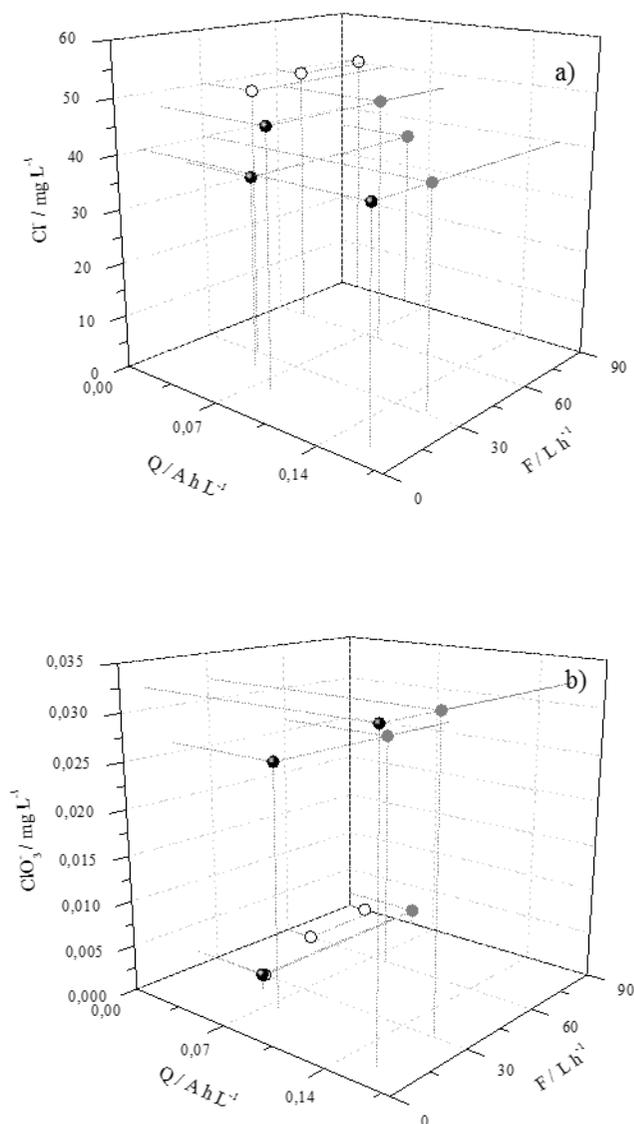


Figure 5.17. Chlorine speciation: a) reduction of chlorides b) production of chlorates following different strategies working in continuous mode. Empty symbols: 1 MIKROZON[®] operated at 30, 60 and 90 L h⁻¹ (section 5.1.2); Degraded symbols: 4 MIKROZON[®] connected in series operated at 30, 60 and 90 L h⁻¹; Full symbols: 4 MIKROZON[®] connected in parallel operated at 7.5, 15 and 22,5 L h⁻¹. Each cell was operated at the same current intensity of 1.2 A.

Thirdly, in order to know more about the mechanisms, it was decided to carry out additional treatments in discontinuous mode (Figure 5.9 c). In this operation mode, water is recirculated through the reactor several times and it is expected that the oxidation of hypochlorite to chlorates and perchlorates will be more important, as compared to the results obtained in continuous mode and single pass. This is because the production of these two species is promoted by the interaction of the hydroxyl radicals formed on the surface of the diamond anodes and the hypochlorite according to the previously described eqs. 5.4-5.6.

Because of the small dimensions of the MIKROZON[®] cells and although the applied currents are within the recommended ranges, it is important to point out that the resulting current densities are extremely high due to the low electrode area. As seen, in general terms the same conclusions can be drawn from the results attained by operating in discontinuous mode although, it is very important to point out that the best results for the MIKROZON[®] were obtained working at the lowest current densities (Figure 5.18).

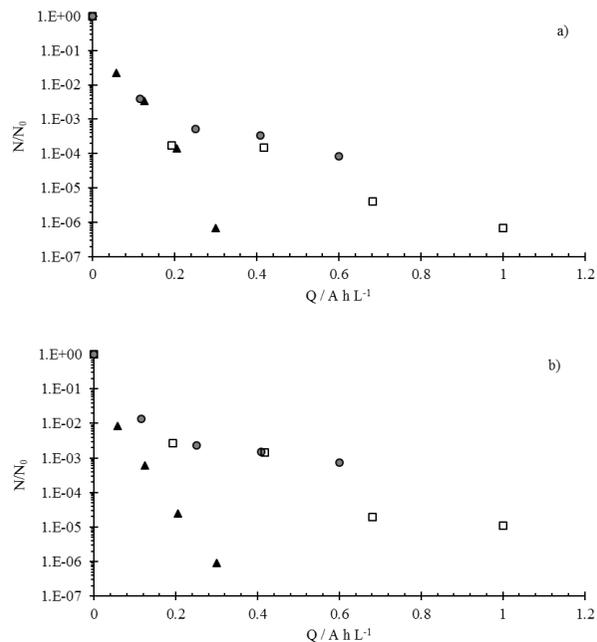


Figure 5.18. Disinfection attained by MIKROZON[®] cell a) Total Coliform and b) *Pseudomonas Aeruginosa* working in discontinuous mode. ▲ 0.3 A; ● 0.6 A; □ 1.0 A.

Equally important as the reduction of microorganisms, which followed the expected trend, is the chlorine speciation attained by the cell (shown in Figure 5.19). As expected, the concentrations are higher than in continuous mode, although in any case the level of the ppm is reached. Hence, these data confirm that the low residence time in the cell (with the subsequent low contact time of the hypochlorite precursors and the hydroxyl radicals produced on the anode surface) is a key to attain an electro-disinfection with nill or low production of chlorates. In this discontinuous mode, the MIKROZON[®] produced a non-negligible amount of chlorates and perchlorates. Thus, these results confirm our previous hypothesis about the key role of the hydraulic residence time in the performance of the cell and the occurrence of disinfection by-products.

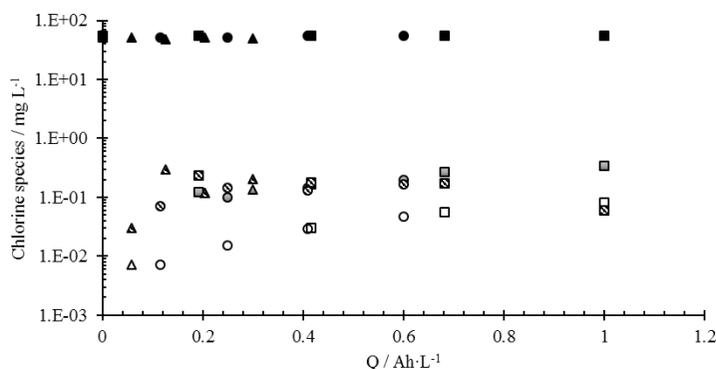


Figure 5.19. Chlorine speciation during the experiments carried out with MIKROZON[®] cell working in discontinuous mode. Chloride: full symbols; chlorate: empty symbols; perchlorate: degraded symbols; hypochlorite: dashed: ▲ 0.3 A; ● 0.6 A; ■ 1.0 A.

Additionally, a simulation of the hydraulic fluxes in the MIKROZON[®] cell was carried out to confirm the role of the internal design of the cell. Figure 5.20 shows the hydrodynamics simulation of this cell at a flow rate of 1.1 L min^{-1} (66 L h^{-1}).

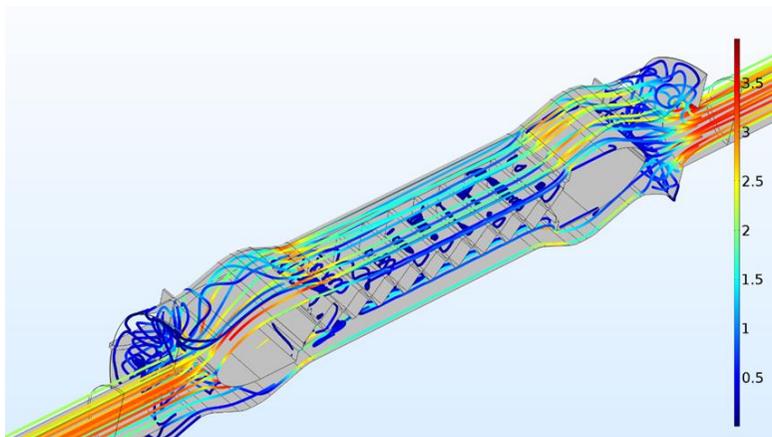


Figure 5.20. Hydrodynamics simulation of flow velocity inside the MIKROZON[®] cell.

As it can be observed, the highest velocity is reached along the electrode meanwhile the lowest velocity is in the electrode trenches. Taking into account the hydraulic simulation, the low production of electrolysis by-products can be explained due to bypass of most volume.

According to these results, both cells using a PEM electrolyte presents a similar performance in the disinfection of synthetic solutions and limit the production of hazardous by-products when proper working conditions are selected. At this point, and as it has been previously explained in this PhD report, it is worth noting that the present work was developed in the framework of the project SafeWaterAfrica. Taking this into account, the higher size of the CabECO[®] devices makes them more suitable than MIKROZON[®] for the targeted treatment flowrate of the project (900 L h⁻¹ for three parallel treatment lines). All in all, due to the similar performance of both MIKROZON[®] and CabECO[®] and the more suitable size of the former, the CabECO[®] cell was selected to perform the optimization the process for the treatment of real wastewater, which results will be presented in the following section.

5.1.4 Conclusions

In the first chapter of this PhD Thesis, three different commercial cells have been studied for the disinfection of water intensified in microorganisms. The main conclusion of this work is that the design of the electrochemical cell and the hydraulic residence time are key variables to assure a high disinfection efficiency and to avoid

the production of hazardous disinfection by-products. Apart from this general comment, the following specific conclusion can be reached:

- The cell design has an important influence on the performance of the electrolysis with diamond electrodes, even higher than that produced by the own electrodic materials.
- The use of PEM cells (CabECO® and MIKROZON®) slightly improves the disinfection performance as compared to non-divided cells (as ECWP®).
- Disinfection is more efficient in continuous than in discontinuous operation mode. The different speciation of chlorine can help to explain the differences observed.
- Formation of chlorate and perchlorates during electro-disinfection can be prevented with the use of PEM electrolytic cells and a continuous operation mode with a single-pass strategy. The low residence time and the different electrolyte used (the solution to be treated in a conventional configuration vs an ionic exchange membrane in PEM devices) are the key to limit the occurrence of hazardous disinfection by-products.
- By connecting cells in series, the disinfection attained can be increased and more than 8-logs have been achieved. In any case the N/N_0 follow the same decay trend respect to the current charge passed regardless of the number of cells attached. Even increasing residence time four-fold, the concentration of chlorates is very low and close to the detection limit of the analytical used.

5.2 Performance of the CabECO® technology for the disinfection of highly fecal-polluted surface water

Taking into account the premises of the earlier section, a more thorough investigation was conducted to better understand the CabECO® cell performance. As the final goal of this chapter was to establish the efficiency of CabECO® technology in the direct disinfection of surface water containing fecal pollution, different operations mode and water matrixes were studied. As well as in the previous experiments Total Coliforms and *Pseudomonas Aeruginosa* were selected as indicators of pathogenicity. In addition, *Total Aerobic Microorganisms* were also monitored in order to determine the effect of the technology not only on disinfection but also on sterilization. The effects of the current density on disinfection efficiency and the formation of undesirable by-products were also evaluated.

The first step was to evaluate the actual composition of the water that can be found in rural areas of South Africa and Mozambique, the target areas of the SafeWaterAfrica project. Thus, Table 5.4 shows the characterization of two real samples taken from the two test sites of the project, Klip River and Hennops River.

As it can be observed, after the physical-chemical and biological analyses of the samples, there are some parameters that present too high values for human supplies. Thus, high turbidity and suspended solids are indicatives of the presence of particles that could be mainly organic if TOC values are taken into account but which could be chemically oxidized looking at the COD values. However, another important point is the large amount of microorganisms that are far from those that can be found in normal conditions in any surface water reservoir in our environment. For this reason, the water used in the test to simulate these water supplies was prepared by merging the inlet of the municipal Water Treatment Plant of Ciudad Real with the effluent of the secondary clarifier of the municipal Wastewater Treatment Plant (WWTP) of Ciudad Real. This mixture was made with several ratios with the purpose of increasing the amount of organic matter and microorganisms. Even an additional test was carried out with an extremely polluted water (using water from the Pretreatment stream of the WWTP) for comparison purposes and in order to establish the limits of the technology.

Table. 5.4 Real water sources analyses.

Parameter	Units	Klip River	Hennops River
Total Coliforms	CFU 100 ml ⁻¹	3940	106100
Pseudomona Aureginosa	CFU 100 ml ⁻¹	61600	266000
Total aerobic microorganisms	CFU 100 ml ⁻¹	31900	532000
Suspended Solids	mg L ⁻¹	46.67	17.5
Total Organic Carbon (TOC)	mg L ⁻¹	5.29	4.68
Inorganic Carbon	mg L ⁻¹	21.9	26.55
Total Carbon	mg L ⁻¹	27.19	31.42
Total Nitrogen	mg L ⁻¹	2.53	4.03
Chemical Oxygen Demand (COD)	mg L ⁻¹	36	19
F⁻	mg L ⁻¹	0.00	0.24
Cl⁻	mg L ⁻¹	35.24	40.60
NO₃⁻	mg L ⁻¹	21.72	2.82
PO₄²⁻	mg L ⁻¹	0.36	0.50
SO₄²⁻	mg L ⁻¹	59.85	36.25
Na⁺	mg L ⁻¹	52.45	57.08
NH₄⁺	mg L ⁻¹	0	12.08
K⁺	mg L ⁻¹	8.18	9.17
Ca²⁺	mg L ⁻¹	31.01	31.56
Mg²⁺	mg L ⁻¹	16.26	13.81

The experimental conditions studied in each of the electrodisinfection experiments carried out with CabECO[®] cell are detailed in the Table 5.5.

Table 5.5. Planning of experiments of electrodisinfection real water with the CabECO® cell.

Test no.	Water matrix (. / .)	Operation mode	Current density/ A m ⁻²	Florate/ L h ⁻¹	Volume of water treated / L	Maximun specific charge passed / Ah L ⁻¹
1	95/5	Continuous	416.7	90	90	0.011
2	95/5	Continuous	833.3	90	90	0.022
3	95/5	Continuous	1666.7	90	90	0.044
4	95/5	Continuous	1333.3	300	300	0.0106
5	95/5	Discontinuous	0	-	5	0
6	95/5	Discontinuous	8.33	-	5	0.0067
7	95/5	Discontinuous	83.33	-	5	0.067
8	95/5	Discontinuous	833.33	-	5	0.29
9	80/20	Continuous	416.7	150	150	0.0067
10	80/20	Continuous	833.3	150	150	0.013
11	80/20	Continuous	1250	150	150	0.02
12	80/20	Continuous	1666.7	150	150	0.027
13	80/20	Continuous	416.7	300	150	0.0033
14	80/20	Continuous	833.3	300	150	0.0067
15	80/20	Continuous	1250	300	150	0.01
16	80/20	Continuous	1666.7	300	150	0.0133

5.2.1 Performance of the CabECO® technology for the disinfection of highly fecal-polluted surface water at discontinuous mode.

A set of experiments were done in discontinuous mode at different current densities from 0 to 833.33 Am⁻². The disinfection was evaluated by the quantification of the microorganisms (Total Coliforms, *Pseudomonas Aeruginosa* and Total Aerobic Microorganisms) present on the samples taken at several experimental times. Figure 5.20 shows the changes in the concentrations of these parameters during the electrolysis of the sample surface water in the discontinuous mode at the three different current densities studied. For comparison, a reference test was also carried out and the results are also included in Figure 5.20. In this reference test, water was passed through the cell at the same flowrate, but no current was applied. The results are plotted on a semi-log scale for improved comparison.

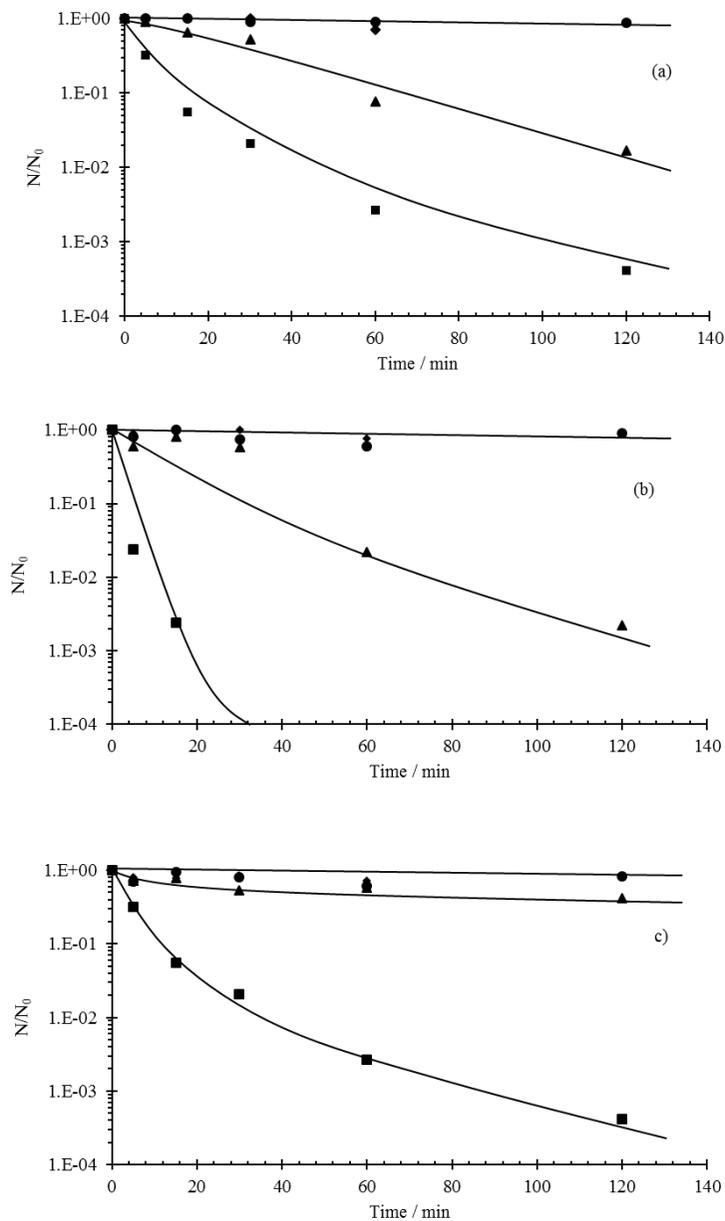


Figure 5.20. Disinfection attained by the CabECO[®] cell working in discontinuous mode at \bullet 0.00; \blacklozenge 8.3; \blacktriangle 83.3; \blacksquare 833.3 A m^{-2} . a) Total Coliforms; b) *Pseudomonas Aeruginosa* and c) Total Aerobic Microorganisms.

As expected, no change in the concentration of microorganisms was observed in the reference test. Likewise, disinfection efficiency with low values of current

density (8.3 A m^{-2}) was negligible because the changes observed in the three biological indicators were almost nil during the entire test. This was not the case for the other two tests carried out at higher current densities. Thus, the disinfection efficiency of the electrochemical technology depends strongly on the applied current density; that is, the higher the current density is, the higher the disinfection rate and the lower the number of microorganisms that remains in the water after the treatment. Hence, high values of current density (above 83.3 A m^{-2}) are required to attain disinfection. Likewise, the treatment time is also an important parameter, and the longer this time, the greater the removal of microorganisms. The treatment time (h) is related to the applied electrical charge (Ah) by equation 5.7.

$$q(Ah) = I(A) \cdot t(h) \quad [5.7]$$

Experimental data of the electrolysis fit well to first order kinetics (linear trend in semi-log plot), except for the tests carried out at the highest current density, where more complex processes may be occurring. Figure 5.21 compares the kinetic constants calculated for the removal of the three biological indicators tested during batch-electrolysis. As shown, the kinetic constants significantly depend on the current density for each biological indicator. The disinfection rate increased almost proportionally with the current density, that is, changing the current density by one log-unit produced an one-fold increase in the removal rate. In comparing the decrease in the three parameters, it can be stated that the total coliforms and *Pseudomonas aeruginosa* were removed approximately 2 times faster than the total aerobic microorganisms, meaning that the electrochemical technology is more efficient for disinfection (removal of pathogens) than for sterilization (removal of any type of microorganisms).

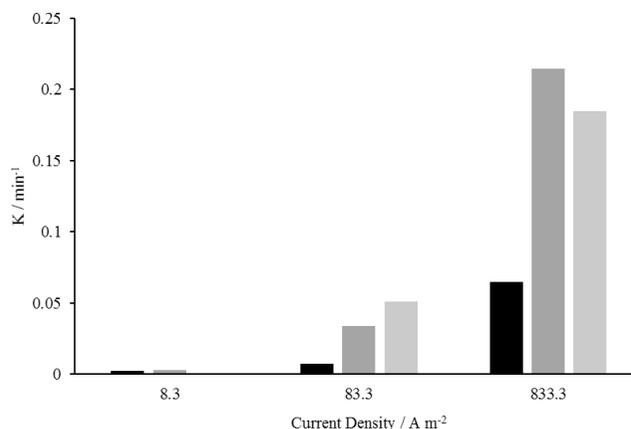


Figure 5.21. Kinetic constants calculated for the pathogens presented in the sample surface water as function of the current density applied during batch-electrolysis. ■ Total Aerobic Microorganisms; ■ Total Coliforms and ■ *Pseudomonas Aeruginosa*.

Figure 5.22 shows the changes in the TOC in the four experiments shown previously. As observed, the TOC decreased with the application of electrical current during the tests, but this decrease did not depend on the applied current densities. In fact, after two hours of electrolysis, the TOC was far from the complete mineralization of the organic load, at about 50% removal. This suggests that, within the range of the applied current densities, the process is not very efficient for TOC removal, and it should not be proposed for the simultaneous disinfection and removal of persistent organic pollutants because the electrical current required would not be cost-effective. It has to be taken into account that the organic load of the treated water comes mostly from the TOC added with the secondarily treated wastewater and typically consists of pollutants that were refractory to the biological treatment. The nil effect of the current density on the depletion of the TOC suggests that the oxidation of this species can be carried out by the ozone produced in the cell. This type of cell is known to produce large amounts of ozone by the reaction of the hydroxyl radical with oxygen (eq. 5.1), even for low current densities, regardless of the salinity of the water electrolyzed. Thus, with the lowest current density, the amount of ozone produced seems to be sufficient for the oxidation, and there is no improvement with the production of higher amounts of ozone.

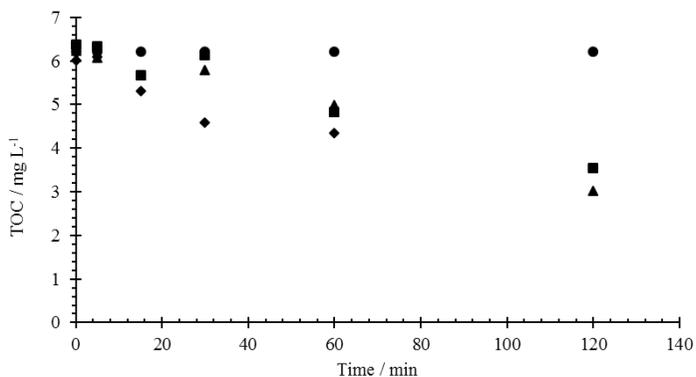


Figure 5.22. Changes in the TOC concentration during the electrolysis carried out in discontinuous mode at ● 0.00; ◆ 8.3; ▲ 83.3; ■ 833.3 A m⁻².

It has to be taken into account that salt content of the water tested in this work was very low, containing only the salts in the raw mixture, and hence the formation of a large amount of other powerful oxidants is not expected. According to the ionic content of the raw water (Table 4.2), chloride was the main anionic species with a concentration of approximately 60 mg L⁻¹, which is quite low compared to the concentration reported in the literature for the removal of organics in wastewater, which are typically in the range of 1000-3000 mg L⁻¹. However, even at low chloride concentrations, the formation of chlorinated disinfectants is expected, which explains the electrochemical disinfection and removal of the organics because the chlorinated disinfectants are very reactive and can attack the organics present in the solution. The concentration of the chloride anion decreases slightly, but it does not undergo very relevant changes (Figure 5.23). This means that after the treatment, the chloride remains the primary chlorinated species in the system.

Chloride is expected to be oxidized to chlorine, which is further transformed into hypochlorite which, in turn, can undergo further oxidation or combination processes. Figure 5.24 shows the distribution of these chlorinated species detected during the electrolysis in the discontinuous mode, classified into the desired (known as disinfectants) and the non-desired species. For comparison, the same units (mmol Cl L⁻¹) have been used in these plots.

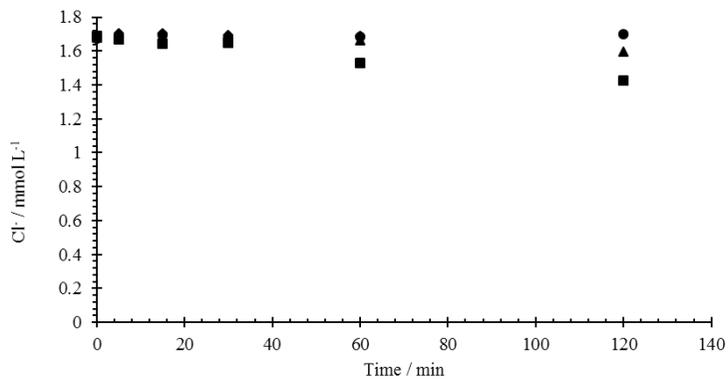


Figure 5.23. Changes in the concentration of chloride during the electrolysis carried out in discontinuous mode at ● 0.00; ◆ 8.3; ▲ 83.3; ■ 833.3 A m⁻².

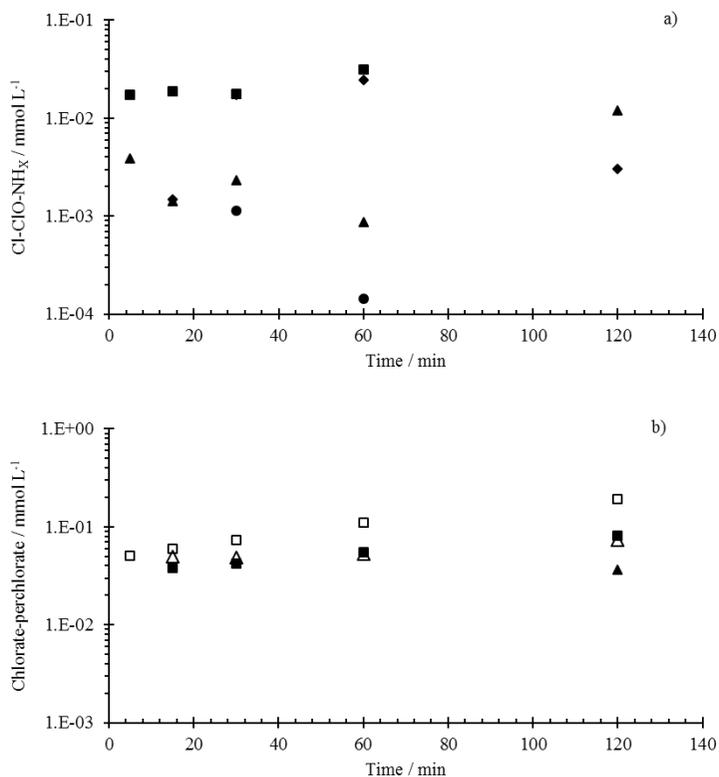
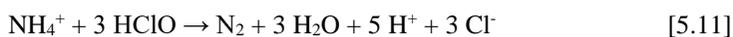
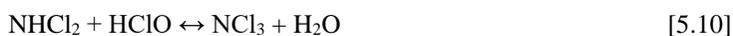


Figure 5.24. a) Changes in the concentrations of disinfectants (chloramines + hypochlorite) during the electrolysis. b) Changes in the concentrations of hazardous chlorinated species (chlorate: empty symbol and perchlorate: full symbol) during the electrolysis. ● 0.00; ◆ 8.3; ▲ 83.3; ■ 833.3 A m⁻².

As expected (Kolosov et al., 2001; Sanchez-Carretero et al., 2011), oxidation of chlorides led to the formation of hypochlorite (eqs. 5.2 and 5.3), which behaves as an intermediate, being further oxidized to chlorite (eq. 5.4), chlorate (eq. 5.5) and perchlorate (eq. 5.6), either via direct oxidation or by mediated oxidation with hydroxyl radicals, depending on the current density applied (Sanchez-Carretero et al., 2011). In fact, as can be observed, hypochlorite did not accumulate in the system and the primary oxidation products of the electrochemical processes were highly oxidized chlorates and perchlorates, especially in the experiments carried out at the highest current densities, which were the most effective in killing the microorganisms. These results agree with those published in the literature, which pointed out the formation of these hazardous species (Cano et al., 2012; Cano et al., 2016). In fact, one of the main strategies proposed in the literature to avoid the formation of perchlorate is the use of a low current density (Cano et al., 2011), under which the massive formation of hydroxyl radicals is not favored, and thus the formation of the highly oxidized chloro-oxyspecies is minimized. This is a drawback of the technology, and more research is required in the future. However, in this case, as the concentration of chlorides in the raw water is not important, the amount of the hazardous species is not very high (under the legal limit) and does not prevent the use of this treated water.

Furthermore, it is well known that hypochlorite is very active and can react with other species present in the solution and that this can affect the formation of the undesirable highly oxidized chlorine (oxychlorinated) species. The raw water tested contains ammonium ions, which may chemically react with the electro-generated hypochlorite to produce chloramines by the well-known breakpoint chlorination (eqs. 5.8 - 5.11). Both, hypochlorite and chloramines promote persistent disinfection, and they seem to be the main species responsible for the disinfection attained during the electrochemical process.



In addition to inorganic intermediates, the formation of organics must be determined. The trihalomethanes (THM) organic compounds are typically formed as by-products when chlorine is used to disinfect drinking water, and they are highly toxic and potentially carcinogenic; thus the formation of THMs must be prevented. Based on this, the presence of short-chain organic acids and organo-chlorinated species was checked by HPLC and Mass-GC. Among them, only chloroform, dichlorobromomethane and bromoform were detected in trace concentrations, and they were always in concentrations below the limits set by Spanish regulations (100 ppb).

In addition to this, the concentrations of other relevant anions and cations present in the raw water (see Table 4.2) were also monitored during the tests. Figure 5.25 shows the concentrations of the different anions monitored in the two tests carried out at the highest current densities.

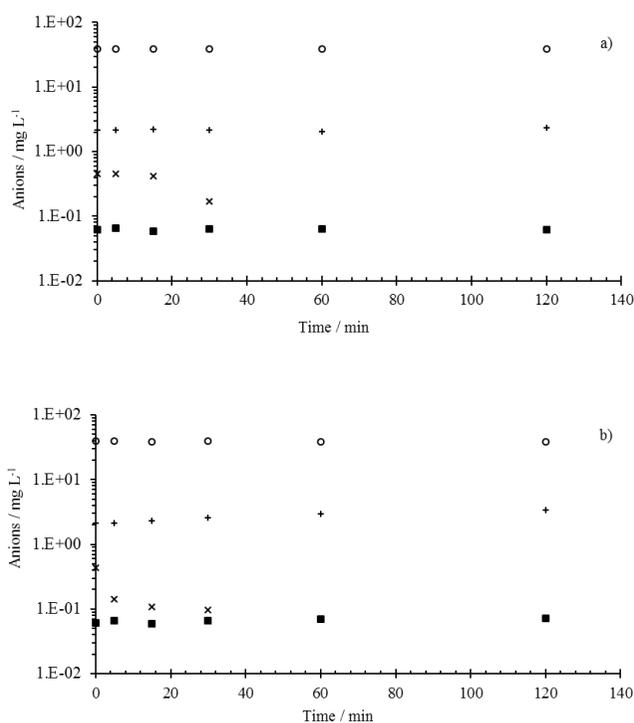


Figure 5.25. Changes in the concentrations of anions during the electrolysis carried out in the discontinuous mode at a) 83.3 A m⁻² and b) 833.3 A m⁻². Anions: ■ F⁻; × Br⁻; + NO₃³⁻; ○ SO₄²⁻.

No relevant changes were observed in the anions monitored, except in the case of bromide, which slightly decreased during the tests due to the formation of the higher oxidation state halo-species, as has been described for chloride. As no bromate or perbromate anions were detected, the most plausible possibility is the formation of bromine, which can be stripped from the system explaining the experimental observation. Likewise, no brominated organics were detected by chromatography. In contrast to bromide and chloride, fluoride anions remained resistant to the treatment. Regarding the other non-halogenated species, the most important observation is that no change in the sulphate concentration was produced during the disinfection. This may mean that, within the conditions applied, no peroxosulphate was formed in the treated water; thus, this important oxidant did not behave as a disinfectant in this process, contrary to observations in previous studies (Cotillas et al., 2016). In addition, the formation of nitrate during the tests was truly surprising. Because this species cannot be formed from the direct oxidation of ammonium ions (Lacasa et al., 2011), the most reasonable mechanism to explain this increase is the oxidation of the organics contained in the water, which is known to produce nitrate from the organic nitrogen contained in the pollutants (Martin de Vidales et al., 2016).

Regarding the concentrations of the cations (Figure 5.26.), it was observed that the concentration of ammonium decreased, which is associated with the production of the chloramines and/or with the stripping of ammonia. Additionally, slight decreases in the concentrations of calcium (14.5% at 83.3 Am⁻² and 24.5% at 833.3 Am⁻²) and magnesium (1.5% at 8.3 Am⁻² and 18.5% at 833.3 A m⁻²) were observed, which may have been associated with scaling in the cathode (formation of a layer of carbonates), although no relevant increase in the cell voltage was observed over the test. The potential operation problem of scaling could be easily overcome by periodically reversing the polarity of the cell. Due to the special design of the CabECO[®] cell, the electrolyte circuit is not affected by the scale of the electrodes because the most active faces of the electrodes are directly in contact with the membrane and not with the water to be treated, and the deposits can only be produced on the other surface of the electrodes.

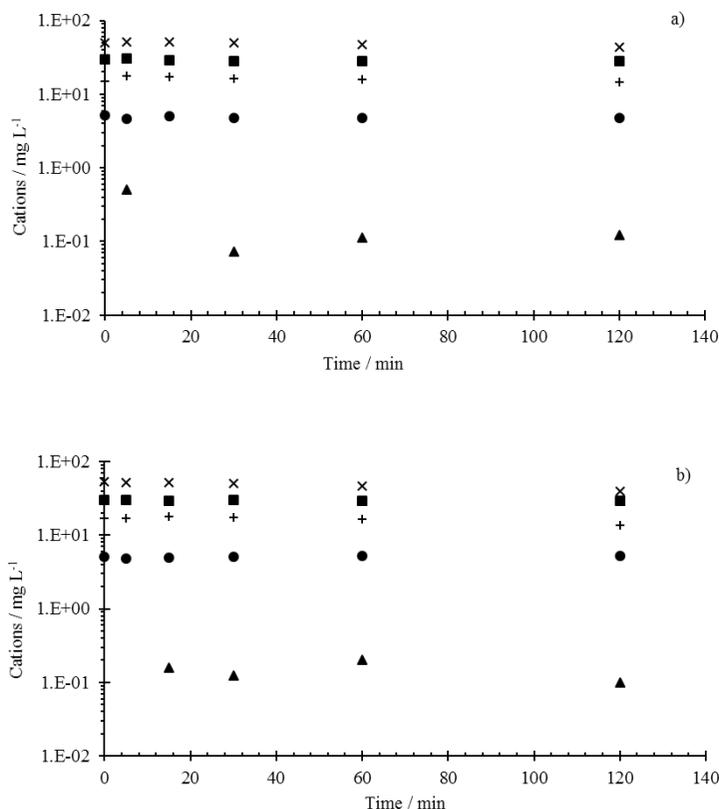


Figure 5.26. Changes in the concentration of cations during the electrolysis carried out in discontinuous mode at a) 83.3 A m^{-2} and b) 833.3 A m^{-2} . Cations: ■ Na^+ ; ▲ NH_4^+ ; ● K^+ ; × Ca^{2+} ; + Mg^{2+} .

5.2.2 Performance of the CabECO[®] technology for the disinfection of highly fecal-polluted surface water at continuous mode

In the search of operation conditions that allow an efficient disinfection and prevent the formation of highly oxidized chloro species, a single pass through the cell was proposed, that is, to operate the electrochemical cell in continuous mode without any recirculation. This means that data obtained during time correspond to transient response and that each experiment only give us a transient response up to the steady state and one relevant point (the steady state value). Figure 5.27 shows the transient response monitored of the concentration of the two pathogens indicators as a function of the current density applied and flowrate. Likewise, Figure 5.28 shows the changes

observed in the Total Aerobic Microorganisms concentration. This latter parameter is not related to disinfection but to sterilization and it may be used to check if the CabECO® technology, under the operation conditions applied, is suitable not only for disinfection but also for sterilization of water.

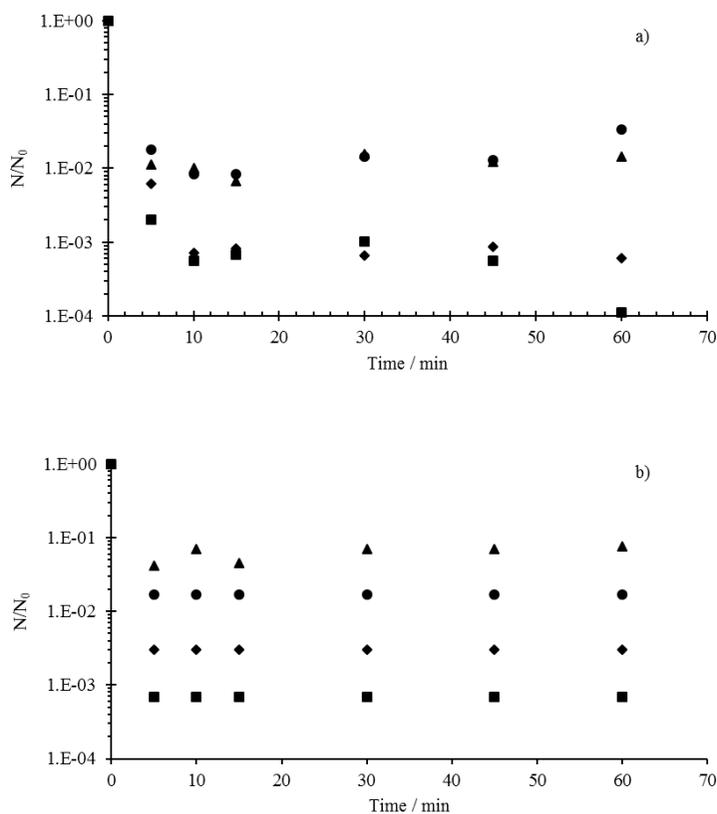


Figure 5.27. Changes during the electrolysis carried out in continuous mode in the concentration of a) Total Coliforms and b) *Pseudomonas Aeruginosa*. Tests: 90 L h^{-1} at \bullet 416.7 , \blacklozenge 833.3 , \blacksquare 1666.7 A m^{-2} and 300 L h^{-1} at \blacktriangle 1333.3 A m^{-2} .

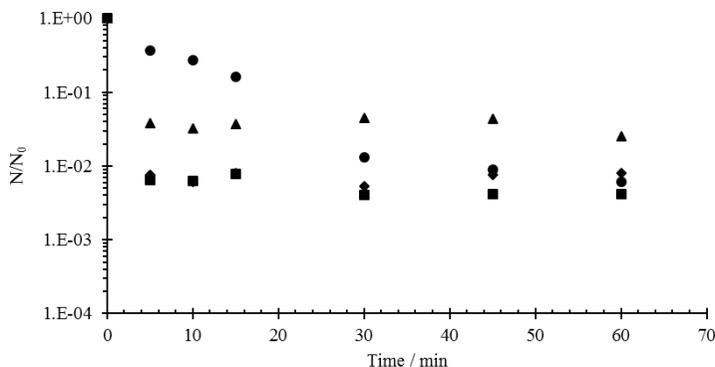


Figure 5.28. Changes during the electrolysis carried out in continuous mode in the concentration of Total Aerobic Microorganism. Tests: 90 L h⁻¹ at ● 416.7, ◆ 833.3, ■ 1666.7 Am⁻² and 300 L h⁻¹ at ▲ 1333.3 A m⁻².

As expected, concentrations decrease progressively down to a steady state value which is reached in less than 10 minutes, indicating that these processes do not need longer times to be started up. Only in the case of the test carried out at the lowest current density, the response seems to be a little bit slower and, in this particular case, it may be explained by the longer time required to generate a suitable amount of oxidants in the reaction media. Anyhow, this slower response was only detected in the case of Total Aerobic Microorganism and it does not apply to the two pathogens indicators monitored (Total Coliforms and *Pseudomonas Aeruginosa*).

$$Q \left(\frac{Ah}{L} \right) = \frac{I(A)}{F \left(\frac{L}{h} \right)} \quad [5.12]$$

In comparing the tests carried out under the same flowrate, it can be pointed out the importance of the operation current density applied. The larger the current density applied, the larger seems to be the decay of microorganisms. These tests were carried out at 90 L h⁻¹ which is the design recommended flowrate for this type of cells. However, the test carried out at 1333.3 A m⁻² does not seem to follow this rule. This test was carried out with a much higher flowrate of 300 L h⁻¹, which is the maximum admissible flowrate of the CabECO[®] cell. This discrepancy can be explained in terms of the different flowrate used in this test. Thus, what it is important in electrodisinfection is not the current density but the specific current charge passed, that is, the relationship between the current intensity applied and the flowrate (eq. 5.12).

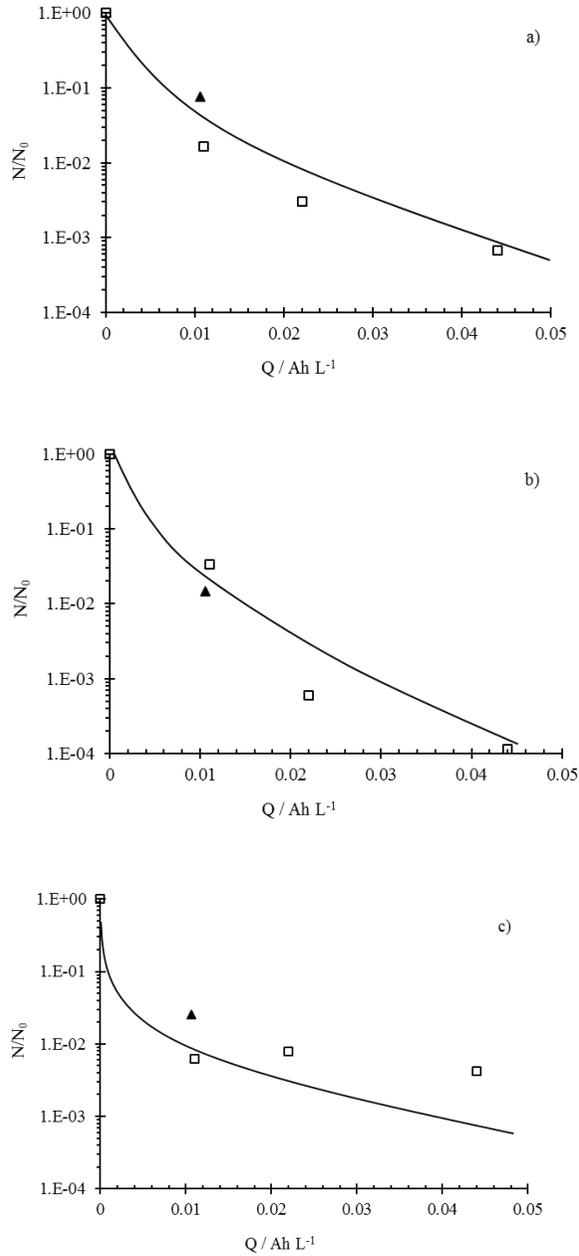


Figure 5.29. Disinfection trend as function of electrical charge passed during electrolysis carried out in continuous mode at 90 L h^{-1} (empty symbols) and 300 L h^{-1} (full symbol).
a) Total Coliforms, b) *Pseudomonas Aeruginosa*, c) Total Aerobic Microorganism.

This can be clearly seen in Figure 5.29, where the steady state values reached in the three parameters are plotted versus the specific charge applied. Here, it is

observed an increasing trend, which includes all tests carried out regardless the flowrate and intensity: the higher the charge applied, the more efficient is the depletion of microorganism. At this point, it is important to remind that in continuous electrochemical processes there is a single value of this parameter if the system is operated at constant flowrate and galvanostatic conditions. This means that information shown in this Figure may be used to size this type of cells, because it relates the depletion obtained with the two main inputs of the process and because the transient response is almost negligible.

Another interesting remark is that the system can obtain up to 4-log unit decay in the population of *Pseudomonas Aeruginosa* and a value slightly lower for Total Coliforms, which are the two main targets in this work, because the technology is evaluated for disinfection (removal of pathogens) not for sterilization (removal of all microorganisms). For removal of *Pseudomonas Aeruginosa* and Total Coliforms the 99.0% of the microorganisms are removed for a charge of 0.02 Ah L^{-1} . Taking into account that the maximum admissible intensity for a single CabECO[®] cell is 4.0 A, this means that the maximum flowrate that could be directly treated in this cell reaching this 2-log decay is 200 L h^{-1} .

One of the side processes which could be of interest during the treatment of water for supply is the removal of organics. Figure 5.30 shows the changes observed in the soluble TOC.

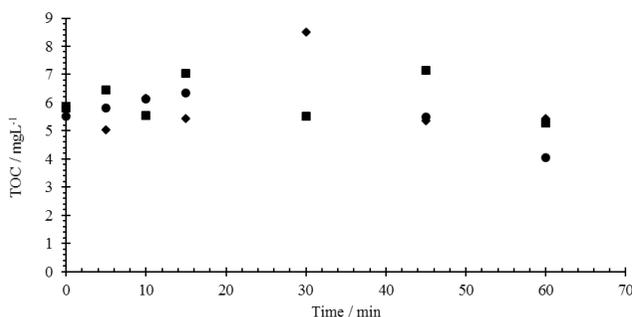


Figure 5.30. Changes during the electrolysis carried out in continuous mode in the total carbon organic concentration. Tests: 90 L h^{-1} at ● 416.7, ◆ 833.3, ■ 1666.7 A m^{-2} .

As seen, no remarkable changes are obtained and, in fact, during one of the tests the soluble TOC did not decrease but it increased. This observation can be explained in terms of the hydrolysis of particulate TOC during the test. Hence, the electrolysis at the conditions applied was not able to remove organics. Initially, this was an expected outcome due to the very low charges applied. The positive point is that there is no formation of organo-chlorinated species and concentration should be below the detection limit of the chromatographic technique used (detection limit of the equipment was 10 ppb).

As expected, this concentration remains almost constant during electrolysis (only a very small decrease is noticed) and only hypochlorite and chloramines were formed. The concentration of other species is much lower. In fact, perchlorate was not detected in any case, and chlorates were only detected at the highest current density applied and the concentrations were not very high. Thus, in comparing these values with other found in the literature (Cano et al., 2011; Cano et al., 2012; Cano et al., 2016), it can be pointed out the low significance, which even can be similar to that of other not electrochemical disinfections technologies. Thus, it is reported the formation of chlorates during the ageing of hypochlorite solution, which contribute to the dosing of this hazardous species in most of the supply systems in which chlorination with chlorine or hypochlorite is the disinfection technology. Hence, it is confirmed that the use of single pass through the cell is a good strategy to prevent the formation of hazardous chlorinated species.

This is a very important observation as the main drawback in the technology, which is the formation of perchlorates, seems to be overcome by operating in continuous mode with only one pass of the water through the cell. Regarding hypochlorite and chloramines, both are known to be good disinfectants and can complement very efficiently to ozone in the disinfection of water. At this point, it is important to point out that the best oxidant is the one that it is produced and react immediately (hence, not being accumulated and detected in the reaction media). That is, once disinfectant is formed, it rapidly reacts with pathogens and organics. In this case, only in the electrolysis carried out at 1666.6 A m^{-2} (in which the disinfection is more effective, and pathogens were almost completely depleted) hypochlorite and

chloramines were detected in concentration around 0.025 and 0.005 mmol L⁻¹ respectively. In the rest of electrolysis, their concentration was even lower.

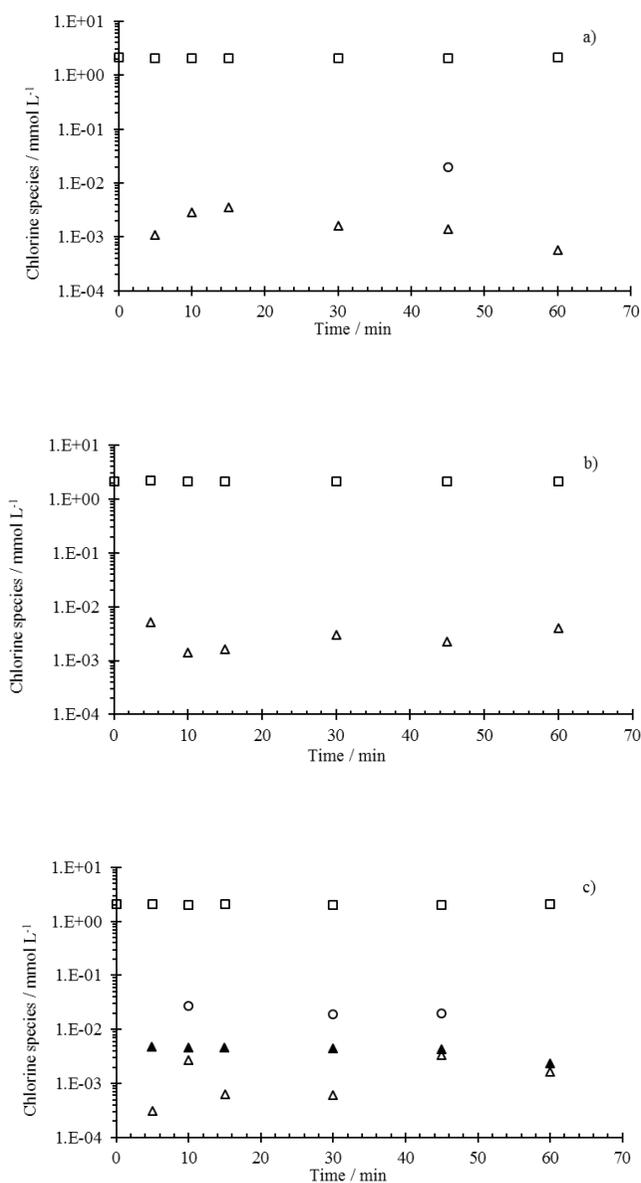


Figure 5.31. Changes in the chlorine speciation during the tests carried out at 90 L h⁻¹ at a) 416.7; b) 833.3; c) 1666.7 A m⁻². Chlorine species: □ chloride; ○ hypochlorite; △ chloramines; ▲ chlorate; ■ perchlorate.

Chlorine anions are not the only species contained in water. There are many others and their concentration remained almost constant all over the tests (in the case of sulfate, phosphate and carbonate). For this reason, this information is not shown. What it is shown, are the changes observed in the concentrations of nitrates and bromides (Figure 5.32). Concentrations decreased slightly, in the first case because of the transformation of nitrates into ammonium, which is later transformed into chloramines by reaction with hypochlorite. Regarding the decrease of bromide concentration, it has to be explained in terms of the formation of bromine and its stripping with the gaseous flow, because bromates were not detected and despite perbromates can be formed with diamond electrodes (Saez et al., 2010), the operation conditions are not suitable for this transformation and it is required harsher oxidation conditions. No brominated organic species were detected over the detection limit of the analytical technique used.

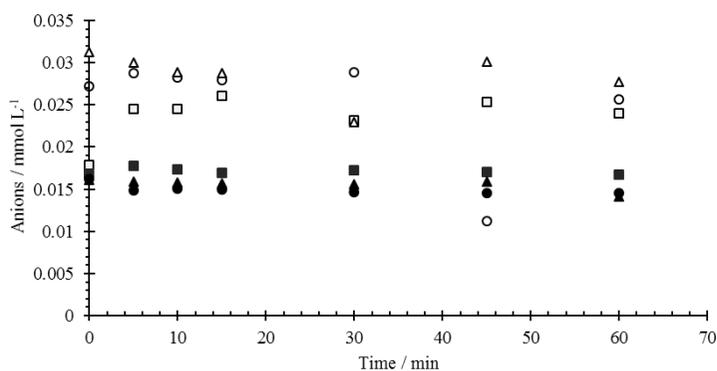


Figure 5.32. Changes in the concentration of nitrates (empty symbols) and bromide (full symbols) during the electrolysis carried out at 90 L h⁻¹: ■ 416.7; ● 833.3; ▲ 1666.7 A m⁻².

Regarding cations, same comments can be done (Figure 5.33). Almost no changes were detected during the different tests pointing out the low impact of carbonate deposits working in continuous operation mode. Only a small decrease in the concentration of ammonium can be noticed, which can be explained in terms of the production of chloramines.

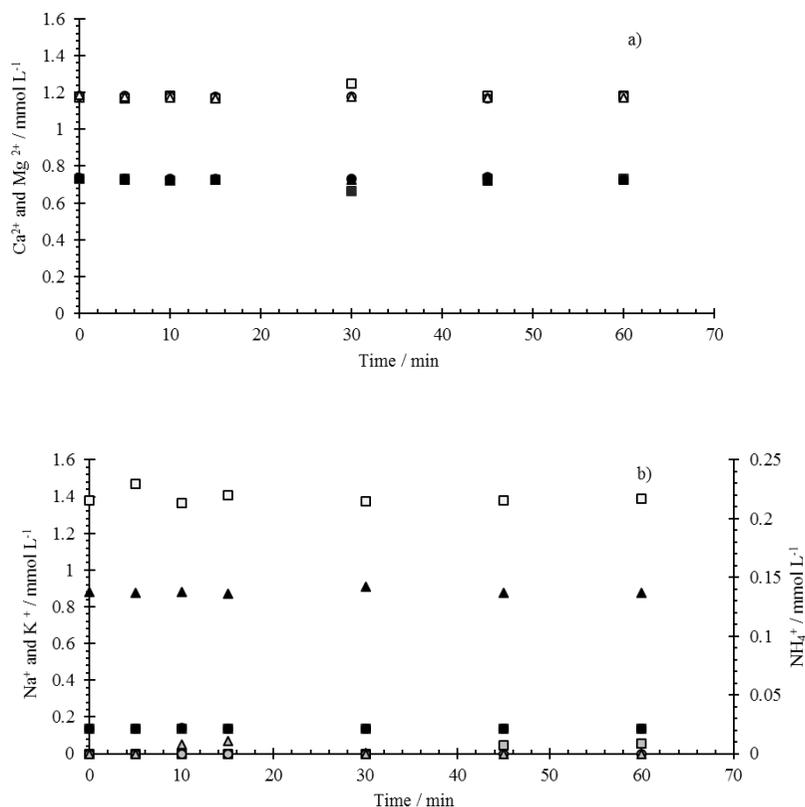


Figure 5.33. Changes in the concentration of calcium, sodium (empty symbols), magnesium, potassium (full symbols) and ammonium (grey symbols) cations during the electrolysis carried out at \blacksquare 416.7 A m^{-2} ; \bullet 833.3 A m^{-2} ; \blacktriangle 1666.7 A m^{-2} .

In order to check the feasibility of using this technology with more strongly polluted water, other tests were made by merging 20% wastewater (from the pretreatment of the WWTP) with 80% surface water (80/20 w/w) instead of the mixture 95/5 which was fed to the previous tests. The idea was to get information about the robustness of the technology for direct disinfection of a source water highly polluted with fecal contamination (as it would be in the worst case of SafeWaterAfrica project), without any further previous treatment. Several tests were carried out at operation current densities ranging 416.7 - 1666.7 A m^{-2} with flowrates of 150 and 300 L h^{-1} (the highest admissible by the CabECO[®] cell) in order to maximize shear stress and avoid the formation of bio-deposits on the surface of the electrodes. Direct disinfection using electrochemical technology is expected to encounter severe problems during the

treatment of highly polluted surface water, with biofouling being the most important. This problem leads to a critical decrease in the efficiency of the disinfection process. This phenomenon is confirmed in Figure 5.34, which shows the effect of the current intensity (I) on the concentrations of total aerobic microorganisms and total coliforms during the treatment of a real highly polluted surface water (20/80 w/w) by a CabECO® unit. In both cases, the graph shows the ratio between the concentration of each type of microorganism at the outlet (N) and at the inlet (N_0) of the electrochemical cell, and the results are plotted on a log scale.

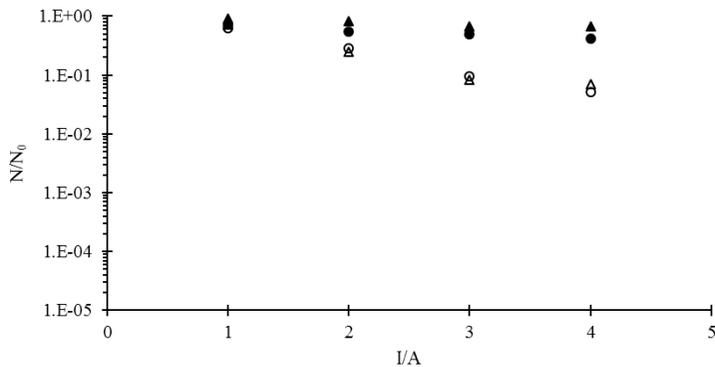


Figure 5.34. Influence of the applied current intensity on the removal of microorganisms by direct application of the CabECO® technology to fecally polluted water (80/20 w/w). ▲ Total Aerobic Microorganisms, ● Total coliforms. Full symbols: 150 L h⁻¹; empty symbols: 300 L h⁻¹

As can be observed, the level of sterilization and disinfection reached depends on the water flow rate treated and the current intensity applied, and the results are not as good as those that can be obtained for the sterilization and disinfection of water when the CabECO® technology is applied to water with a lower solid content; in the latter case, this technology is able to attain more than 3 logs of disinfection even for very high flow rates. Thus, the direct treatment of this highly polluted water sample with the CabECO® system leads to poor results in terms of inactivation of microorganisms, with a maximum removal of only 1 log unit, which is much lower than the values that are typically reached with other methods of diamond electrolysis described in the literature (Cano et al., 2011; Cano et al., 2012; Lacasa et al., 2013; Cano et al., 2016). In fact, this fouling also helps to explain why the performance at higher flow rates was much better than that at lower flow rates (despite the higher volume of water treated): the shear

stress caused by the flow on the surface of the electrodes assists in cleaning the electrode surfaces. This effect has also been observed in other studies in which surface-based treatment technologies were applied to highly polluted water (Zouboulis et al., 2014; Julio et al., 2015). In the system investigated here, one log unit of removal can be attained for total aerobic microorganisms, and slightly over 1 log unit can be reached in the case of total coliforms when a high flow rate is treated. A comparison of the two microbiological indicators shows that both sterilization and disinfection are performed with very similar efficiency, and no remarkable differences are found.

As seen, the presence of higher pollution is a real drawback for the direct application of the electro-disinfection process. Thus, the efficiency falls down to unacceptable values for disinfection, regardless of the current density applied respect to the population of total coliforms and it is even worse when results are compared in terms of sterilization, because in this case removal efficiency of total aerobic microorganisms population is completely negligible. In addition, in order to compared this results with those obtained in a test with the cleaner fecal water in the Figure 5.35 are represented the best disinfection efficiencies achieved in each case.

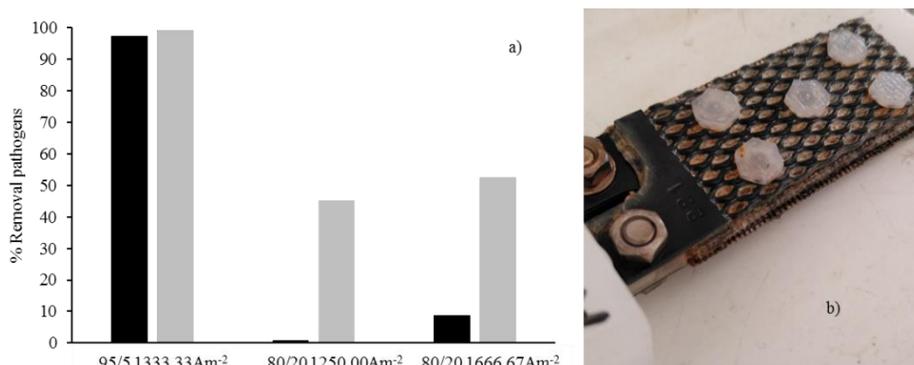


Figure 5.35. Performance of the disinfection and sterilization with different qualities of water: a) Efficiency of the removal; b) picture of the membrane-electrode assembly after the use with fecally polluted water (80/20 w/w) ■ Total aerobic microorganism, ■ Total coliforms.

As it can be seen in Figure 5.35 b), electrodes biofouling is responsible for this bad performance and it can be explained in terms of the sluggish biofilm on the surface of the electrode which blocks the productions of the oxidants needed for sterilization or even for disinfection and also covers the surface of the membrane. Anyhow, due to the

special design of the cell this biofouling does not affect to the cell voltage, meaning that water oxidation and reduction are not greatly affected and that connection between electrodes and the membrane is not affected. Hence, in case of highly polluted water, this disinfection technology cannot be applied alone and it should be combined with suitable pre-treatment operations.

5.2.3 Conclusions

The main conclusion of the present chapter is that CabECO[®] cell, based in the use of PEM technology, performs efficiently regarding disinfection for low polluted wastewater but its performance is highly affected when water with high fecal pollution is treated. Additionally, more specific conclusions can be summarized as follows:

- CabECO[®] can disinfect efficiently fecal-polluted water in both discontinuous and continuous mode.
- Steady state operation is attained in less than 10 minutes and disinfection depends on current charge applied.
- Decays up to 4- log units in pathogens can be attained with a single CabECO[®] at 90 L h⁻¹ with a mixture of 95/5 (surface water/wastewater)
- No THM or perchlorates are produced within the operation conditions applied.
- Technology cannot be applied if water is very strongly polluted because of electrodes' fouling and a pre-treatment is needed to assure the proper disinfection of the effluent.

5.3 Development of a Pre-disinfection unit.

As concluded in the previous sections, the presence of solids may become a handicap in order to obtain highly efficient disinfection processes. Thus, it is necessary to design a pre-disinfection treatment step in order to improve results of the electro-disinfection. This need for pre-treatment is also common outside electrochemical methods, and pre-treatment has been used in many other water treatment approaches (Pio et al., 2015; Im et al., 2018). Typically, the treatment of surface water consists of a sequence of coagulation-flocculation, sedimentation, filtration and disinfection. Hence, the basic goal of this chapter is to design and develop a home-made compact system using low cost materials to combine into a single process all the unit operations required to pre-treat highly polluted surface water before disinfection. After this pre-treatment, it is expected to obtain sufficiently high-quality water to be connected to a CabECO[®] cell, thus protecting the electrode surfaces and avoiding the blocking of the electrochemical cell. The pre-disinfection system has been called pre-disinfection column (PREDICO) and its details are described in Section 5.3.1. A scheme of the experimental set-up designed in this section is shown in the Figure 5.36.

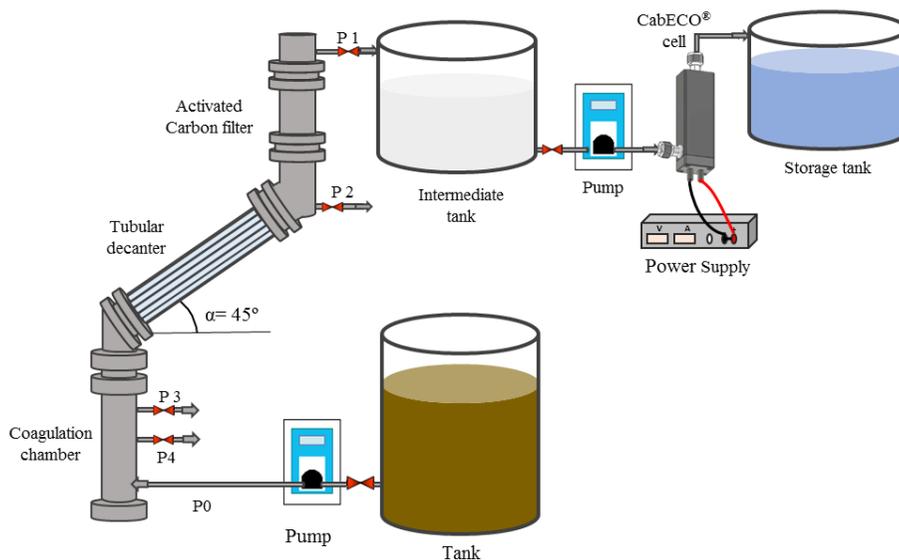


Figure 5.36. Experimental set-up scheme including PREDICO system (left) and disinfection process (right).

In addition, taking into account that the PREDICO system will be settled in remote areas where it is very difficult to provide chemical compounds, it is proposed the coagulant dosage by electrochemical means. That is, change the manual addition of iron salts, which had been chosen as coagulant in this case, by an electrocoagulation reactor. Although the electrocoagulation is a well-known technology, there are not many works focused on the development of new reactor approaches for iron dosing. For this reason, it was decided to undertake the design of novel coagulant dosing systems. Thus, in order to attain the required dose we have evaluated different proofs of concept, including the use of iron powder in the first device developed, called “ECU”(Electrochemically-assisted Coagulant – production & dosing Unit) to iron sheets in the second, named “i-ECU” (improved- ECU).

The experimental conditions studied in the experiments carried out with the PREDICO system are detailed in the Table 5.6.

Table 5.6. Planning of experiments in PREDICO system.

Test no.	Water matrix	Prototype	Flowrate / L h⁻¹	Superficial load rate / cm min⁻¹
1	tap water	Bench scale	10	8
2	tap water	Bench scale	20	17
3	tap water	Bench scale	30	25
4	tap water	Bench scale	40	34
5	tap water	Bench scale	50	42
6	80/20	Pilot plant	50	3
7	80/20	Pilot plant	100	6
8	80/20	Pilot plant	150	9
9	80/20	Pilot plant	300	18

The experimental conditions studied in each of the PREDICO pre-treated water electrodisinfection experiments carried out with the CabECO cell are detailed in the Table 5.7.

Table 5.7. Planning of experiments of electrodisinfection of PREDICO pre-treated water with the CabECO® cell.

Test no.	Water matrix	Operation mode	Current density / $A m^{-2}$	Florate / $L h^{-1}$	Maximum specific charge passed / $Ah L^{-1}$
1	80/20 pretearted	Continuous	416.7	150	0.0067
2	80/20 pretearted	Continuous	833.3	150	0.013
3	80/20 pretearted	Continuous	1250	150	0.02
4	80/20 pretearted	Continuous	1666.7	150	0.027
5	80/20 pretearted	Continuous	416.7	300	0.0033
6	80/20 pretearted	Continuous	833.3	300	0.0067
7	80/20 pretearted	Continuous	1250	300	0.01
8	80/20 pretearted	Continuous	1666.7	300	0.0133

The experimental conditions studied in the experiments carried out with the ECU system are detailed in the Table 5.8.

Table 5.8 Experimental conditions applied in the tests carried out with ECU cell.

Test no.	Water matrix	Conductivity / $\mu S cm^{-1}$	Operation mode	Flowrate / $L h^{-1}$	Maximum specific charge passed / $Ah L^{-1}$
1	tap water	400	Continuous	15	0.027
2	tap water + ultra pure water	100	Continuous	15	0.027
3	Na ₂ SO ₄	1000	Continuous	15	0.027
4	NaCl	1000	Continuous	15	0.027

5.3.1 Develop and design of a PRE-DIinfection COLUMN (PREDICO)

The PRE-DIinfection COLUMN (PREDICO) system combines into a column the three operation units required to pre-treat surface water before disinfection: coagulation-flocculation tank, tubular decanter and GAC filter. This PREDICO system makes use of the relative position of each unit to increase the performance of the whole device. Then, the bottom of the pre-disinfection column consists on a coagulation chamber that simultaneously acts as the concentration zone of the lamellar decanter,

while the top of the lamellar decanter acts as a reservoir for the granulated activated carbon (GAC) filtering.

A bench scale PREDICO was constructed with PVC consumables to characterize the performance of the system. For this, the effect of the flow rate was selected as a parameter to examine, which is particularly important in the sedimentation stage of the unit. Thus, it is important to search for the maximum water flow rate in which the flocs are remaining below the Surface Loading Rate (SLR). In this way, it is intended to avoid the loss of solids formed during the coagulation in the lamellar sedimentation stage of the PREDICO unit. Taking into account that the solids to be settled arise from the effluent of a coagulation step with an iron-based reagent (hence, iron hydroxide is the primary species in their composition), a preliminary study was carried out in a bench-scale plant in order to determine the maximum permissible SLR that should be applied to the lamellar settler to efficiently retain the solids produced during the coagulation stage. Results are shown in Figure 5.37.

As can be seen, when the water flow increases, the quality of the effluent becomes worse. In fact, operating at a flow below 20 cm min^{-1} seems to be a good practice in order to prevent the loss of solids from the unit. Regarding the concentration of coagulated sludge at the bottom of the lamellar decanter (which is the coagulation-flocculation chamber), as the flow rate increases, the sludge blanket becomes larger and solids become less concentrated. This phenomenon may have a negative impact on flocculation because of the lower possibility of collisions between flocs. However, when working at fluid velocities under 20 cm min^{-1} , the sludge concentration is greater than 1 g L^{-1} , which is high enough to assure good flocculation results (Zaleschi et al., 2012).

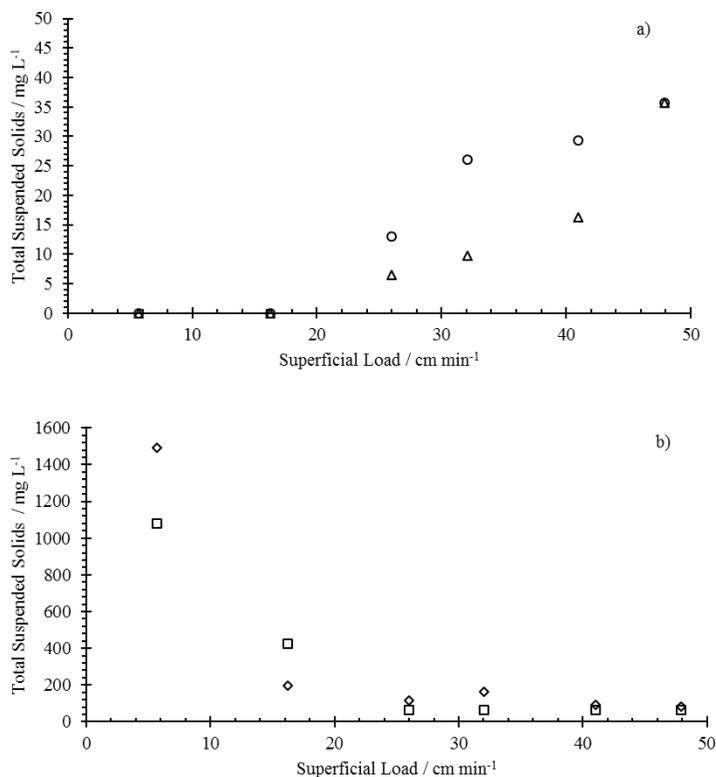


Figure 5.37. Influence of the SLR on the performance of the lamellar decanter contained in the PREDICO system in tests carried out at the bench scale. Total suspended solids: a) \triangle P 1 at the clarified liquid and \circ P 2 at the inlet of the GAC filter unit (empty for these experiments) and b) \square P 3; \diamond P4 at the bottom of the decanter (coagulation chamber).

Once the range of flow velocities through the system had been established, a prototype (pilot plant) was sized and constructed for 300 L h⁻¹, and additional tests were carried out in the pilot plant with flow rates ranging from 50 to 300 L h⁻¹ to confirm whether the scale-up had been executed properly. This pilot plant was sized so that the fluid velocity through the cell (SLR) at the maximum flow rate was less than 20 cm min⁻¹, hence avoiding the loss of solids from the decanter and helping to increase the service lifetime of the filters. Figure 5.38 shows the iron measured at different points of the set-up during the initial coagulation test. The results obtained confirm that particles are retained in the system and that only negligible concentrations of iron are lost during treatment. Therefore, the use of the SLR as a scale-up parameter for the separation units of PREDICO is confirmed for a scale-up ratio of 15 (20 L h⁻¹ in the

bench-scale plant vs 300 L h⁻¹ in the pilot plant). Similarly, sludge is successfully concentrated in the coagulation chamber of the pilot plant (which simultaneously acts as the bottom of the tubular decanter), allowing good flocculation performance because of the mixing conditions attained and the increased floc concentration.

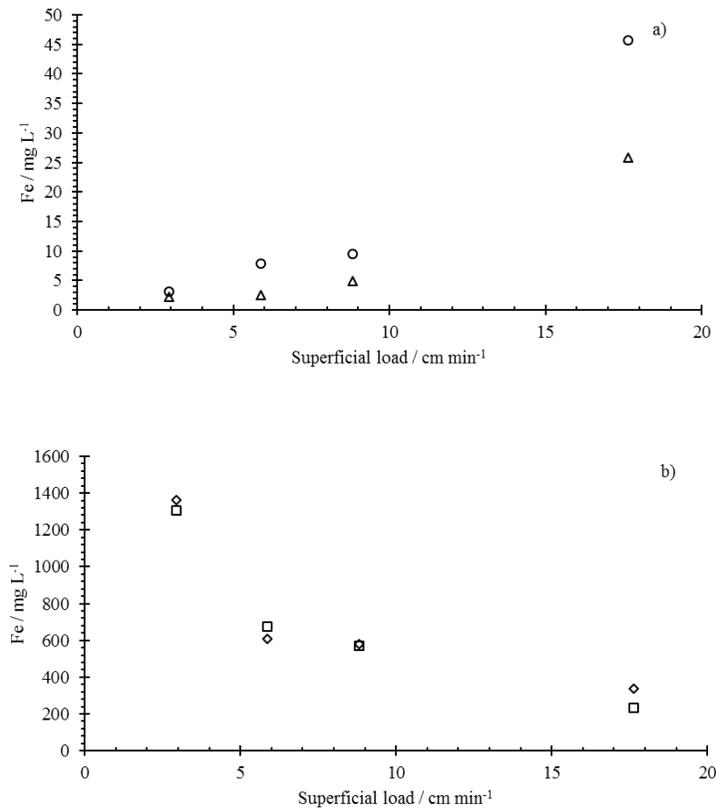


Figure 5.38. Influence of the SLR on the performance of the lamellar decanter contained in the PREDICO system in tests carried out at the bench scale. Iron concentration : a) △ P 1 at the clarified liquid and ○ P 2 at the inlet of the GAC filter unit; b) □ P 3; ◇ P 4 at the bottom of the decanter (coagulation chamber).

The coagulation of colloids and the removal of solids by sedimentation and filtration is expected to remove microorganisms from the water, as pointed out in previous studies published by our group (Zaleschi et al., 2012; Zaleschi et al., 2013) and by other researchers (Chon et al., 2014; Kpan et al., 2017). Thus, the treated highly fecal-polluted water, which was made by merging 20% raw wastewater with 80% surface water, was passed through the PREDICO system at different flow rates, and the

removal of microorganisms between the inlet and outlet was measured. Figure 5.39 shows the changes observed in the steady-state value reached in each test in which flow rates from 50 to 300 L h⁻¹ were passed through the system (resulting in a HRT in the coagulation chamber ranging from 4.5 to 27.2 minutes).

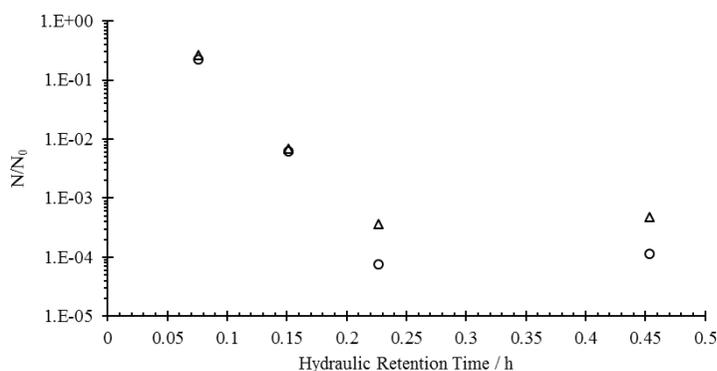


Figure 5.39. Influence of the hydraulic retention time on the removal of microorganisms by direct application of the PREDICO technology to fecal-polluted water (80/20 w/w), expressed as the ratio between the microorganisms contained in the effluent (N) and in the influent (N₀) △ Total aerobic microorganisms; ○ Total coliforms.

As can be seen, there is a reduction in microorganisms (sterilization) by more than 3 log units and a reduction in pathogens by more than 4 log units (disinfection), and the efficiency depends on the HRT in the coagulation chamber. Up to 13.6 minutes, there is a clear log decrease in the microorganism concentration. At that HRT, the maximum disinfection capacity is reached, and no further improvements are found. At this point, the concentration of microorganisms in the treated effluent is quite low; however, this PREDICO process does not inactivate microorganisms but simply concentrates them into the iron hydroxide sludge, so it is necessary to purge this sludge and to inactivate the microorganisms in a later stage (Zaleschi et al., 2012; Zaleschi et al., 2013). This process can be easily and simply performed by acidifying the sludge in order to solubilize the iron, which can be neutralized and used again in the system to avoid the use of new iron.

As the concentration of microorganisms at the outlet of the PREDICO unit was very low, the preliminary test for the evaluation of the CabECO® technology was not completely successful in terms of characterization of the technology (total depletion

of microorganisms was obtained, but initial concentrations were rather low; therefore, no relevant conclusions were found). Hence, to investigate the capability of the CabECO® process to disinfect highly microbially-loaded water, the outlet of the PREDICO system was amended with coliforms and pseudomonas by adding *Pseudomonas aeruginosa* and *E. coli* from pure cultures, up to concentrations similar to those contained in the non-pre-treated water. Figure 5.40 shows the effect of the current intensity and flow rate on the steady-state disinfection attained by the CabECO® system.

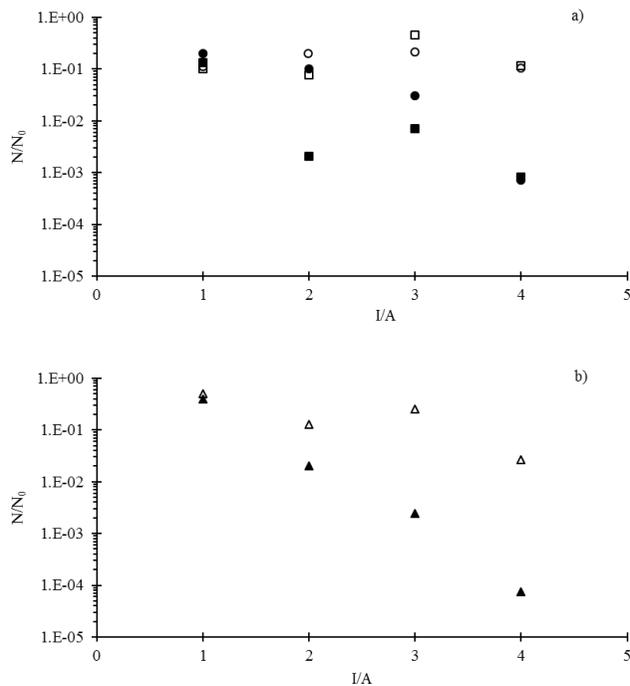


Figure 5.40. Influence of the applied current intensity on the removal of microorganisms by direct application of the CabECO® technology. a) Disinfection. ● Total Coliforms; ■ *Pseudomonas Aeruginosa*; b) Sterilization. ▲ Total Aerobic Microorganisms. Full symbols: 150 L h⁻¹; empty symbols: 300 L h⁻¹.

As observed, the results are much better than those obtained during the treatment of the raw water before the PREDICO process (see section 5.2.2), and in this case, the effect of the flow rate is exactly as expected: higher disinfection rates are attained when treating lower flow rates of water. Obviously, no fouling was observed

on the electrode surface after the treatment, and hence, in addition to the 3-4 log units of disinfection that the PREDICO system can attain, up to 3 log units of total aerobic microorganism removal (sterilization) and 4 log units of coliform removal (disinfection) can be attained, ensuring the complete treatment of almost any type of water with the combination of the PREDICO and CabECO® technologies. Thus, from the results obtained here, the combination of these pre-disinfection and disinfection units is a promising and feasible choice because it guarantees a highly efficient treatment method that is capable of efficiently improving the quality of very poor water.

In the way to get an autonomous water treatment plant, in the next section the design of new electrocoagulation reactors as coagulant dose is addressed as an essential element for the pre-treatment of highly fecal-polluted surface.

5.3.2 Electrochemical Coagulant Dosing Unit (ECU)

The first device proposed in this research work was called Electrochemically-assisted Coagulant – production & dosing Unit (ECU). It was designed to provide a long-time operation and an easy system for replacing the iron bed that is being dissolved, trying to reduce the operating costs and to enhance the real applicability of the device. The performance of the ECU device was compared to that of a conventional chemical iron dosing (in the form of FeCl_3). In order to cover the wide range of potential surface waters that exists in the natural environment, four water matrixes with different conductivities were studied: a mixture of tap and ultrapure water with a conductivity of $100 \mu\text{S cm}^{-1}$, tap water (aprox. $400 \mu\text{S cm}^{-1}$), NaCl solution ($1000 \mu\text{S cm}^{-1}$) and Na_2SO_4 solution ($1000 \mu\text{S cm}^{-1}$). Figure 4.41 shows a scheme of the ECU system.

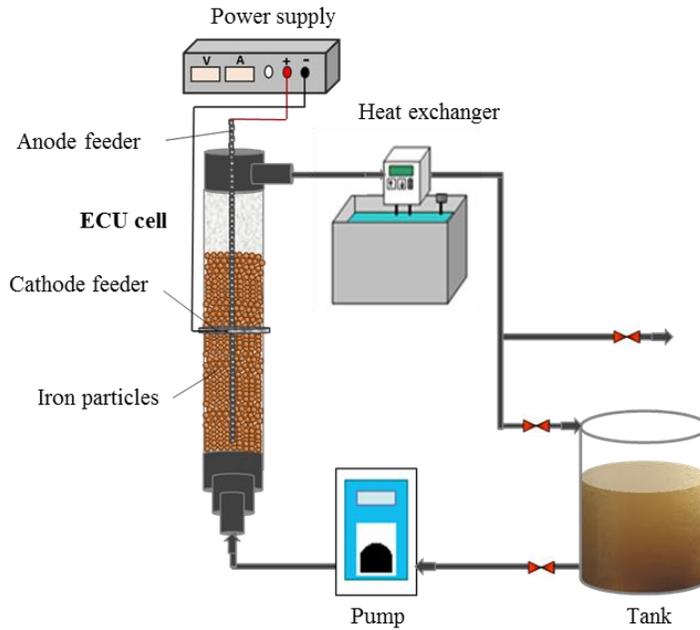


Figure 5.41. Schematic plot of the ECU set-up.

One of the main points to evaluate when an electrochemical device is developed, is its relation between the intensity and the voltage. Thus, Figure 5.42 shows the relation between the intensity and voltage of the ECU cell obtained for the four water matrixes with different conductivities used as models in this work.

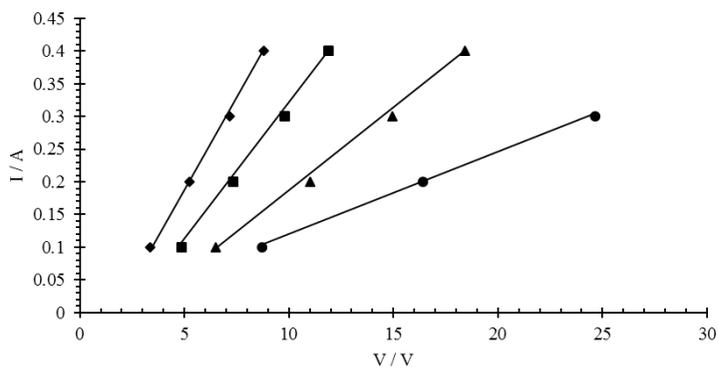


Figure 5.42. Relation between intensity and voltage for (ECU): ● $100 \mu\text{S cm}^{-1}$; ▲ tap water; ◆ $1000 \mu\text{S cm}^{-1}$ SO_4^{2-} media and ■ $1000 \mu\text{S cm}^{-1}$ Cl^- media.

The almost linear relation of intensity vs voltage indicates that this process works in the region of ohmic polarization within the range of conductivities tested in the present work. As expected, the slope of the plot increases for higher ionic conductivities, as the resistance of the electrolyte decrease (Wang et al., 2011; Ma et al., 2016; Ren et al., 2016; Arenas et al., 2017). Hence, for the same cell voltage applied, higher currents can be obtained, and hence higher amounts of coagulants are expected to be produced. Unexpectedly, sulfate solution leads to better performance than chloride and this has to be explained in terms of the complex chemistry of chloride anions.

Interestingly, one of the key aspects of the cell is its ability to dissolve the required iron concentration. Thus, Figure 5.43 represents the iron produced in these tests, together with the iron dosing predicted by Faraday's Law, considering oxidation of metal iron to Fe^{2+} (Parga et al., 2005; Moreno-Casillas et al., 2007; Sasson et al., 2009).

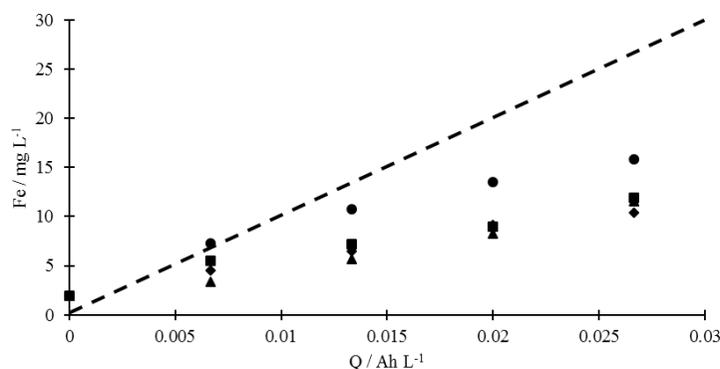
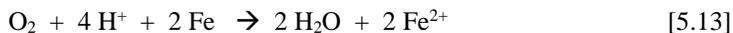


Figure 5.43. Fe concentration at the outlet of the ECU: ● 100 $\mu\text{S cm}^{-1}$; ▲ tap water; ◆ 1000 $\mu\text{S cm}^{-1}$ SO_4^{2-} media; ■ 1000 $\mu\text{S cm}^{-1}$ Cl^- media; Dashed line: Fe predicted by Faraday's Law.

As observed, the amounts of iron produced are under the expected values, pointing out the occurrence of parasitic reactions, specifically the well-known oxygen evolution (Cañizares et al., 2007; Sasson et al., 2009). The exception to this general behavior is the concentration of iron dissolved (1.3 mg L^{-1}) when no current is passed through the system. As an aerated solution is passed through the cell, some oxidation of iron by the dissolved oxygen is expected in this system (eq. 5.13), explaining the

slight concentration of iron that was found for null applied electric charge. This behavior has been previously described not only for iron but also for aluminum electrocoagulation (Cañizares et al., 2005).



Moreover, it can be observed that the highest efficiency in the dissolution of iron was found for the lowest conductivity solution ($100 \mu\text{S cm}^{-1}$) meanwhile the ECU device exhibits a more similar efficiency with the rest of test waters, just with a slightly lower efficiency in the case of tap water. It is worth mentioning that iron can be dosed to the solution even at very low conductivity, demonstrating the applicability of the device to be used in a wide range of different water matrixes. As it will be explained later on, the lower ionic strength of this water produces a larger change in the pH and conductivity, which can help to explain this higher efficiency in the production of iron coagulants. In addition, the more complex composition of the tap water (in particular with the presence of bicarbonates) can help to explain the slightly lower production of iron in that case.

One of the most important parameters to control in real drinking water treatment processes is pH, a variable that should be kept close to neutrality. The evolution of this variable is gathered in Figure 5.44, which represents the pH at the outlet of the ECU device (Figure 5.44 a) compared to the pH after dosing the same concentration of iron as FeCl_3 , (Figure 5.44 b).

As it can be observed in Figure 5.44.a, the change in the pH for the ECU device is almost negligible except for the solution of the lowest conductivity, in which the value of the pH increased from 7 to 9.5, which may be explained in terms of the lower ionic strength of this water and, in turn, can be one of the causes of the higher iron production. On the contrary, the chemical addition of FeCl_3 to the solution causes a decrease of the pH in the entire range of conductivities tested. The decrease in the pH was less accused for tap water due to the well-known buffer capacity of carbonates. For the rest of tests, the final pH was lower than 4 after adding a dose of iron equivalent to that dosed electrochemically. This is one of the key advantages of the electrochemical dosing of iron compared to the conventional chemical addition of iron salts. In this

latter case, a subsequent neutralization step should be required, increasing the economic and environmental impact of the treatment.

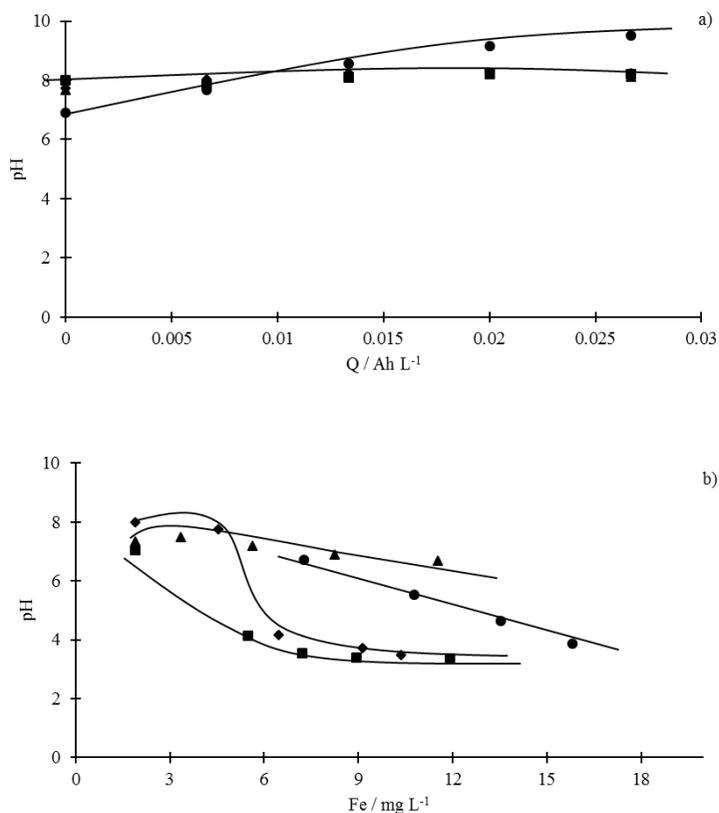


Figure 5.44. a) Comparison of final pH change of ECU and b) conventional coagulation for similar iron dosing. ● 100 $\mu\text{S cm}^{-1}$; ▲ tap water; ◆ 1000 $\mu\text{S cm}^{-1}$ SO_4^{2-} media; ■ 1000 $\mu\text{S cm}^{-1}$ Cl^- media.

Next, both processes (electrochemical and chemical dosing) were compared in terms of conductivity, an additional key variable to be controlled in real drinking treatment processes. As it is commented in the experimental section, a neutralization step was carried out after the addition of iron in order to simulate a real treatment process in the case of chemical dosing of FeCl_3 . Results (expressed as the ratio of final vs initial conductivity) are gathered in Figure 5.45.

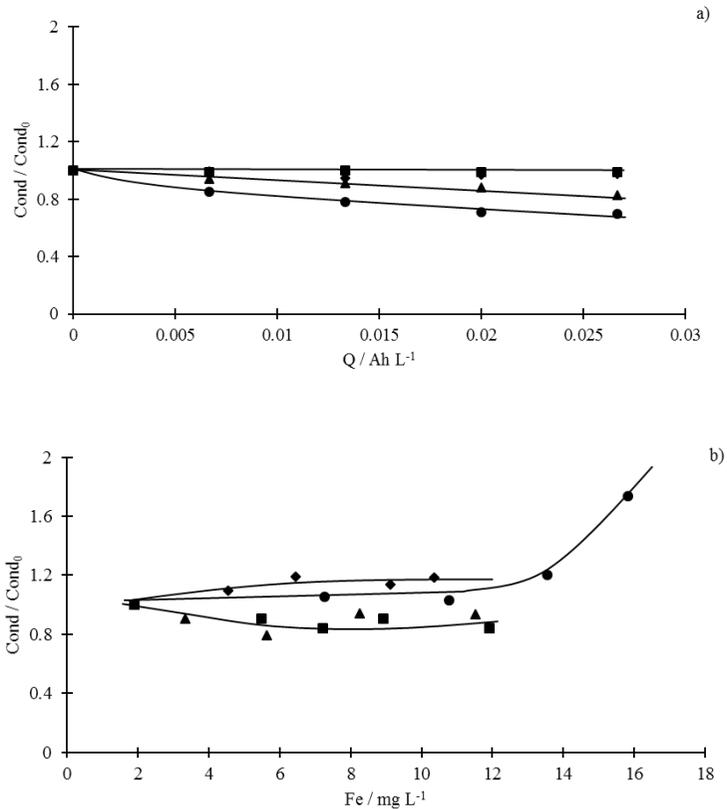


Figure 5.45 a) Comparison of relative conductivity of ECU and b) conventional coagulation-neutralization for similar iron dosing. . ● 100 $\mu\text{S cm}^{-1}$; ▲ tap water; ◆ 1000 $\mu\text{S cm}^{-1}$ SO_4^{2-} media; ■ 1000 $\mu\text{S cm}^{-1}$ Cl^- media. Neutralization by adding NaOH.

As it is observed, the electrochemical dosing of iron provokes a slight decrease in the conductivity, being the relative decline observed in this parameter higher for lower initial conductivity. In many works, it has been reported the capacity of iron precipitates to remove a wide variety of ions mainly by adsorption on the growing flocs (Lacasa et al., 2011; Jadhav et al., 2015; Elazzouzi et al., 2017; Kim et al., 2017; Mamelkina et al., 2017). In the case of chemical dosing-neutralization, an increase in the relative conductivity of the effluent was observed for all the effluents tested except for the tap water. In these cases, the addition of ions in the form of FeCl_3 and sodium hydroxide (in the neutralization stage) overcomes the flocs ability to adsorb the ions present in the solution. The exception in this behaviour of tap water is expected due to

the lowest decrease in the pH previously explained in the stage of iron dosing, which requires a negligible addition of sodium hydroxide to neutralize the solution.

Finally, in order to compare the chemical speciation of the iron dosed in both systems, Figure 5.46 shows the redox potential at the outlet of the ECU device (Figure 5.46 a) and after a comparable chemical dosing of iron and neutralization (Figure 5.46 b).

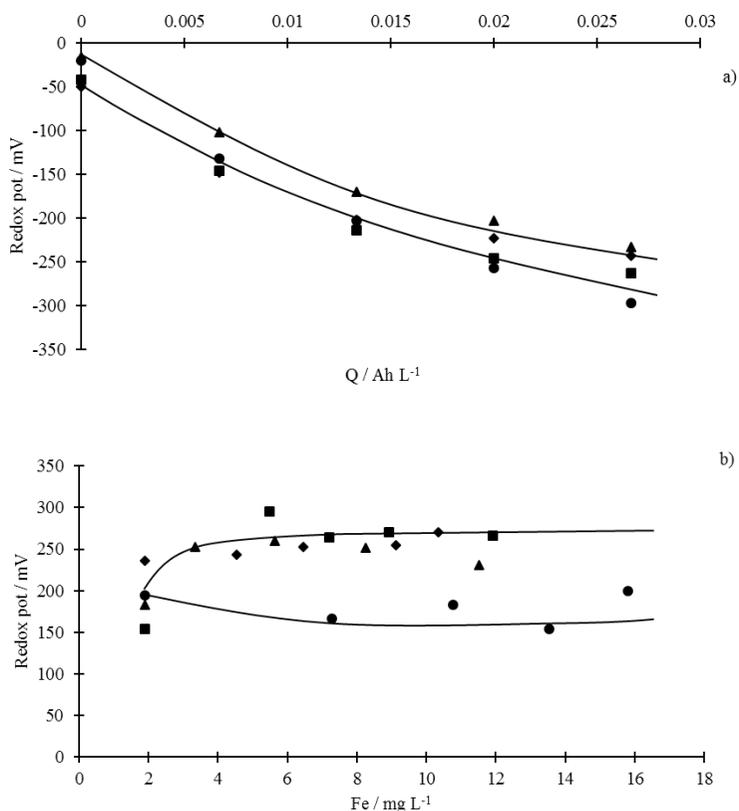
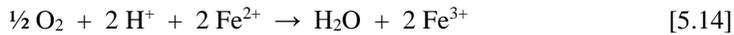


Figure 5.46. Final redox potential of: a) ECU and b) Conventional coagulation-neutralization for similar iron dosing. . ● 100 $\mu\text{S cm}^{-1}$; ▲ tap water; ◆ 1000 $\mu\text{S cm}^{-1}$ SO_4^{2-} media; ■ 1000 $\mu\text{S cm}^{-1}$ Cl^- media. Neutralization by adding NaOH.

Figure 5.46 shows the dissimilar behaviour of both systems in terms of final redox potential. In the case of the ECU device, there exists a decrease in the redox potential for increasing the applied charge. This decrease in the redox potential means a higher reductive capacity of the effluent, what can be directly related to a higher

$\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio (Gadd et al., 2010). In the case of chemical dosing, the redox potential remains positive, indicating a high proportion of Fe^{3+} in the iron speciation.

As it is widely known, chemical dosing of iron in a coagulation process should be performed under energetic agitation, giving a solution saturated in oxygen. In a saturated solution and at pH values over 5, the quick oxidation of Fe^{2+} to Fe^{3+} by dissolved oxygen (Eq. 5.14) is performed with high efficiency (Xu et Zhu, 2004; Kakshmanan et al., 2009). In the case of the ECU unit, the solution is not directly in contact with atmospheric air so it should be expected that the amount of dissolved oxygen may be lower than in a stirred tank used in conventional coagulation. This higher speciation of Fe^{2+} increases the potential applicability of this device to processes different from coagulation, as it is the case of Fenton-related technologies.



Anyhow, after tested the novel device presented in this chapter it can be drawn that it could be perfectly integrated in the pre-treatment of surface water sources as it exhibits a very good performance in the iron dosed covering a wide range of water conductivities ($100\mu\text{S cm}^{-1}$ - $1000\mu\text{S cm}^{-1}$). In addition, the ECU device presented clear advantages vs chemical coagulation, in particular with respect to the pH control, changes in the ionic conductivity and ratio $\text{Fe}^{2+}/\text{Fe}^{3+}$ in the coagulant produced. Due to the good results obtained from the design of the ECU device, three ECU units (Figure 5.47) were designed, built and sent to the South African partners to be connected to the prototypes that were developed in the framework of the SafeWaterAfrica project.



Figure 5.47. Three ECU units built and delivered to be used in the SafeWaterAfrica prototype.

Unfortunately, several drawbacks about the technology was reported by our South African partners after the three ECU's was installed and tested at the prototype. The first one was related with the amount of iron dose, it was not enough to remove the high concentration of particles found in some South African rural areas. A new target value of coagulant was fixed in 15 g h^{-1} . Another problem was related with the iron bed, which particles had been agglomerated because of the humidity remaining due to they were tested here. Anyway, as the maximum iron dose rate generated was around 200 mg h^{-1} , it is clear that this first design should be scale to be able to supply the amount of iron required of 15 g h^{-1} . It means that the reactor size should be increased at least 10 times. Then, it will be so much large and heavy. This led to change the strategy, used iron sheets instead of iron power. In the next section it will be faced the development of a reactor with this later concept.

5.3.3 Improved Electrochemically Coagulant dosing Unit (i-ECU)

To face the increase in the production of iron with a system that does not increase the size unnecessarily up to unmanageable sizes and, at the same time, meets the features of the ECU related to simplicity, low cost and easiness of operation, a new reactor design strategy was looked for. In this search, different types of electrochemical cell concepts were manufactured and tested, being some of them shown in Figure 5.48. Many preliminary tests were carried out with each prototype, although only the most relevant results are going to be shown in this Section, because most of them were used to make sequential changes in order to improve the final target design.

The first prototype developed (Figure 5.48 a) consisted of a cylindrical cell with the same structure than the ECU, although in this case the external stainless steel cathode was replaced by a rod located closer to the anode feeder rod, with the aim of reducing the ohmic resistance of the system. This prototype was able to produce coagulant although, unfortunately, it failed in producing much higher amounts than the previous ECU and the same problem of iron particles agglomeration appeared. In addition, it did not prevent the increase in the ohmic resistance by accumulation of metal hydroxide particles in the bed when using the system for long times. This meant that this geometry failed and that a more innovative cell based on a different approach had to be used.

For this reason, a completely different prototype concept was proposed, by changing the types of the sacrificial electrodes installed from iron powder to iron sheets, trying to avoid the problems related to agglomeration and, at the same time, the increase in the ohmic losses associated to the production of iron hydroxide precipitates in the pores of the iron bed (Figure 5.48b).

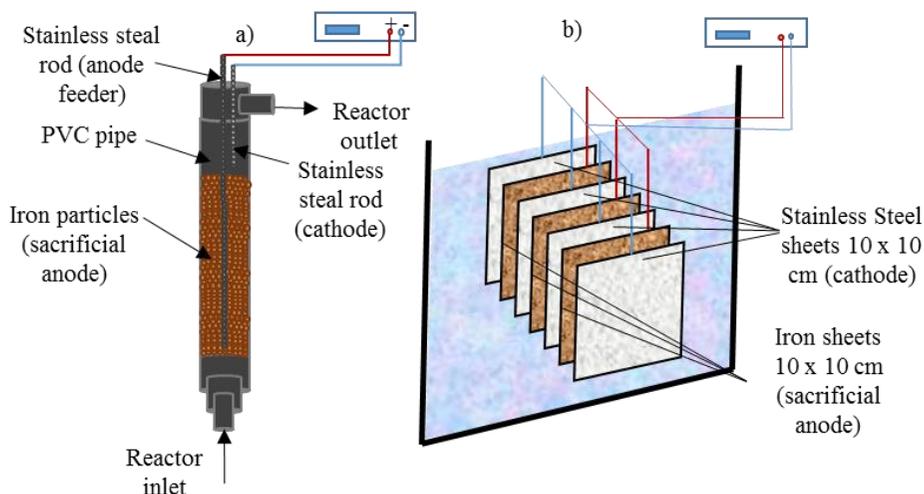


Figure 5.48. Different prototypes constructed during the development of the i-ECU.

a) modified ECU; b) monopolar plates in parallel connection.

The first prototype equipped with this new type of electrodes used a series of five cathodes and anodes sheets placed alternatively and powered individually (monopolar connection). The key operative problem found in its development was the way in which the current feeder was connected to the electrodes: the contact point between the wire and the electrode was in contact with water and it underwent a fast corrosion. In addition, it was found that a minimum gap between electrodes of 3mm was needed in order to prevent clogging problems, which may not appear in the short operation times of the lab-scale tests but it may be important in longer operation periods such as those aimed to be used in the real application.

Thus, it was studied an improved prototype in which the individual powering of electrodes was avoided. The monopolar connection used in the previous prototypes was replaced by bipolar connection. To do this, two outer Metal Mixed Oxide (MMO)

electrodes were connected to the power supply and the sacrificial iron electrodes were placed between them. Thus, the outer electrodes were monopolar and the inner ones were bipolar. This means that electrons go from one side to the other and that each face becomes counter electrode of the electrodes that it faces (Hakizimana et al., 2017). As only the MMO electrodes were connected to the power supply, this technology had a clear advantage regarding the systems developed previously.

Previous experiments with this technology were successful and, hence, it was decided to carry out a more detailed assessment of the cells. Thus, a set of experiments were carried out to evaluate the influence of the conductivity of the electrolyte on the current exerted. The first prototype tested contained 5 internal iron sheets (Figure 5.49 a) and it was tested in a discontinuous mode. Figure 5.50 shows the relationship between intensity and voltage for different electrolytes. The voltage is represented in log scale.

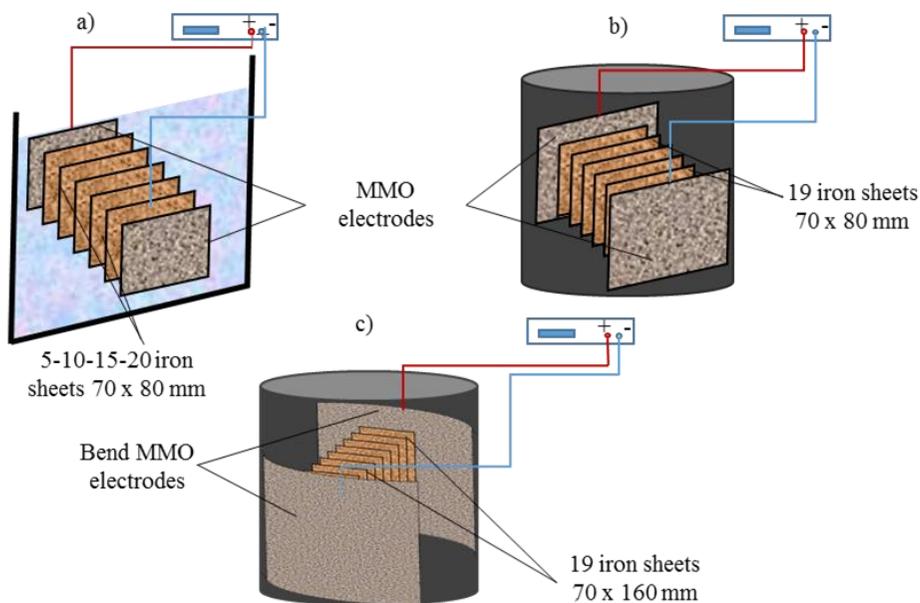


Figure 5.49. Sequential steps in the i-ECU development. a) Electrode arrangement; b) first i-ECU c) last i-ECU.

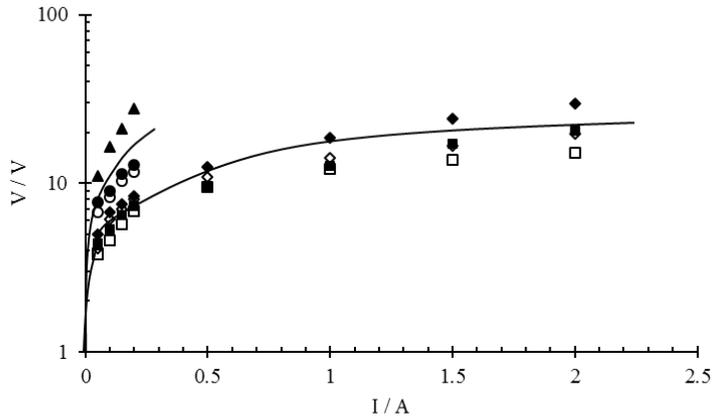


Figura 5.50. Relation between intensity and voltage for electrochemical coagulant dosing unit (ECU). ▲ tap water ● tap water + 0.5 g/L; ◆ tap water + 2.5 g/L, ■ tap water + 5 g/L. (Full symbols: sulphate medium; Empty symbols: chloride medium).

As expected, for the same applied intensities, lower values of voltage are reached as the amount of salt added is increased, which can be explained in terms of the higher ionic conductivity of the solutions, which in turn produced a lower ohmic resistance. As it can be observed, the chlorine medium presented a slightly better performance than the sulphate media, but both electrolytes were found suitable to increase the conductivity of the system. This is important because the dosing unit is not aimed to be fed with the water to be coagulated but with a synthetic solution that is transformed into the coagulant reagent to be added in the coagulation chamber of the PREDICO where the water to be treated is flowed.

Another important input for this prototype was the number iron sheets placed between the main electrodes. In order to evaluate its influence, tests with 5, 10, 15 and 20 iron sheets were carried out. As expected, the intensity and, hence, the amount of iron produced increased with the number of electrodes placed (Table 5.9). It is important to note that the values of voltage and intensities shown corresponds with the global values monitored in the power supply and they do not account for the internal intensities produced in each of the bipolar electrodes.

Table 5.9. Total system intensity evolution with the number of iron sheets.

N° sheets	V / V	I / A
5	20	3.33
10	20	5.12
15	20	8.90
20	20	8.24

Once the system based on bipolar electrodes was found to be operating properly, the sheets were placed in a home-made PVC reactor vessel in order to make the cell concept come true for the project purpose. Consequently, the design has to follow the same premises than its precursor: the cell was thought to be an easy to manipulate, in order to allow an easy replacement of iron sheets and it was made with cheap materials. After various mechanical trials, the final design carried out is shown in Figure 5.49c. Mechanical details are shown in Figure 5.51.

**Figure 5.51.** i-ECU mechanical details.

As seen, the new prototype included as driving electrodes two bend MMO electrodes following the geometry of the reactor. It is important to point out that all materials needed to manufacture the cell, except for the MMO electrodes, can be purchased in a hardware store at a low price (lower than 250 €).

A set of experiments were carried out with this final design. Figure 5.52 shows variations of the intensity and iron electrogenerated in the electrochemical process with increasing concentrations of salt added. The dashed line correspond with the expected value if the process was purely electrochemical (assuming the only anodic process is the metal oxidation). The reactor was tested in discontinuous mode under potentiostic conditions fixing a voltage of 31 V.

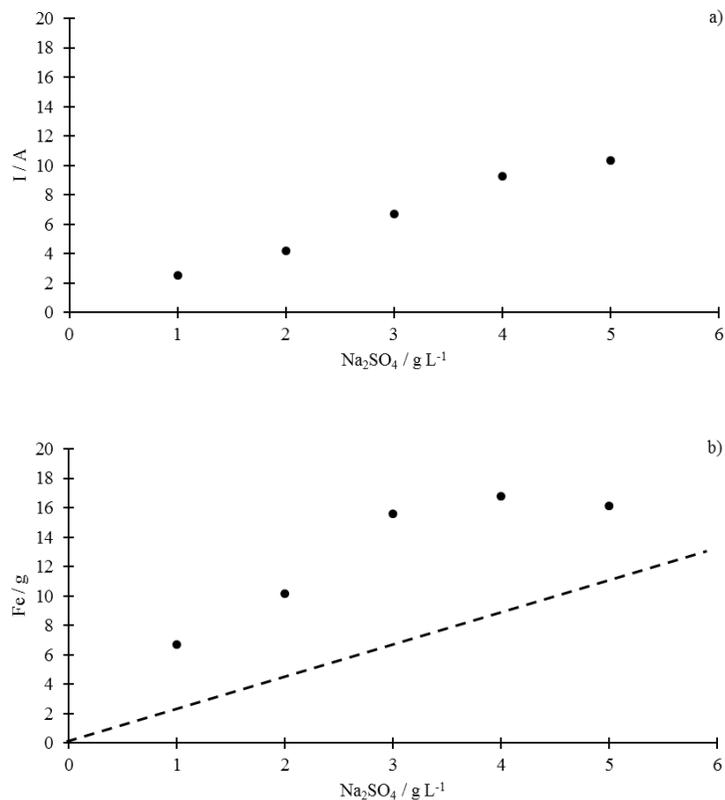


Figure 5.52. a) Relation between the intensity and concentration of salt added. b) Evolution of total iron generated after one hour of i-ECU operation with the concentration of salt added; dashed line: Fe predicted by Faraday's Law.

As can be seen, the intensities achieved increases linearly with the amount of salt added (Figure 5.52 a). Consequently, the amount of iron electro-dissolved also increased, being the experimental values greater than the values calculated if the process is considered to be purely electrochemical (according to Faraday's Law). The differences observed can be explained by considering the bipolar connection of the iron electrodes. Intensity measured only accounts for the oxidation and reduction that take place on the MMO electrodes (mainly for oxidizing and reducing water) and not for iron dissolution. It is important to emphasize that no great differences in the generation of iron are obtained in using salt concentrations higher than 3 g/L. For this reason, from this moment on, this value was taken as the reference to evaluate the following operation modes and to be used in the real application. Regarding other important parameters, Figure 5.53 shows the values of the conductivity and pH of the samples taken at the final of each of the experiments (one hour of electrolysis).

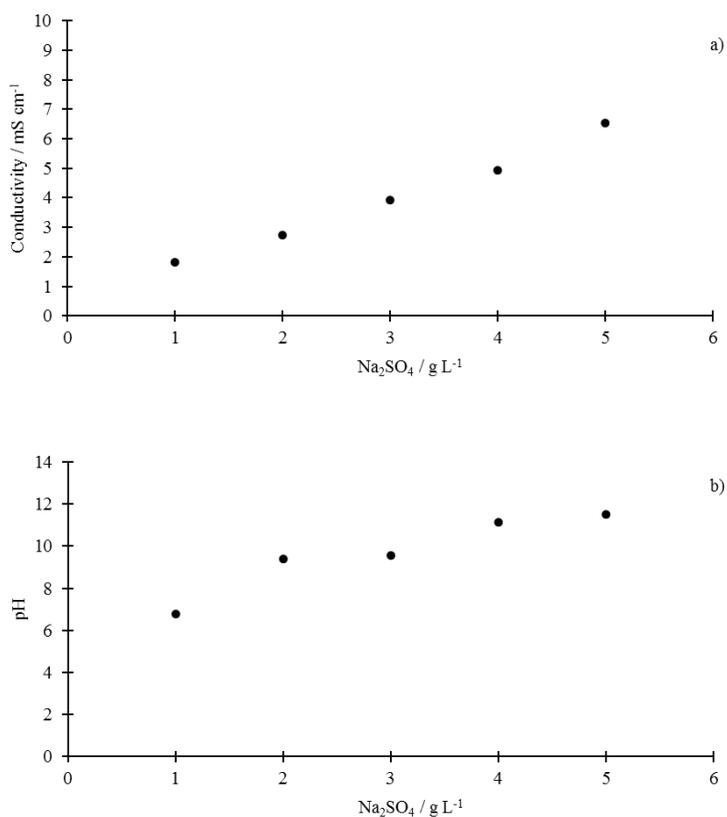


Figure 5.53. Evolution of a) Conductivity and b) pH with the concentration of salt added.

As expected, there is a linear relation between the amount of salt added and the changes in the conductivity and pH. It is important to take in mind that variations in both parameters are not only related to iron dissolution but to water oxidation and reduction on the MMO electrodes and to the complex chemistry of coagulant formation. With a salt concentration of 3.0 g L^{-1} , pH is around 9.0, which is a good value to produce iron precipitates once the iron (II) produced anodically is oxidized to iron (III).

The results showed in the Figure 5.52 b point out that the i-ECU system can dissolve around 15.5 g h^{-1} . In successive tests, this production was increased to 19.17 g h^{-1} by increasing the cell voltage to 33V, which was a value over the target for the project.

Then, the following step consists of changing the operation mode from discontinuous to continuous, with only one pass of the electrolyte throughout the reactor. It was decided to feed 10 L h^{-1} of 3.0 g L^{-1} sodium sulphate solution. The production of iron coagulant reached under this operation mode was 19.59 g h^{-1} , which confirms that the change in the operation mode did not change the production of iron. Voltage and current intensities recorded during the test are shown in Table 5.10. The set point for the voltage was 40 V but as the intensity increases up to the maximum value supplied by the power supply, voltage decreased to 34 V during operation. Anyway, production of iron hydroxide was maintained. Further tests confirms the good results and hence, a successful prototype was confirmed.

Table 5.10. Experimental results of i-ECU operating at continuous mode.

Exp. Time / h	I / A	V / V
0	6.09	40
0.12	8.17	39
0.33	8.17	34
0.67	8.17	34
1	8.17	34

Once obtained the cell, it was necessary to develop the complete layout of the plant, with a venturi aerator to favour the transformation of the iron (II) produced electrochemically into iron (III). In addition, it was found some accumulation of coagulant in the reactor vessel and a wash up procedure with an electro-valves system

was proposed to invert the direction of the fluid each five minutes, which was found to be a suitable reversion time to prevent this accumulation. In the Figure 5.54, it is shown a complete scheme of this process.

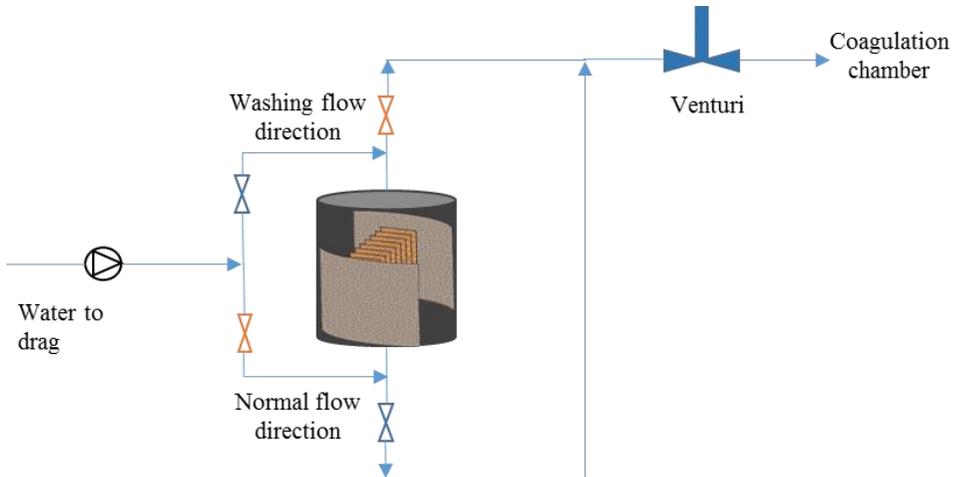


Figure 5.54. Scheme of the final process.

This system is specially designed to generate iron (III) hydroxide in the coagulation chamber and not in the dosing unit maximizing the entrapment of pollutants into the growing floc. It is important to point out that this electrocoagulation reactor is a completely new concept not described before in literature.



Figure 5.55. Two i-ECU units built and delivered to be used in the SafeWaterAfrica prototype.

From this work, two i-ECU reactors were manufactured and delivered to SafeWaterAfrica prototype. They were successfully employed in the final stage of the project, although results are not included here because they were obtained by other partners and are under confidentiality.

5.3.4 Conclusions

In this chapter it was developed two types of systems: on the one hand the so-called PREDICO (PRE-DIinfection COLUMN) and on the other hand the family of devices named Electrochemically Coagulant dosing Unit (ECU and i-ECU). After designed and tested the different process, the following conclusions can be drawn:

- The PREDICO system is a compact and modular pre-treatment process which can easily be assembled, disassembled, and transported, which can be easily integrated with electrodisinfection. In addition, it helps to prevent fouling in later electrodisinfection processes, achieving excellent disinfection rates in the pretreatment of highly polluted water (3-4 log units).
- ECU device efficiently doses iron even for solutions with very low conductivity. The amount of iron dose was not enough for design purposes, but its performance overcomes the behaviour of traditional chemical iron dosing.
- The completely new concept not described before in literature i-ECU is able to dose a higher amount of coagulant than ECU and, thus, to better satisfy the requirements for the treatment of the African natural sources tested.

5.4 Re-engineering PREDICO for treating groundwater

In order to check the robustness and flexibility of the PREDICO system, a final set of experiments was carried out for the treatment of other type of source of water, groundwater, which composition differs from that of surface water.

Modification of PREDICO to face the softening of groundwater consisted of

- 1) transforming the coagulation chamber into a chemical reactor in which lime is added to promote the formation of precipitates by its reaction with calcium, magnesium and carbonates and
- 2) including a sequence of two resins (first anionic and second cationic) at the outlet of the process to exchange nitrates by chlorides and calcium and magnesium by sodium.

A scheme of experimental set-up of the PREDICO re-engineering is shown in Figure 5.56.

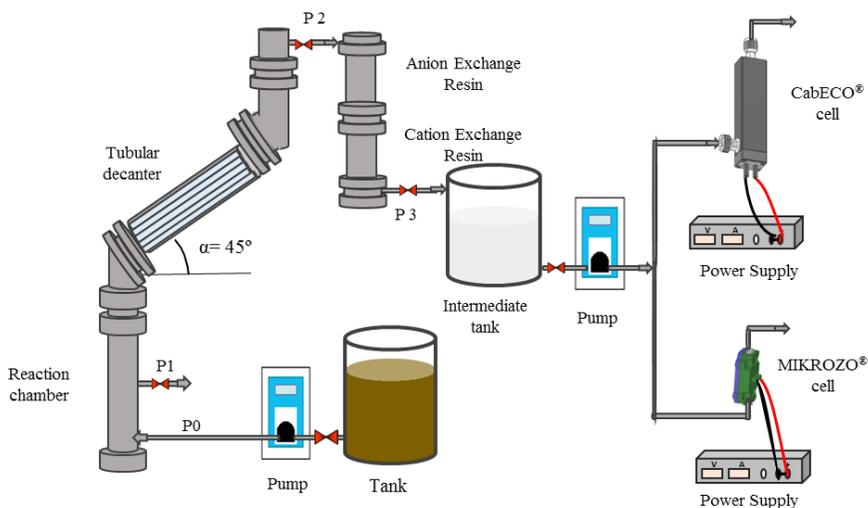


Figure 5.56. Experimental set-up scheme. PREDICO re-engineering (left); disinfection process (right).

Figure 5.57 shows the detail of the design of the re-engineering PREDICO in operation, including details of both the tubular decanter and the reaction chamber.



Figure 5.57. a) Tubular decanter detail; b) reactor chamber detail.

Three set of experiments were scheduled, trying to determine the best operation conditions of the re-engineering PREDICO technology. For each of these experiment water pre-treated was divided into two flows for evaluating the performance of the CabECO® and MIKROZON® cells. In addition, because of the low time-constants of the system, each disinfection tests were sequentially made with two different current densities: the design and the maximum current densities of each of the two electrochemical cells tested. Table 5.11 shows the operation conditions applied to each set of experiments.

Table 5.11. Operation conditions applied during the evaluation of PREDICO+DISINFECTION.

Test no. (PREDICO system)	Flowrate/ L h ⁻¹	Test no. (CabECO)	Current density / A m ²	Flowrate / L h ⁻¹	Test no. (MIKROZON)	Current density /A m ²	Flowrate / L h ⁻¹
1	100	1.1.a	833.33	25	1.1.b	5333.33	25
		1.2.a	1666.67	25	1.2.b	10666.67	25
2	200	2.1.a	833.33	50	2.1.b	333.33	50
		2.2.a	1666.67	50	2.2.b	10666.67	50
3	300	3.1.a	833.33	75	3.1.b	5333.33	75
		3.2.a	1666.67	75	3.2.b	10666.67	75

Figure 5.58 shows the influence of the treatment flowrate (from 100 L h⁻¹ to 300 L h⁻¹) in the efficiency of the PREDICO system for the removal of turbidity in four

different parts of the PREDICO system. The evolution of this parameter is related to the formation of precipitates by the interaction of lime with carbonates and bivalent cations contained in the water and to the efficiency of the whole system to remove the formed solids.

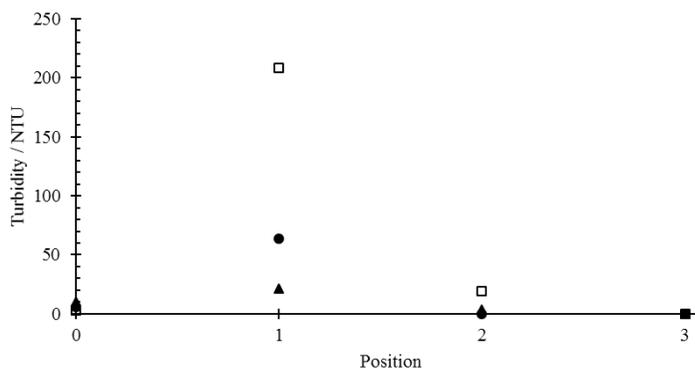


Figure 5.58. Turbidity values vs sample position in steady-state during the pre-treatment carry out at ▲ 100 L h⁻¹; □ 200 L h⁻¹; ● 300 L h⁻¹. Position 0: inlet of water; Position 1: reaction chamber; Position 2: outlet of tubular decanter; Position 3: outlet of ion exchange resins bed.

As seen, the turbidity in the position 1 increases very importantly due to the formation of a high number of solids in the reaction chamber. The high dispersion of the measurements in this position is due to the high heterogeneity of this chamber, what makes difficult to make an accurate sampling procedure. Anyway, it is clear that the tubular decanter is efficient enough to remove most of the particles, which are completely exhausted after the treated water passes throughout the resin bed, as it is observed due to the nil turbidity measured at the position 3.

Next, Figure 5.59 focuses on the changes in the cation concentrations during the pre-treatment of groundwater in the modified PREDICO system at the three different flow rates studied in this task.

As it can be observed in the Figure 5.59, almost a total exchange of calcium and magnesium by sodium is produced for the three flow rates studied. It is important to point out that the highest efficiency is expected to be achieved for the lowest flowrate, due to the higher effective retention time.

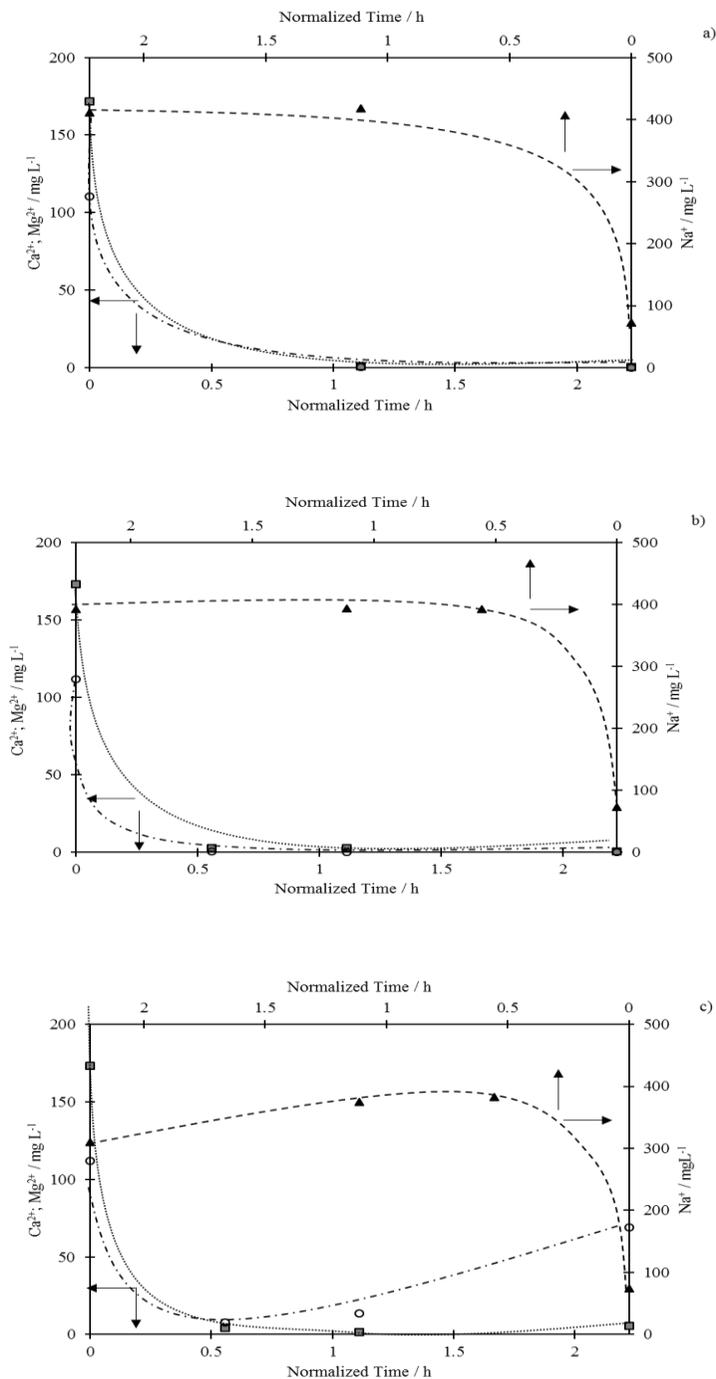


Figure 5.59. Changes in the concentration of the cations during the pre-treatment carried out at a) 100 L h^{-1} ; b) 200 L h^{-1} and c) 300 L h^{-1} . $\blacktriangle \text{ Na}^+$; $\blacksquare \text{ Ca}^{2+}$; $\circ \text{ Mg}^{2+}$.

The decrease observed in the efficiency in the last experiment, performed at 300 L h^{-1} (Figure 5.59 c), for increasing times (higher concentration of magnesium for increasing times) can be explained in terms of the saturation of the cationic resin, because the resin was not regenerated at any time during the experiments and they were carried out sequentially from 100 L h^{-1} to 300 L h^{-1} . Hence, the capacity of the technology for softening water is demonstrated with this set of experiments and only a regeneration stage would be needed as it is the case of any conventional ion exchange process.

On the other hand, the water denitrification is also an important aspect to consider in any water treatment plant due to the harmful effects of nitrate for the human health. Figure 5.60 shows the evolution of nitrate concentration in the three experiments when water pass through the anionic resin placed in the PREDICO system. In this case, the nitrates are exchanged by chloride anions.

As can be seen, the lower is the flow rate the higher are the exchange efficiencies obtained, as it was expected. Thus, considering the Figures 5.60 a and b, it can be observed that almost the total depletion of nitrates concentration is reached when flow rates applied are under 200 L h^{-1} . However, is important to remark that, at least, an 85% of removal is achieved in the worse scenario (corresponding to the highest flux), being the final concentration of nitrates under 5 mg L^{-1} in all cases.

Hence, in observing results, it is clear the capability of the readapted PREDICO technology to face the removal of the target ions, being demonstrated in this case the denitrification and softening of the water.

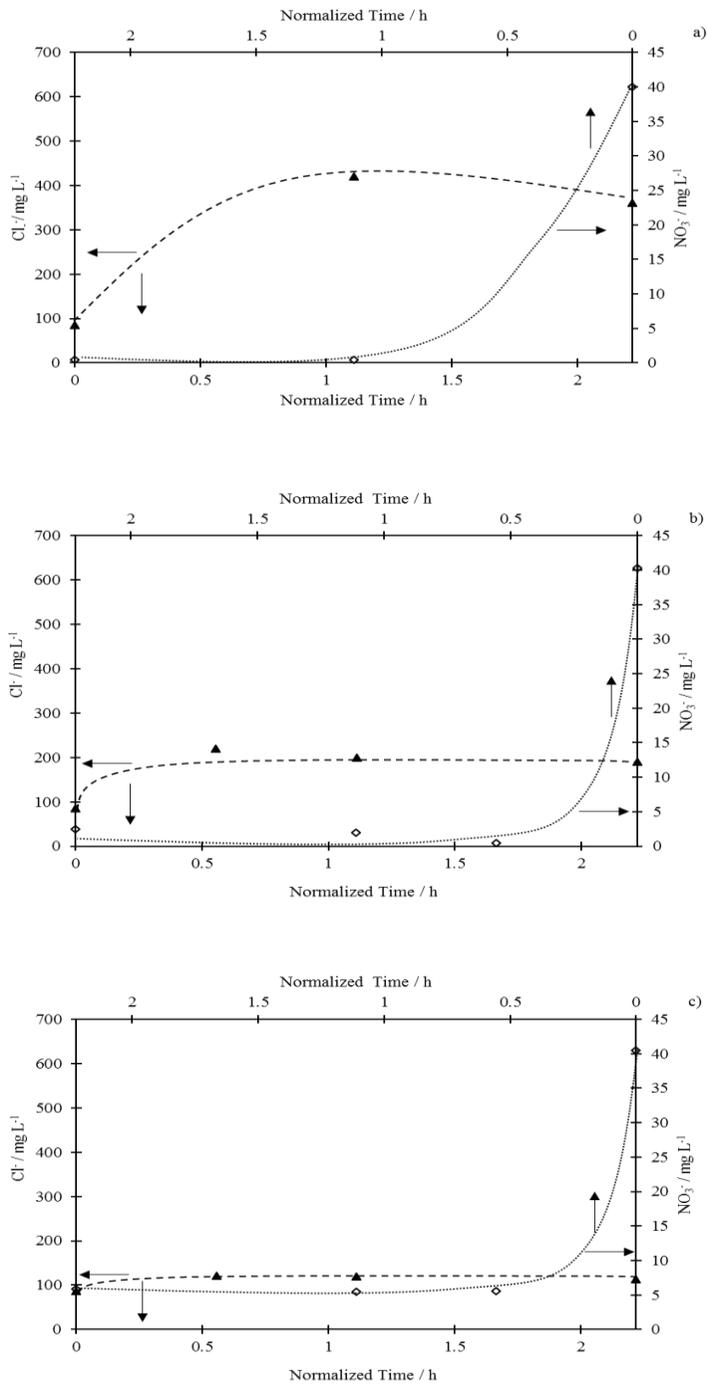


Figure 5.60. Changes in the concentration of the anions during the pre-treatment carry out at a) 100 Lh⁻¹; b) 200 Lh⁻¹ and c) 300 Lh⁻¹. ▲ Cl⁻; ◇ NO₃⁻.

The evolution of pH and conductivity in the different positions of the re-designed PREDICO system was also monitored. This evolution is shown in Figure 5.61. As expected, no relevant changes are observed, as the ion-exchange process (the stage that could affect both variables) was designed to remove calcium, magnesium and nitrate and exchange these ions by sodium or chloride but not as a demineralization process (which would imply exchanging the target ions by H^+ and OH^-).

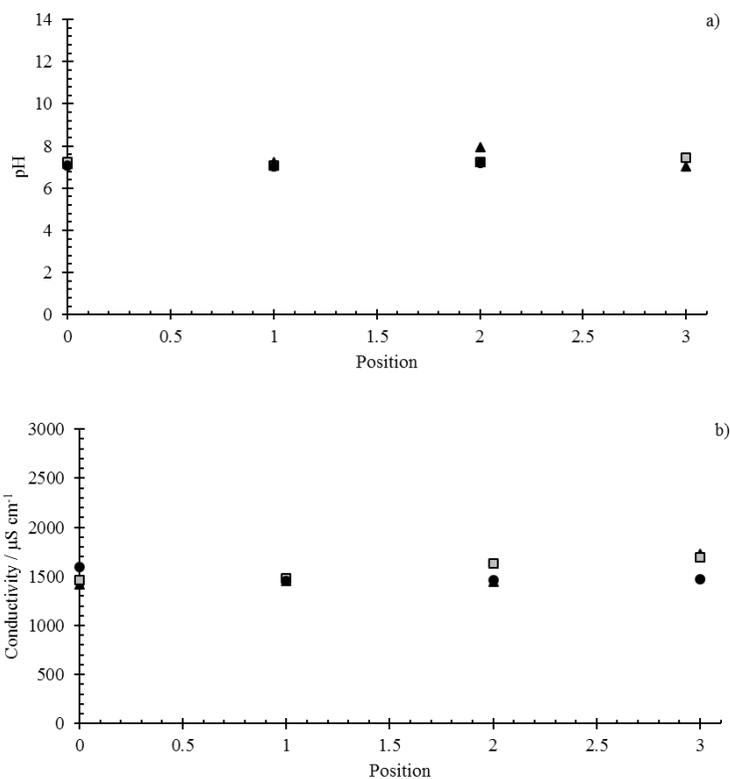


Figure 5.61. Changes in the a) pH and b) conductivity vs sample position in steady-state during the pre-treatment carry out at \blacktriangle 100 L h⁻¹; \square 200 L h⁻¹; \bullet 300 L h⁻¹. Position 0: inlet of water; Position 1: reaction chamber; Position 2: outlet of tubular decanter; Position 3: outlet of ion exchange Resins bed.

As previously explained in section 5.3.1, the PREDICO technology applied on surface water was able to obtain a coarse disinfection in enmeshing pathogens into growing flocs and then transferring the hazardousness to the flocs, which is a very convenient process, because in the sludge it is easier to manage the problem of

disinfection and let water in conditions to be used. Initially, the mechanisms involved in the treatment of groundwater should not achieve any disinfection, but it was considered interesting to measure the targeted microorganisms before and after the modified PREDICO pre-treatment (Figure 5.62). As it is shown in Figure 5.62, the number of pathogens studied did not undergo any significant changes during the PREDICO treatment, confirming our initial assumption. At this point, it is worth noting that the lime precipitates did not enmesh efficiently microorganisms.

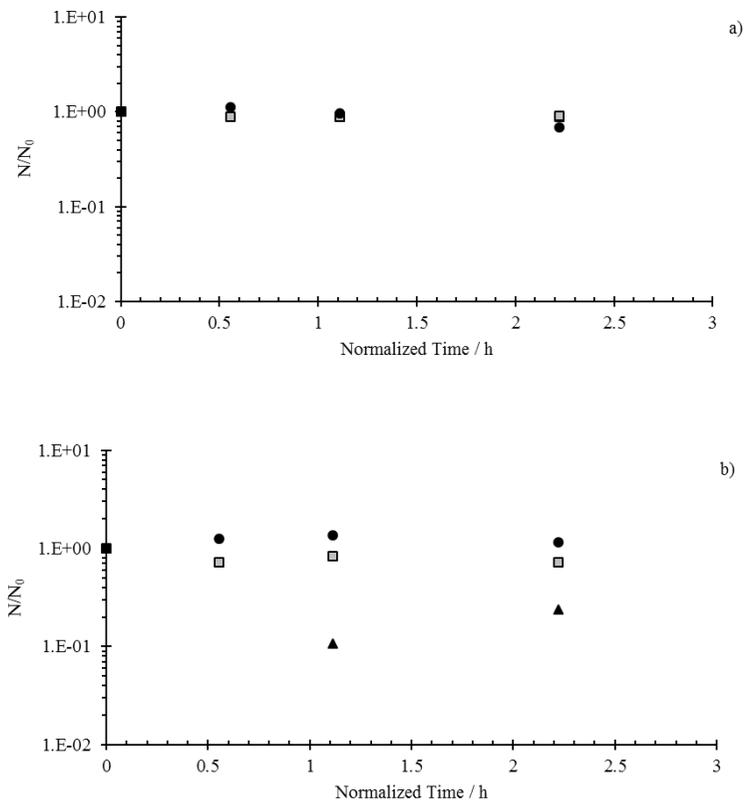


Figure 5.62. Changes in the concentration of microorganisms a) Total Coliforms; b) *Pseudomonas Aureginosa* during the pre-treatment carry out at \blacktriangle 100 L h⁻¹; \square 200 L h⁻¹; \bullet 300 L h⁻¹.

The effluents of the PREDICO were distributed into two different electrochemical cells: the CabECO[®] and the MIKROZON[®], which were fed at three different flowrates in order to obtain as much information as possible. Figures 5.63 and

5.64 show the evolution of the microorganisms concentration with the electrical charge applied for each experiment at steady state. Thus, plotted values correspond with a sample taken 40 minutes after the test start up, where it was confirmed that steady state was reached.

As it can be observed, there are not significant differences between the performance of the CabECO® and the MIKROZON® cells and the treatment is very efficient working at flowrates lower than 50 L h^{-1} with removals of pathogens near 4-logs. In the case of the higher flowrate, the efficiency was lower. This can be explained in terms of the very different water matrix as compared to that of the experiments carried out when characterizing the treatment of surface water. Anyway, more than one-log of disinfection capability is observed event at these non-convenient conditions.

If we focused on the performance of the MIKROZON® cell, it is important to remark the good response obtained for the second flow rate tested (Figure 5.63 and 5.64 b), that, as can be observe, achieved 3 logs of removal in the pathogens studied.

It is important to point out the electrical problems appeared in the last experiment (Table 5.11 exp 3.2 b) carried out with the MIKROZON® related with the increasing of the cell potential. It could be related with the small size of the compartments and the effects of solids particles that can mask the electrode surface. These problems were not detected when working with the CabECO® cell, what means that the CabECO® design presents a better potential behaviour for long-term tests than the MICROZON® cell.

Regarding the chlorinated species generated during the electrochemical processes, Figure 5.65 shows the changes in the chlorate and perchlorate concentration formed during the treatment. As already pointed out in previous sections, both species are detrimental to health and hence their presence should be minimized.

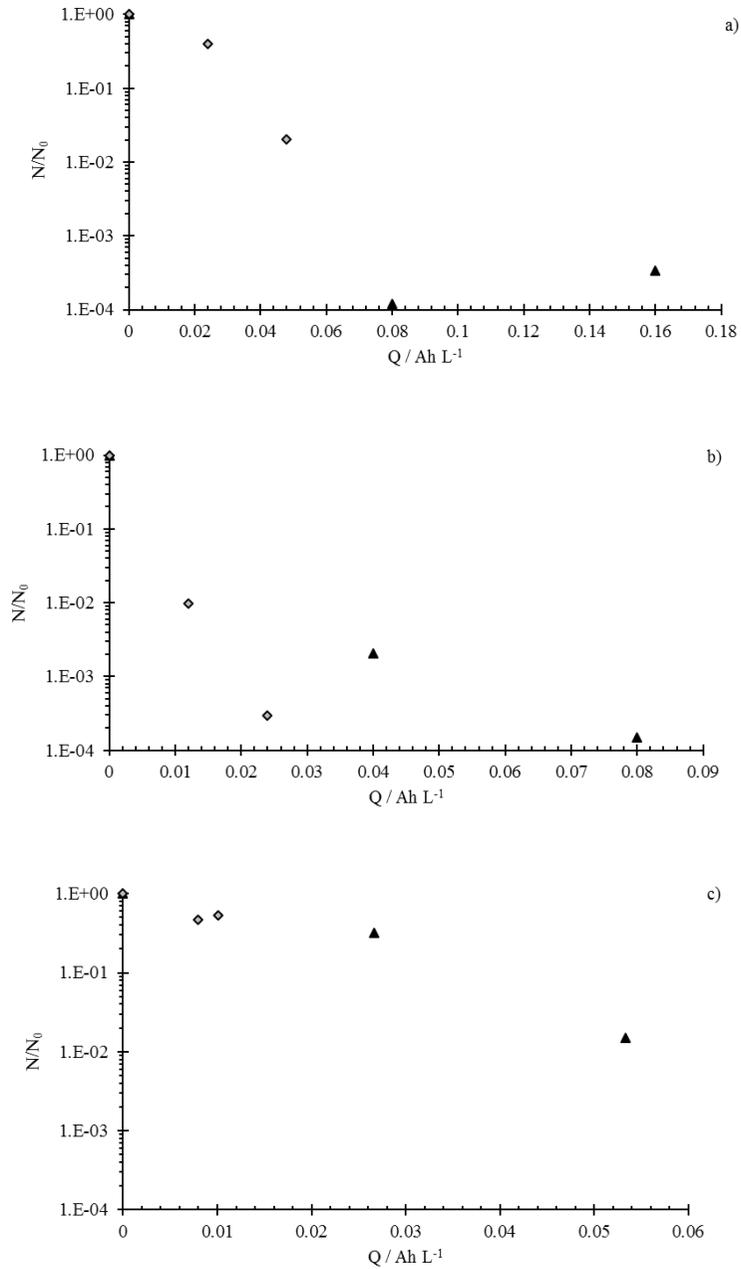


Figure 5.63. Changes in the concentration of Total Coliforms during the electrolysis carry out at a) 25 L h^{-1} ; b) 50 L h^{-1} and c) 75 L h^{-1} with ▲ CabECO and ◊ MIKROZON cells.

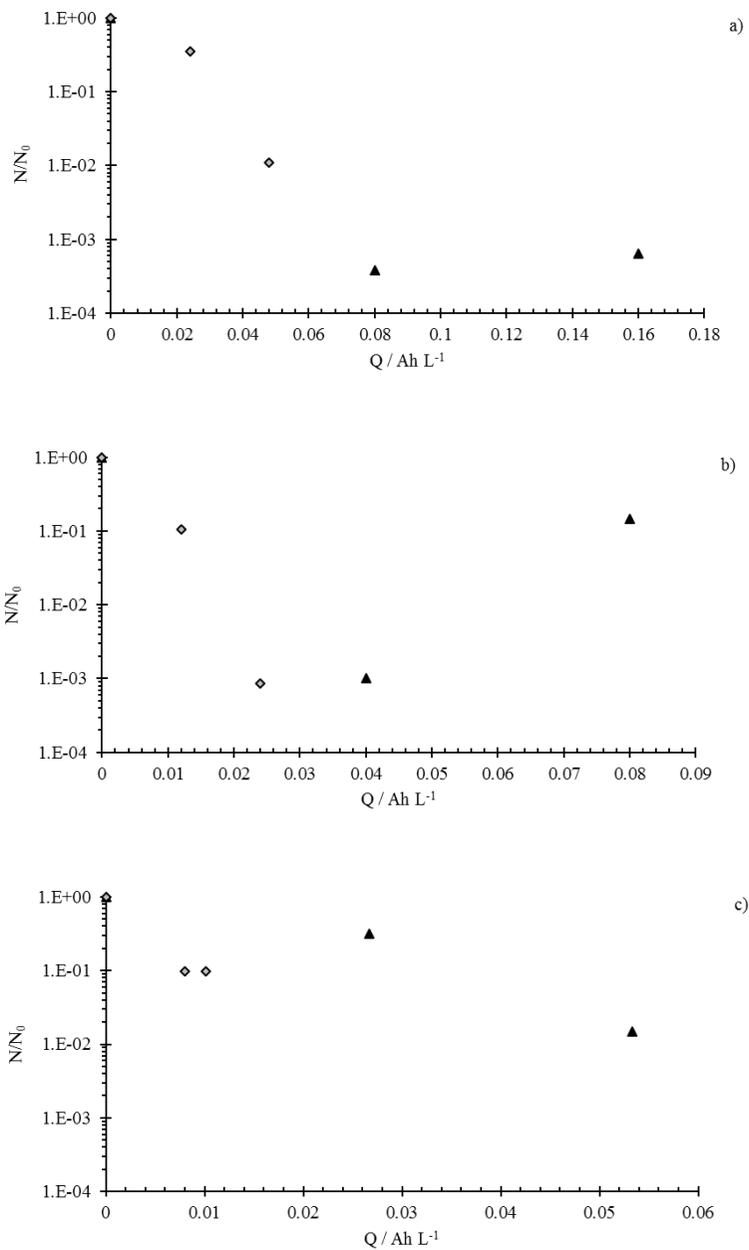


Figure 5.64. Changes in the concentration of the *Pseudomonas Aureginosa* during the electrolysis carry out at a) 25 L h⁻¹; 50 L h⁻¹ and 75 L h⁻¹ with ▲ CabECO and ◊ MIKROZON cells.

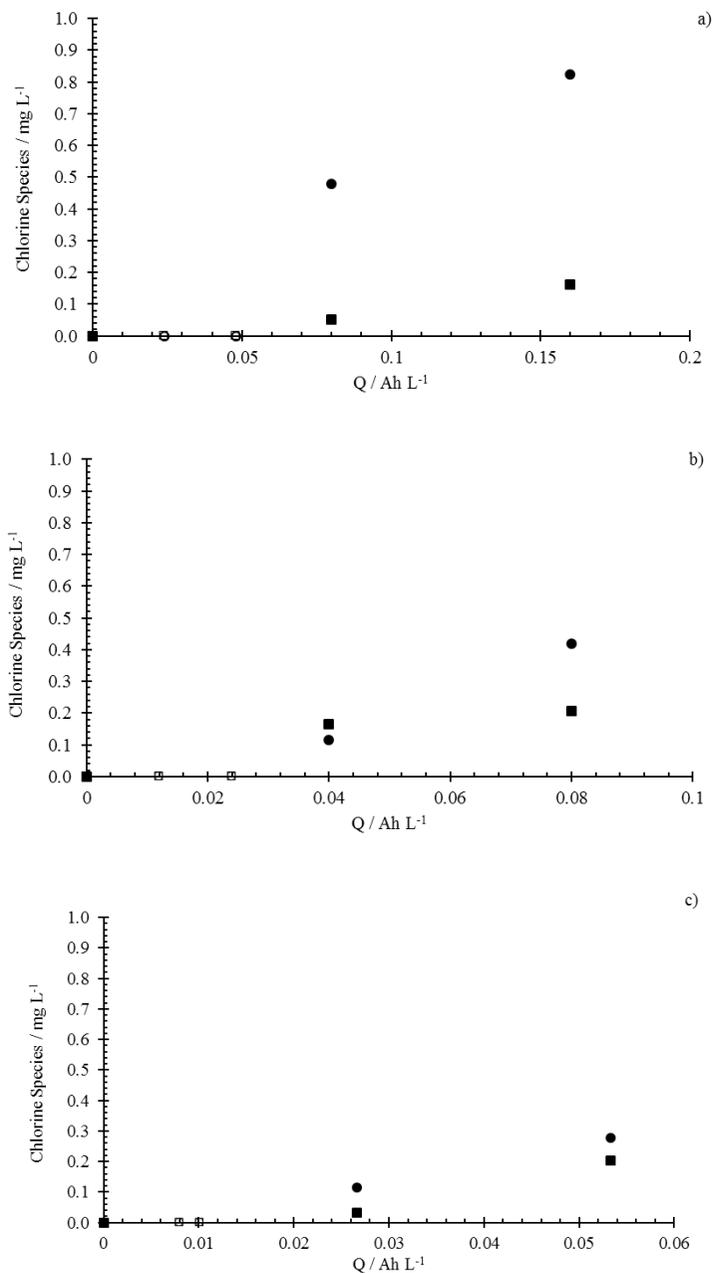


Figure 5.65. Changes in the concentration of the chlorine species (● Cl-CO₃⁻ ■ Cl-CO₄⁻) for the different current densities applied in the electrolysis carry out at a) 25 L h⁻¹; b) 50 L h⁻¹ and c) 75 L h⁻¹ with the CabECO: full symbols; MIKROZON: empty symbols.

In this case, the initial concentration of chloride in the PREDICO's effluent that is fed to the cells goes from 130 to 380 mg L⁻¹ due to the action of the anionic resin, which is a very high value which can promote the formation of these hazardous species, in particular when compared with the concentrations of chloride found during the treatment of surface water.

At it can be observed, no significant concentration of chlorate and perchlorate were produced during the electrochemical process carried out using the MIKROZON cell. Meanwhile, in the case of the CabECO[®] electrolysis, chlorate and perchlorate were detected but in very low concentrations in most cases. Thus, the higher amount of perchlorate observed was under 0.85 mg L⁻¹ corresponding with the experiment carried out at the lowest low rate of 25 L h⁻¹ when is applied a current density of 1666.67 A m⁻². In the remaining cases, the concentration of perchlorate was under 0.5 mg L⁻¹. The chlorate detected was always under 0.25 mg L⁻¹. This means that even in those non-optimal initial conditions, the disinfection is suitable and do not lead to unsuitable concentrations of these hazardous species.

5.4.1 Conclusions

In this chapter, the pre-disinfection column PREDICO, originally designed for the treatment of surface water, was adapted to treat groundwater. The following conclusions can be drawn:

- Re-engineering consisted of transforming the coagulation chamber into a reactor where lime, instead of coagulant, was used for a first softening of water. The tubular decanter, used in the original configuration to separate the flocs and concentrate them into the coagulation chamber, can face the separation of the precipitate formed and concentrated it into the reactor, favouring an efficient performance. In addition, two resin beds (one anionic and one cationic) were additionally added at the outlet the system, also contributing to exhaust the solids from the effluent acting as a filter. These resins, which can be targeted for the removal of different ions, have demonstrated to efficiently exchange divalent calcium and magnesium by monovalent sodium (softening) as well as to exchange nitrate by chloride.

- Pre-treated water can be efficiently disinfected by CabECO and by MIKROZON reaching disinfection as high as 4 logs and 3 logs in the removal of E. Coli and P. Aeruginosa, respectively.

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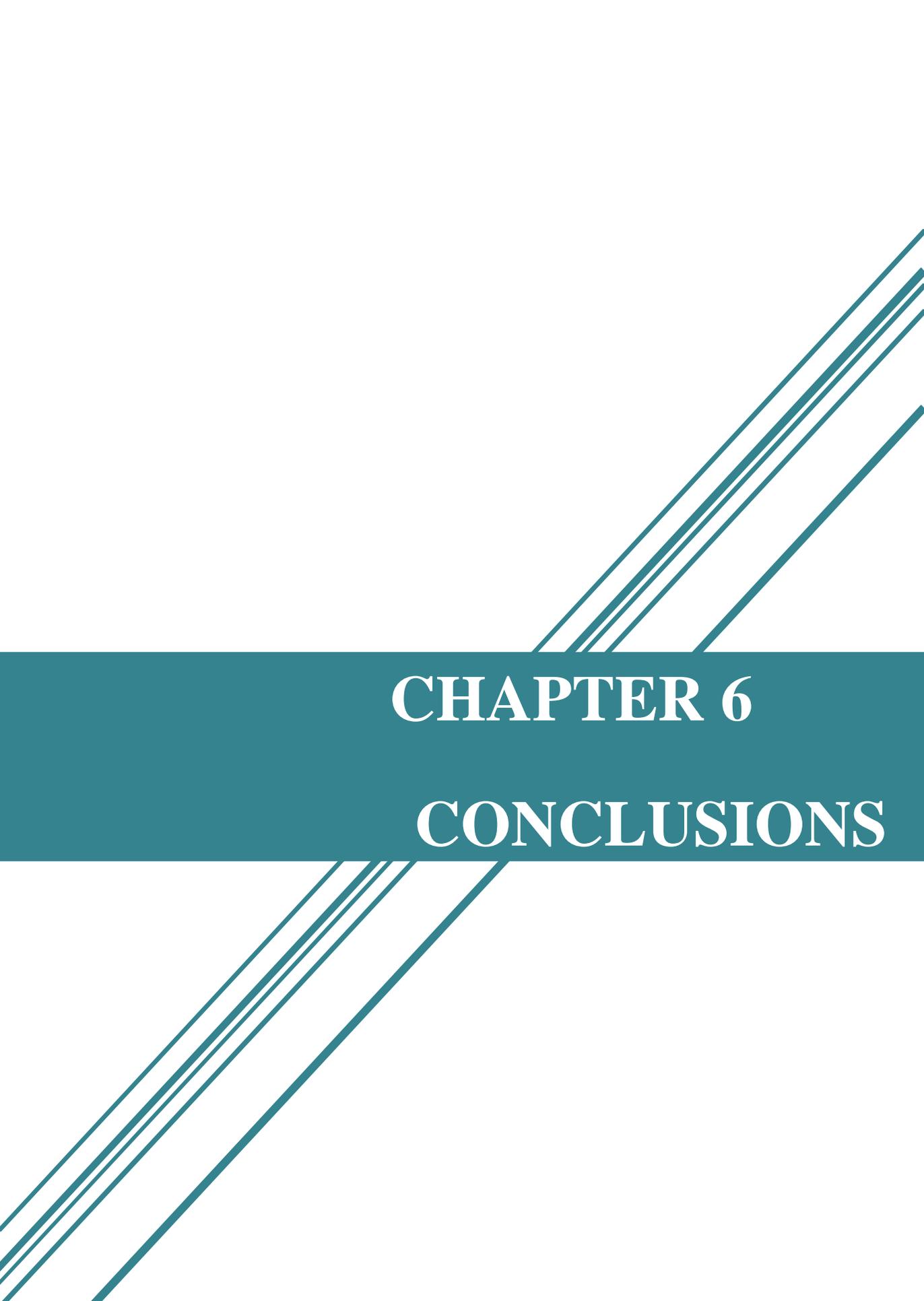
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CHAPTER 6

CONCLUSIONS

In this PhD thesis, the development of an autonomous safe water supply system in line with the European project SafeWaterAfrica grand agreement No. 689925 has been done. Within the tasks of the project, our group was part of the team in charge of designing the technical side of the system. Thus, after the discussion of the result obtained, in this section it will be given a global view of the mayor milestones reached.

The study of the behavior of different commercial cells equipped with diamond electrodes is essential to determine the most suitable electrochemical cell for its application in disinfection of surface water. Results showed that the cell design has an important influence on the performance of the electrolysis, even higher than that produced by the own electrodic materials. The three cells evaluated (ECWP[®], CabECO[®] and MIKOZON[®]) were very effective and allows to reach disinfection levels of several logs. In general terms, the percentage of removal depends on the flowrate used and the electric charge applied.

However, the formation of chlorine hazardous species is a key factor that affect convencional cells (ECWP[®]) more acutely. Otherwise, with the use of PEM electrolytic cells (CabECO[®] and MIKROZON[®]) the production of chlorates and perchlorates drops significantly. Nevertheless, this negligible concentration can be prevented with very low contact time between water and the electrode, and a single-pass strategy. Finally, CabECO[®] was selected as the best option for our purposes due to its structural stability and its technical specifications.

At that point, a more in-depth study of the CabECO[®] cell pointed out that the main responsible for the disinfection process was the mixture of oxidants formed during the electrolysis, including ozone (which was the key oxidant in the design of the cell) and persistent disinfectants such as hypochlorite and chloramines. Besides, in all cases, the THM concentrations were low and significantly below the limits set by Spanish regulations (100 ppb). In addition, the use of continuous mode with a single pass through the cell, CabECO[®] is able to eliminate the microbial contamination of surface water intensified with fecal pollution (95/5v/v) attaining efficiencies of 3 and 4-log unit in disinfection and 2-log units in sterilization. These facts confirmed the hypthothesis of the good purposes of the disinfection performance of the CabECO[®]

technology. The main drawback is related with the fouling of the electrodes when very strongly polluted water (80/20 v/v) is treated. This indicates the necessity of a pre-treatment unit to assure the proper disinfection of the effluent.

An efficient system, the so-called PREDICO (PRE-DIinfection Column) system, was developed and evaluated. When operating this system with an surface loading rate (SLR) of less than 20 cm min^{-1} and a hydraulic residence time (HRT) of more than 13.6 minutes, the PREDICO system can exceed 3 log units of removal of total aerobic microorganisms (sterilization) and 4 log units of removal of coliforms (disinfection) and can prevent the fouling of the downstream electro-disinfection cell when treating highly polluted surface water (made by mixing 80% surface water with 20% raw urban wastewater). These results supplement those obtained by electrolytic disinfection (more than 4 log units) and result in a highly efficient combined treatment. The PREDICO system has been carefully designed so that it can be easily and economically applied in rural communities in poor countries by manufacturing and replicating it using common hardware store materials (mainly pipes of different diameters).

In addition, two electrochemical dosing reactors to supply coagulant to the coagulation tank of the PREDICO system have been developed. They follow the premises of providing long-operation time, easy operation, easy for replacing electrodes and low cost. The first of them, called ECU, is capable to produce and dose the iron species needed in the pre-treatment of surface water sources. It can be successfully used with water matrixes with ionic conductivities within the range $100 \mu\text{S cm}^{-1}$ - $1000 \mu\text{S cm}^{-1}$. In addition, this device overcomes the behaviour of a conventional chemical dosing (in the form of FeCl_3) because it attains a better pH control and it produces a decrease in the effluent conductivity. However, the necessity of providing higher iron dosing rates and avoiding the agglomeration of iron particles when the device is not operated within long time periods, led to the development of an improved ECU system (i-ECU). This last device is able to dose coagulant at higher rates, thus attaining better treatment of the African natural resources tested.

Finally, a reingennering of the PREDICO system were done for the pretreatment of groundwater, including a lime bed instead of coagulation tank and resins filter

instead of GAC filter. Results demonstrated that re-designed PREDICO can successfully remove carbonates and salts contained in groundwater. Additionally, pre-treated water can be efficiently disinfected by CabECO® and by MIKROZON® reaching disinfection as high as 4 logs in the removal of *Total Coliforms* and *Pseudomonas Aeruginosa*.

The system designed was finally implemented to supply safe water in Africa sites. Figure 6.1 shows some pictures of the prototype constructed and operated.



Figure 6.1. SafeWaterAfrica project final prototype