UNIVERSIDAD DE ANTIOQUIA

TREATMENT OF FLORENCIA-CAQUETÁ MUNICIPAL WASTEWATER BY THE COMBINATION OF BIOLOGICAL PROCESSES AND FENTON-TYPE ADVANCED OXIDATION PROCESSES

Autor

Lis Manrique Losada

Universidad de Antioquia

Facultad de Ingeniería

Medellín, Colombia

2020

Treatment of Florencia-Caquetá municipal wastewater by the combination of biological processes and Fenton-type advanced oxidation processes

Lis Manrique Losada

Tesis de doctorado como requisito para optar al título de:

Doctora en Ingeniería Ambiental

Director

Ricardo Antonio Torres Palma
Ph.D. Químico

Universidad de Antioquia
Facultad de Ingeniería
Medellín, Colombia
2020

TREATMENT OF FLORENCIA-CAQUETÁ MUNICIPAL WASTEWATER BY THE COMBINATION OF BIOLOGICAL PROCESSES AND FENTON-TYPE ADVANCED OXIDATION PROCESSES

LIS MANRIQUE LOSADA

FACULTAD DE INGENIERÍA
DOCTORADO EN INGENIERÍA AMBIENTAL
MEDELLIN
2020

TREATMENT OF FLORENCIA-CAQUETÁ MUNICIPAL WASTEWATER BY THE COMBINATION OF BIOLOGICAL PROCESSES AND FENTON-TYPE ADVANCED OXIDATION PROCESSES

LIS MANRIQUE LOSADA

Thesis submitted in partial fulfillment of the requirements to obtain the degree of Doctor in Environmental Engineering

Advisor:

Ph.D. Ricardo Antonio Torres-Palma

GRUPO DE INVESTIGACIÓN
en Remediación Ambiental y Biocatálisis

DOCTORADO EN INGENIERÍA AMBIENTAL
MEDELLIN
2020

To my beloved and remembered dad, ***Jorge***

To my beloved mom and sister, ***Lucía y Bell***
To my brother, ***Dan***
To my daughters and princesses, ***Victoria y Violeta***
To my dear husband, ***Rafael***

ACKNOWLEDGMENTS

This thesis became a reality thanks to the support, accompaniment, and teachings of many people. I want to express my sincere and profound gratitude to everyone for making it possible. I further grateful for the advice and encouragement provided by countless doctoral fellows, classmates, colleagues, students, friends, and family members.

First, I want to express my eternal gratitude to the ex-rector of the Universidad de la Amazonia, magister Leonidas Rico Martinez, under his administration, who supported the beginning of my doctoral studies. In this way, the doctoral thesis presented herein was sponsored by Universidad de la Amazonia in the framework of the "*Programa de formación doctoral de la Universidad de la Amazonia*". The support provided by Universidad de la Amazonia included the tuition fee, research internship, and the tools, capacities, and infrastructure necessary to develop this Ph.D. project.

I especially want to thank my thesis advisor, Prof. Ricardo Antonio Torres Palma, who in spite of the particular circumstances surrounding the development of my doctorate, agreed to be my guide and supervisor during this time. I thank Prof. Ricardo for the opportunity he gave me to work with him, many times from a distance. His support and trust allowed the long journey of constant learning and the completion of this thesis. Thank you for sharing your invaluable knowledge and for guiding me to improve my research. Prof. Ricardo allowed me to be part of the GIRAB group, where I was fortunate to receive support from such extraordinary people as Prof. Javier Silva Agredo, Paola Villegas, Efraim Serna, Dayana Jojoa and Marcela Paredes. They shared their knowledge and experience with me during my time in Medellin at the beginning of my Ph.D. studies. Thanks to all the GIRAB group for being an example of work, discipline, and solidarity. I would like to express my sincere gratitude to Efraim for all the scientific support and advice during the writing of this thesis.

I will be eternally grateful to many people from the Universidad de la Amazonia, especially from the Faculty of Sciences and the Chemistry Department, including all the teachers and students. Many contributed to this achievement from their everyday tasks. Thanks to Hernán García, Jaime Velasquez, and Marlon Peláez, former deans and friends. Thanks to Professor Alberto Fajardo Oliveros, who as Vice-Rector of Research, promoted the equipping of the Environmental Chemistry

laboratory, and also the development of this thesis. Also special thanks to my fellow researchers at the CIMAZ-Macagual research center: Paola García, Alejandro Reyes, Wilson Rodríguez, Faver Alvarez, Juan Carlos Suárez, Lida Galindo and Gustavo Celis, who contributed to keeping the research dynamic in such difficult times. I also thank Claudia Gonzalez, coordinator of the teaching laboratory, for her support and for facilitating the use of the instruments available in these spaces.

Thanks to the researchers from the research group Materiales, Ambiente y Desarrollo – MADE, and to my students of the POHAGUAS research seedbed projects. They joined me in this challenge of researching the Universidad de la Amazonia. Thank you for supporting all the processes that were achieved during the development of the thesis: presentation of projects to calls, development of projects, management of degree projects, generation of research products, creation, provision and implementation of ISO17025 norm in the Environmental Chemistry laboratory, among others.

Thanks to Heidy Santanilla, Brayan Muñoz, Elkin Suárez, Steffannia Gonzalez, Sergio Cerón, Santiago Monje, Paola Castiblanco, Jairo Gómez, Tatiana Guaje, Karen Murcia, Juan Camilo Arriola and Alejandra Gasca, my chemistry program students who supported the development of this thesis. With their tireless work, we succeed. I wish you all much successes in your future professional life. I would like to especially thank Carolina Quimbaya, my student and now a research assistant, who became a fundamental part of the Environmental Chemistry Laboratory of the Universidad de la Amazonia. Thank you for your discipline, hard work, and support during this thesis.

I also want to thank the research group BPNA for their collaboration with the analysis of total phenols content on the extracts of Amazonian fruits. I would like to thank especially to Natalia Cuellar who made it possible, and Francis Sánchez for his support in the study of the influence of chemical structure on the extent of biodegradation.

I would like to thank Prof. Sixto Malato and Dr. Isabel Oller for supporting me at the different stages of my research internship at the Plataforma Solar de Almería (PSA) – Spain. Thank you for giving me the confidence to pursue the thesis when I needed it. I would like to thank Prof. Sixto for allowing me to undertake my research internship at PSA, without knowing me. Thank you for sharing all your experience and knowledge during my stay. I am grateful for the trust place in me, it was invaluable in this life experience that was my doctoral studies. I would like to express my most sincere gratitude to Isabel for teaching me everything about photo Fenton and a lot about life in our talks, which fortunately were not only academic. I thank them both for allowing the Colombian community of advanced oxidation processes,

to count on your valuable support and willingness to maintain strong cooperation networks. Thanks for teaching me so much.

I am also indebted to all the academics and staff members of the water treatment unit of PSA. My time at PSA left me as many friends as I can remember. It left me expertise, knowledge but also taught me about tolerance, respect, discipline, and solidarity. I would like to thank Elisa Ramos, Isabel Fernandez y Francisco for their invaluable support in the laboratory, so much that I wanted to bring them to Colombia. I also want to thank Agustin Carrion because I was fortunate enough to meet him before his PSA farewell, and he taught me how to work harder and overcome problems, thanks for everything Agustin. I am also thankful to the PSA Ph.D. students: Ilaria, Dennis, Irene, Ana, Samira, Melina, and Laura for making my time at PSA pleasant and enriching. From each one, I learned not only about photo electro Fenton, ozonolysis, disinfection, heterogeneous photocatalysis, filtration membranes or UPLC, but also what the best wine is. Thanks for all that guys, I carry you in my heart. I also want to especially thank the new friends who, like me, were research interns at PSA and with whom I established an academic relationship and, of course, a friendship: Giusy, Gema, Enrico, Diego, Afsoon, Ariadna. I especially thank Ilaria, Giusy, Gema, and Dennis for letting me become part of their lives for a short time, and I love you very much.

Additionally, I express my sincere thanks to those whose essential collaboration allowed me to complete this thesis. In this way, I thank Dr. Ana Agüera, Dr. Ana Martinez and Dr. Patricia Plaza all from CIESOL Solar Energy Research Center of University of Almería for their support in determining the pharmaceutical concentration present in the sludge used in experiments of this thesis. Likewise, to Dr. Ana Botero and Dr. Felix Hernandez of the Research Institute for Pesticides and Water (IUPA) of University Jaume I for the cooperation for the quantification of 38 pharmaceuticals present in municipal wastewater from Florencia Caquetá.

I want to thank the reviewers of this thesis, Dr. María Isabel Mejía, Dr. Henry Zúñiga and Prof. Sixto Malato for reading and evaluating this thesis, for their valuable observations that contributed to improving the quality of the final document.

I would like to express my most sincere gratitude to the following people:

- I do not have the right words to thank my dear Maurin Salamanca. It would never be enough to thank her for driving the "remote" idea of pursuing doctoral studies after so long for me. Thank you Maurin for believing that I could and should do it for making me see the research in the best way for all the scientific and emotional support, for so many teachings and for being my friend. I love you so much.

- Of course, my dear friends Oscar Gamba and Jaime Gallego, since I had the luck to meet them as professors of the Chemistry Department and creating the research group. They followed my progress from a distance and have supported me in the difficult moments. I thank you for not forgetting me, and I am sorry for not being able to share your special moments. I think we will have time now, and I carry you in my heart.

- Likewise, my friends from the Colombian community of advanced oxidation processes, Miguel Angel Mueses and Fiderman Machuca, thank you very much for watching my process, advising and encouraging me during the writing stage of this thesis. I want to make a special mention to my fellow undergraduate and Master's in Chemical Engineering, Silvia Ochoa, Mario López and Gerónimo Matallana, for allowing this friendship to be sustained over time and distance and for serving as a reference to continue my training. I carry them all in my heart.

- Finally and more important, I want to thank my family. This journey did not begin five years ago, the idea of pursuing a Doctoral Degree came up in conversations with my dad, more than 20 years ago. The goal was there over the years, during good and bad times. Today, after a difficult and enrichment journey, I fulfilled my dad's dream, which he shared with my mom and my sister. Although my dad is no longer physically with us, I want to think that he is with us from heaven and that he will receive this gift. Thank you, dad, for having loved and taught me so much, this achievement is my gift to you because we dreamed it together. I love you and I miss you. I am eternally indebted to my mom and Bell, for being my faithful admirers, for supporting and loving me always. I love you, Manrique girls. Thanks Dan, for protecting me from heaven. I love you too. I will always be thankful to my beautiful daughters, my princesses, Victoria y Violeta, for enduring my absence for months and still demonstrate me their unconditional love. Thanks for making sense of everything. You should prepare yourselves because the best is yet to come. I love you, princesses of my life. I am very thankful to my husband for sharing more than 13 years of our lives. Thank you for your patience, and for believing in my capacities. Thank you for going through life with me and for being part of achievements. I love you. A thousand thanks with all my heart to my brother-in-law Camilo Hernandez, I will never forget all the support received by opening the doors of his home and his heart to me. I love you too much.

CONTENTS

Page

LIST OF TABLES

Page

LIST OF FIGURES

Page

SUMMARY

In developing countries, small cities such as Florencia-Caquetá (Colombia), municipal wastewaters (MWW) are directly disposed on environmental aqueous media without any treatment. Consequently, contaminants of emerging concern (CECs) as pharmaceuticals reach natural water bodies. These CECs have the potential risk for the environment due to their persistence properties and biological activity. Under such context, research about technologies to treat MWW and eliminate CECs are needed.

Considering the absence of efficient municipal wastewaters treatment plants in Florencia-Caquetá, the present doctoral thesis was focused on the treatment of MWW by alternative and conventional processes considering local economic and environmental conditions. It was evaluated the combination of biological treatments with solar photo-Fenton (SPF) at near neutral pH.

The thesis is organized in six chapters. Chapter 1 contains the research background, i.e., the problem statement, the conceptual framework about biological processes and photo-Fenton, the objectives as well as the new contributions of the thesis. In Chapter 2 is presented the characterization of MWW from Florencia-Caquetá in terms of global parameters (e.g., chemical oxygen demand, pH, organic matter content, conductivity, etc.) and presence of relevant CECs (e.g., pharmaceuticals). In Chapter 3 is depicted the treatment of MWW from Florencia through two biological systems (aerobic or anaerobic) at lab-scale. Initially, the acclimatization of microorganisms to the water sample was studied. Afterwards, the action of the stabilized biological systems to remove four representative pharmaceuticals (selected from Chapter 2) and biodegradable organic matter in the MWW from Florencia was established. The processes efficiency was tested by monitoring the concentration of pharmaceuticals, the removal of total organic carbon (TOC) and evolution of nitrogen forms (NH_4^+, NO_3^-).

In Chapter 4, the application of solar photo-Fenton process for treating the representative pollutants at lab-scale is presented. Also, the improvement of SPF performance by Amazonian fruit extracts is considered. This chapter analyzes the limitations of classical photo-Fenton for degrading the target pharmaceuticals and it

shows the possibility of addition of Amazonian fruit extracts (copoazu, canangucha and coffee) as complexing agents of iron to enhance the degrading ability of SPF process for treating MWW. The performance of process was evaluated as a function of removal efficiency of organic matter and pharmaceuticals present in MWW from Florencia. Additionally, the evolution of dissolved iron and peroxide consumption were monitored.

Chapter 5 deals with the combination of the biological processes with SPF for treating MWW from Florencia. It was evaluated the effect of combination order (first biological process and second SPF or vice-versa) at lab scale. In Chapter 6, it is initially described the acclimatization of a pilot biological reactor (which was operated under non-controlled conditions of temperature, humidity and pH). Then, the combination at pilot scale of the SPF process (in presence of an extract of Amazonian fruit) and a biological system to treat MWW from Florencia is shown. It was evaluated the ability of combination to remove target pollutants and organic matter, in addition to evolution of nitrogen species.

The development of this research work provides new information about: i) the occurrence of CEC in raw MWW from Florencia-Caquetá (which could be used as a primary indicator of pollution of water environment of the Colombian Amazonia); ii) A green solar photo-Fenton process at natural pH promoted by Amazonian natural products as iron complexing agents; iii) the use anaerobic treatment in combination with SPF for the elimination of CECs and mineralization of organic matter present in MWW; and iv) combination of an anaerobic biological process with SPF at pilot-scale, which represents a useful background for the construction of systems at a bigger scale and its subsequent application to MWW in Florencia or other towns belonging to Colombian Amazonia.

CHAPTER 1. THESIS BACKGROUND

1.1 Problem statement

Florencia-Caquetá is the largest urban settlement on the Colombian Amazonian region. Consequently, this zone discharges high amounts of pollution into the aquatic environment. Unfortunately, the most of the municipal effluents are disposed on *La Perdiz* river (the local river), which flows into *Hacha* river (Figure 1). These rivers are a hydrographic basin that surrounds Florencia city and flows into others regional environmental waters. Hence, the presence of many contaminants in Amazonian-Andean aquatic ecosystems could generate unbalance in the natural media.

It has been estimated that Florencia produces 0.6 m^3 s^{-1} of municipal wastewater (MWW). Additionally, Florencia has no a central municipal wastewater treatment plant (MWWTP), which generate a direct negative impact over its aquatic and land biodiversity. This city suffers an enormous sanitation deficit and lack of qualified personal for treatment of MWW (Manrique-Losada & Pelaez Rodriguez, 2010). Florencia had two small MWWTP: "*La Ciudadela"* and "La Gloria". "*La Ciudadela"* was closed because it was a focus of pests and environmental problems and "La Gloria" did not work properly. Both plants presented mistakes of design and poor maintenance. Currently, Florencia has a small wastewater treatment plant with low efficiency for the local agro-industrial activities (SERVAF, 2013).

The water service company from Florencia (SERVAF S.A. E.S.P.) has reported to environmental authority (Corpoamazonia) 80 points of direct discharges of MWW on water sources (28 points on *Hacha* river, 37 on *La Perdiz* river and 15 on *La Sardina* river, Figure 1, (SERVAF, 2013)). Rivers in Caquetá are affected by anthropic

intervention, which lead to a high contamination into aquatic ecosystems, bad water quality and an impossible of use to drink and recreation.(Manrique-Losada & Pelaez Rodriguez, 2010). For example, *La Perdiz* river collects 42.5% of all discharges of the city. This aquatic ecosystem receives a charge of 3150.95 kg d^{-1} of chemical oxygen demand and 1418,11 $kg.d^{-1}$ of total suspended solids (SERVAF, 2013).

It can be mentioned that the MWW from Florencia are a mix of domestic, hospital, institutional, commercial and agro-industrial wastewaters. Such MWW contain compounds as carbohydrates, fats, proteins, pesticides, inorganic ions, surfactants and pharmaceuticals. MWW typically have a BOD_5/COD ratio between 0.4 and 0.5, which implies they can be treated by biological processes to remove biodegradable compounds (as carbohydrates, fats or proteins), but at the same time MWW have recalcitrant compounds (e.g., pharmaceuticals or pesticides) that cannot be eliminated by biological processes or in natural aquatic ecosystems (Pepper & Gerba, 2015). Indeed, some of these recalcitrant substances can be toxic in the environment and induce other adverse effects on aquatic organisms, even permanent damages to animal or humans (European Cooperation in Science and Thecnology, 2017; Rizzo et al., 2019).

Nowadays, it is recognized worldwide that MWWTPs are among the main sources for releasing to natural media emerging concern contaminants (CECs, pollutants at trace levels, which cannot be completely transformed by conventional biological processes and their effects on environment and health are not well-known until now (Aziz et al., 2019; Jonstrup et al., 2011; Polesel et al., 2015; Sikosana, Sikhwivhilu, Moutloali, & Daniel, 2019; Vidal et al., 2019)). Unfortunately, MWWTPs are not designed to remove CECs and conventional treatments require to be complemented with other processes to deal with CECs and limit their discharge into the environment (Rizzo et al., 2019).

The combination of biological treatment with advanced oxidation processes (AOPs) has been utilized as an interesting option for the removal of biodegradable organic matter (Bandala et al., 2010; De la Cruz, Giménez, Esplugas, Grandjean, De Alencastro, et al., 2012; Nikolaus Klamerth, Malato, Agüera, Fernandez-Alba, &

Mailhot, 2012; Moreira et al., 2016) and degradation of CECs in MWW (Alvarino, Suarez, Lema, & Omil, 2014; W. H. Chen, Wong, Huang, Chen, & Lin, 2019; Huang, Guo, Yan, Gong, & Fang, 2019; Martínez-Hernández, Meffe, Herrera López, & de Bustamante, 2016; Novelo et al., 2016).

According to Rizzo *et al*., the best technology to reduce the releasing of CECs into the environment must be done based on the local conditions (e.g., available space and solar energy, cost of electricity, etc.) and water characteristics (Rizzo et al., 2019).

Likewise, there are widely studied possibilities for biological treatment such as stabilization lagoons and natural or artificial wetlands, which have shown moderate efficiencies depending on the goal of the MWWTP (Sikosana et al., 2019). The main advantages of this treatment are the relative low construction and operation costs. Nevertheless, vast areas of land and permanent plague control are required (Mendonca, 2001). The most common biological treatment in MWWTP is the activated sludge (aerobic treatment), which reach high mineralization efficiencies but at high operational costs because it requires a permanent air supply (Ramalho, 2003; Romero-Rojas, 2001).

In search of low-cost treatments, efficient and sustainable alternatives with low land area requirements are desirable. Anaerobic treatment emerges as a viable option fulfilling these requirements. In fact, successful applications of anaerobic systems have been demonstrated in tropical developing countries (Bandara et al., 2012; Orozco-Gaviria, Triviño-Cabrera, & Manrique-Losada, 2014; Padrón-Páez, Almaraz, & Román-Martínez, 2016; Romero-Rojas, 2001; Torres-Lozada, 2012). Additionally, according to the literature, biological treatments do not remove completely CECs present in MWW (Bueno et al., 2012; De la Cruz et al., 2012; Klamerth et al., 2010; Miralles-Cuevas, Oller, Sánchez Pérez, & Malato, 2014) and then, it is necessary to consider other processes such as AOPs to degrade CECs.

There is a significant number of AOPs with high efficiency in CECs degradation. UV/H_2O_2, ozone, TiO_2/UV, sonochemistry, direct and indirect electrochemistry, and Fenton based processes are some examples. Some of them are improved with the

mediation of UV or sunlight (Chong, Sharma, Burn, & Saint, 2012; Papoutsakis et al., 2015; Sathishkumar, Mangalaraja, & Anandan, 2016; Sirés, Brillas, Oturan, Rodrigo, & Panizza, 2014).

The main advantage of these processes is the high efficiency for CEC elimination due to the formation of HO radicals. Nevertheless, the high implementation costs at pilot or real scale are major limitations. The solar photo-Fenton process is highly efficient and simply needs an external iron source and H_2O_2; which are innocuous in operational concentrations (Klamerth, Malato, Maldonado, Agüera, & Fernández-Alba, 2011a; Méndez-Arriaga et al., 2009). The main disadvantage of using conventional SPF is the pH required for an optimal operation of the process. A high efficiency is achieved at acidic pH (Kositzi, Poulios, Malato, Caceres, & Campos, 2004; Malato, Blanco, Vidal, & Richter, 2002). However, to develop strategies to use SPF at natural pH and degrade CECs present in MWW is a need and then, an area of growing interest (Klamerth, Malato, Agüera, & Fernández-Alba, 2013; Klamerth, Malato, Maldonado, Agüera, & Fernández-Alba, 2011b; Villegas- Guzman et al., 2017; Villegas-Guzman, Giannakis, Torres-palma, & Pulgarin, 2017).

In this context, during biological treatment, biodegradable organic matter can be removed; while using solar photo-Fenton elimination of CECs can be achieved. Therefore, the combination of both processes constitutes an interesting alternative to reach both goals. In fact, the combination of photo-Fenton with a biological treatment reduces the operating costs (Bautista, Mohedano, Casas, Zazo, & Rodriguez, 2008; Cassano et al., 2011; Oller, Malato, & Sánchez-Pérez, 2011b; Ponce-Robles, 2018). In this sense, previous studies have showed the feasibility of combining the two processes at pilot and real scale in agricultural and industrial wastewaters (Oller et al., 2011b). In addition, other works have successful evaluated the application of photo Fenton at acidic or near neutral pH in effluents of municipal wastewater treatment plants (Klamerth et al., 2013, 2012, 2010; Papoutsakis et al., 2015a, 2015b) and the treatment of raw municipal wastewaters by solar photo-Fenton followed by biological oxidation (Prieto-Rodriguez et al., 2012). Therefore, it is necessary to evaluate the combination of these processes to treat the municipal

wastewater of Florencia (Caquetá) in order to promote its mineralization and the elimination of CECs at lower operating costs.

Additionally, considering the case of Florencia-Caquetá (where local socio-economic and environmental conditions request the implementation of low cost, sustainable and simplified wastewater treatment systems), it is necessary to study on adaptable technologies for efficiently treating their MWW. Consequently, this doctoral thesis was performed around the development of a combination of biological systems with photo Fenton solar at natural pH to treat MWW from Florencia at lab and pilot scale.

1.2 Conceptual framework

1.2.1 Contaminants of emerging concern – CECs

Contaminants of emerging concern (CECs) are a heterogeneous group of chemicals that includes pharmaceutically active compounds (PhACs), personal care products, surfactants, pesticides, endocrine disrupting chemicals (EDCs), nanoparticles (NPs) and industrial chemicals (such as flame retardants, plasticizers and food additives) (Giannakis, Franco, Vives, & Grandjean, 2015). This group of substances are typically detected in wastewater and aquatic ecosystems at low concentrations (ng L^{-1} – µg L^{-1}) (Rizzo et al., 2019). CECs are ubiquitous and present potential risks to human health and the environment, although their toxicological effects are not yet fully known in many cases (Martín-pozo et al., 2019). In the case of PhACs, once administered, a portion of them are excreted and released into wastewater and subsequently reach natural water bodies, where may cause environmental problems due to their persistence and critical biological activity (Serna-Galvis et al., 2019).

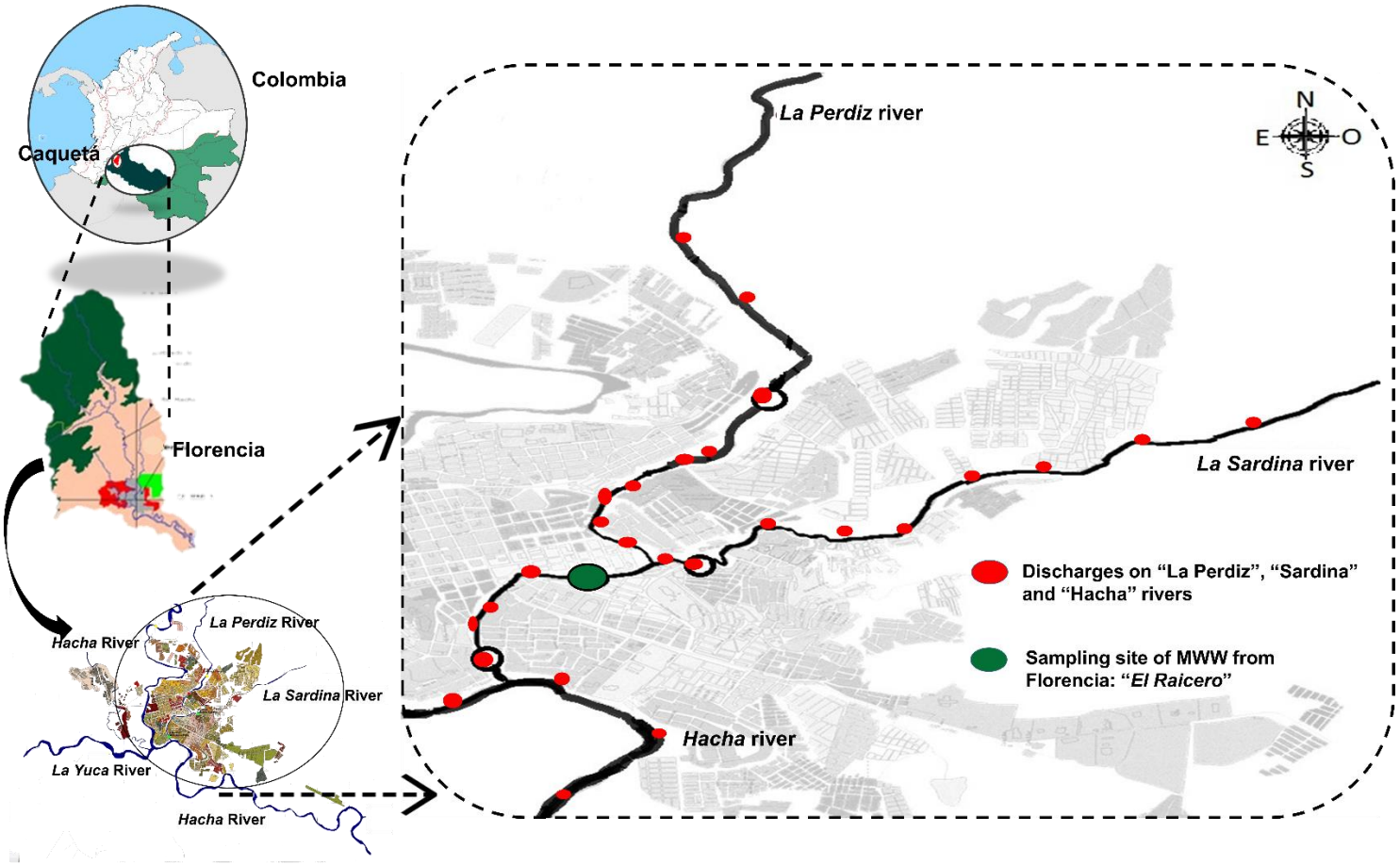


Figure 1. Some discharges located over the urban area of Florencia and sampling site selected to this work. *Source: Diagram prepared by the author of this thesis, based on information reported by SERVAF et al. (2013), Manrique-Losada et al. (2010), Manrique-Losada et al. (2013) and updated through fieldwork of this thesis.*

Frequently, PhACs are found in MWW and its limited biodegradability have been demonstrated (Vasiliadou et al., 2018, Madakka et al., 2019). On the other hand, it has been shown that some PhACs or combination among them can be present at high non-lethal concentrations in biological reactors (Aydin et al., 2015). Additionally, under that conditions, some PhACs like antibiotics can promote development/proliferation of antibiotics resistant bacteria (which is considered a serious public health problem in XXI century) (Botero-Coy et al., 2018; Bouki, Venieri, & Diamadopoulos, 2013; Krzeminski et al., 2019; Novelo et al., 2016; Velásquez, 2014). Thus, PhACs are CECs that demand special attention and application of effective processes to eliminate them, and them are the main subject of this work.

1.2.2 Biological processes for wastewater treatment

Biological processes for the treatment of wastewater take advantage of the microbial metabolism for the transformation of organic compounds present in the water. Thus, organic matter is converted into small molecules (e.g., CO_2, CH_4, water, inorganic ions) and energy for growth, cell maintenance and reproduction of microorganisms (Show & Lee, 2017).

Microbial metabolism can be carried out under aerobic or anaerobic conditions. In the aerobic treatment, microorganisms oxidize organic matter in the presence of oxygen. This involves three main stages: fermentation/respiration (or oxidation), biosynthesis, and endogenous respiration. The final products of oxidation process are carbon dioxide, water, and inorganic ions as sulfate and ammonia. Eq. 1.1 represents the main general aerobic reaction of organic compounds (COHNS).

$$COHNS + O_2 + aerobes \rightarrow CO_2 + H_2O + NH_3 + energy \quad \text{(Eq. 1.1)}$$

$$COHNS + O_2 + energy + aerobes \rightarrow new\ cells \quad \text{(Eq. 1.2)}$$

During the fermentation step, biodegradable organic compounds are transformed into volatile fatty acids (VFAs) and in a second process (respiration) the aerobic microorganisms convert VFAs into CO_2, water and energy by using oxygen as an electron acceptor (Eqs. 1.3–1.4) (Lazcano-Carreño, 2016). Then, as microorganisms consume dissolved oxygen in the water, the oxygen must be constantly supplied to the bioreactor to guarantee the conversion of organic matter and new cells that accumulate in the biological system (Gerba & Pepper, 2014; Show & Lee, 2017).

$$\text{COHNS} + \text{aerobes} \rightarrow \text{VFAs} + CO_2 + \text{energy} \quad \text{(Eq. 1.3)}$$

$$\text{VFAs} + O_2 + \text{aerobes} \rightarrow CO_2 + H_2O + \text{energy} \quad \text{(Eq. 1.4)}$$

The biosynthesis stage involves the formation of cellular structures (growth of microorganisms and reproduction), consuming energy and organic matter (Eq. 1.2). Meanwhile, the endogenous respiration stage is achieved when the organic matter is finished under conditions of oxygen saturation and the microorganisms consume other cells. Normally this last process is used to reduce the biomass accumulated in bioreactors during the biosynthesis stage (Show & Lee, 2017; Sikosana et al., 2019; Virkutyte, 2017).

In turn, anaerobic treatment promotes the degradation of organic matter towards final products as CH_4. In this treatment, acceptors of electrons different to molecular oxygen are used (e.g., NO_3^-, SO_4^{2-} and CO_2, which have a lower reduction potential than O_2), therefore less energy is generated in this metabolism compared to an aerobic process, even when both start from the same substrates (glucose, amino acids, triglycerides). In anaerobic treatment, 90% of the energy produced in the process is retained as CH_4 (Aziz et al., 2019; Derlon, Wagner, da Costa, & Morgenroth, 2016).

The anaerobic process is developed by two types of bacteria: acidogenic that act in the early stages of the process and methanogenic that produce the final compounds. Four stages have been proposed for anaerobic process: hydrolysis, acidogenesis

acetogenesis and methanogenesis. In the hydrolysis, complex molecules (e.g., carbohydrates, lipids and proteins) become simpler ones (e.g., monosaccharides, fatty acids an amino acids). Then, in acidogenesis CO_2, H_2 and organic acids (such as acetic, propionic, butyric, valeric acids, etc.) are produced. In the third stage (acetogenesis), acetogenic bacteria generate acetate, carbon dioxide and hydrogen from organic acids. Finally, in the methanogenesis, bacteria reduce CO_2 and acetate to form CH_4 (Figure 1.2) (Aziz et al., 2019; Bhatti, Maqbool, Malik, & Mehmood, 2014; Derlon et al., 2016).

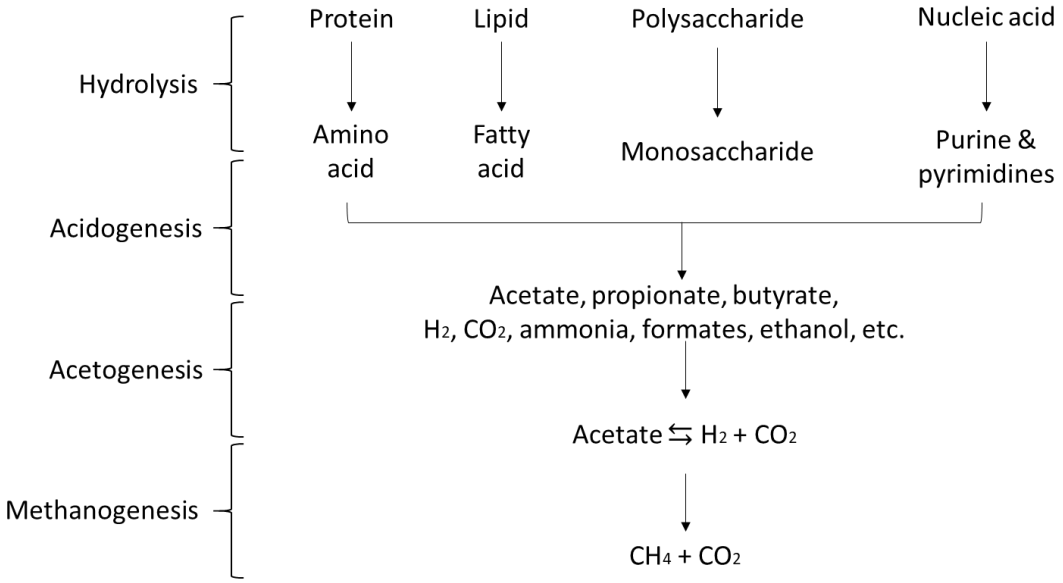


Figure 2. Steps involved in anaerobic metabolism. Reprinted from Aziz *et al.* (Aziz et al., 2019)

The described biological treatments have demonstrated high effectiveness toward transformation of biodegradable organic matter in wastewater (Show & Lee, 2017; Sikosana et al., 2019). Nevertheless, the non-elimination of recalcitrant or not biodegradable pollutants as PhACs in MWWTP by biological processes could be a serious problem (Maddakka et al, 2019), which should require the use/combination with complementary technologies to reach an efficient treatment of MWW.

1.2.3 Principles of photo-Fenton process

AOP are based on generation and utilization of short lived and highly reactive radical species (mainly hydroxyl radical, HO•, which is a strong oxidant, E°: 2.80 V, (Armstrong et al., 2013)) to eliminate recalcitrant organic pollutants. Among different ways to produce the hydroxyl radical, we have catalytic AOPs such as photo-Fenton (Miklos, Remy, Jekel, Linden, & Hübner, 2018), which initially comprises the reaction of Fe (II) with hydrogen peroxide (Eq. 1.5). Then, the Fe (III) produced can be reduced in the aqueous medium by the action of UV-Vis light, producing extra hydroxyl radicals (Eq. 1.6) and making the system a catalytic process (Pignatello, Oliveros, & Mackay, 2006). This process has gained a high attention of researchers due its operational easiness and possibility of solar irradiation utilization (Clarizia, Russo, Somma, Marotta, & Andreozzi, 2017; Rahim Pouran, Abdul Aziz, & Wan Daud, 2015).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO\bullet + HO^- \qquad \text{(Eq. 1.5)}$$

$$Fe^{3+} + H_2O + h\nu_{(UV\text{-}vis)} \rightarrow Fe^{2+} + HO\bullet + H^+ \qquad \text{(Eq. 1.6)}$$

Photo-Fenton process has shown to be very efficient in the degradation of pollutants in MWW (Papoutsakis, Pulgarin, Oller, Sánchez-Moreno, & Malato, 2016). However, the photo-Fenton process at pH higher than 3.0 is limited by Fe^{3+} precipitation (Eq. 1.7) (Villegas-guzman, Giannakis, Torres-palma, & Pulgarin, 2017). Interestingly, some organic compounds can complex iron (III) keeping it in soluble forms allowing to work at near neutral pH conditions (Clarizia et al., 2017). Furthermore, many Fe^{3+}-organic ligand complexes are able to absorb light in the near-UV and visible regions more efficiently than aquo-complexes and undergo photo-reduction through a ligand-to-metal charge transfer (LMCT). As a results, ferrous ion regeneration (Eq. 1.8) and the production of other radicals (Eqs. 1.8-1.9), which could contribute to the

organic matter oxidation occurs (Clarizia et al., 2017; Miralles-Cuevas, Oller, Sánchez Pérez, & Malato, 2014; Villegas-guzman et al., 2017).

$$Fe^{3+} + HO^{-} \rightarrow Fe(OH)_{3\ (insoluble\ solids)} \quad \text{(Eq. 1.7)}$$

$$[Fe^{3+}\text{-}L]_{\ complex} + h\nu \rightarrow Fe^{2+} + L\bullet \quad \text{(Eq. 1.8)}$$

$$L\bullet + O_2 \rightarrow\rightarrow\rightarrow O_2\bullet^{-} \quad \text{(Eq. 1.9)}$$

Carboxylic acids (e.g., oxalic, malic, succinic, citric and gluconic acids) are among the most common organic compounds used as iron complexing agents (J. Chen & Browne, 2018; N. Klamerth, Malato, Maldonado, Agüera, & Fernández-Alba, 2011; Liu et al., 2010; Nogueira, Souza, Dezotti, Boaventura, & Vilar, 2017; Villegas-Guzman et al., 2017). Polyphenols are also able to complex ferric ions and increase its solubility in aqueous solutions at near neutral pH values (Papoutsakis et al., 2016). Moreover, some polyphenols can also act as photosensitizers and promote the formation of reactive oxygen species (ROS) (Clarizia et al., 2017; Papoutsakis et al., 2016; Villegas- Guzman et al., 2017).

In most cases, the photo-Fenton process enhancement with organic complexing agents requires the addition of these compounds to the reaction system. For this reason, recent works have been addressed to search for non-toxic and biodegradable chelating compounds, which must be environmentally sustainable and inexpensive to propose a large-scale photo-Fenton process at natural pH. (N. Klamerth, Malato, Agüera, & Fernández-Alba, 2013). In this context, some natural products rich in polyphenols and organic acids could have an interesting potential in the application of solar photo-Fenton (SPF) at natural pH. Indeed, juices of orange or lime and coffee extract have been evaluated as SPF enhancers with promising results for the elimination of CECs and bacteria (Villegas-guzman et al., 2017).

1.2.4 Natural products from Colombian Amazonia as potential iron complexing agents

Some abundant native products from the Amazonian region of Colombia contain organic acids and polyphenols (Cantergiani, Andlauer, Heeger, & Kosin, 2016; Genaro-Mattos, Maurício, Rettori, Alonso, & Hermes-Lima, 2015; Geremu, Tola, & Sualeh, 2016; Mussatto, 2015), which could act as iron complexing agents. Therefore, in this thesis three typical products of this region were considered: copoazu (*Theobroma gramdiflorum*), canangucha (*Maurita Flexuosa*) and husk coffee (*coffea arabica*).

Copoazu and canangucha are typical fruits of the Amazon region (Contreras-Calderón, Calderón-Jaimes, Guerra-Hernández, & García-Villanova, 2011; Galeano, 2011; Koolen, da Silva, Gozzo, de Souza, & de Souza, 2013; Nobre et al., 2018; Rogez et al., 2004), these have been used in the food industry in Brazil and Peru. In the Colombian Amazon region, copoazu and canangucha are part of the nascent agro-industry. Likewise, coffee is an emblem of the national economy of Colombia, it is also cultivated and marketed in Caquetá.

In Florencia-Caquetá, copoazu is widely used in the production of candies. For this purpose, part of the pulp is used and the rest is discarded. Copoazu pulp contains polyphenols and organic acids in concentrations such as those listed in the Table 1. The concentrations vary according to the procedure for obtaining the extract (Tauchen et al., 2016).

Table 1. Concentration of total phenols and organic acids present in diverse copoazu extracts.

Type of extraction	Total phenols	Citric Acid (mg 100 g-1 DW)	Malic Acid (mg 100 g^{-1} DW)	Ascorbic acid (mg 100 g^{-1} FW)	Reference
Enzymatic extraction from ripe fruits	410.00±3.00 (mg GAE 100 g^{-1} of DW)	71.79±12.03	16.04±3.03	---	(Díaz et al., 2017)
Methanolic extraction from ripe pulp	40.3±0.57 (mg of GAEs 100 g^{-1} of FW)	---	---	7.05±0.00	(Contreras-Calderón et al., 2011)
Juice pulp from ripe fruit	226±26 (µg tannic acid g^{-1} of DW	176±3	48±2	---	(Pérez-mora, Jorrin-novo, & Melgarejo, 2017)
Ethanolic extraction from ripe pulp	163.0±8.1 (mg GAE g^{-1} extract)	---	---	---	(Tauchen et al., 2016)

- --- Not measured; ND Not detected; DW Dry weight; FW Fresh weight

In the case of canangucha, it is also very common part of food industry in the Colombian Amazon. According to its characterization, canangucha contains phenolic compounds as caffeic acid, chlorogenic acid, quercetin, kaempferol, miricetin, narigenin, vixetin, scoparin, rutin, cyanidin-3-rutinoside, cyanidin-3-glucoside (Koolen et al., 2013; Nobre et al., 2018). Table 2 shows reported concentrations of polyphenols and ascorbic acid in Canangucha fruit.

Table 2. Concentration of total phenols and ascorbic acid present in extract from pulp of canangucha.

Type of extraction	Total phenols	Ascorbic acid (mg 100 g^{-1} FW)	Reference
Extraction with hexane from green fruit	378.07±3.12 (mg GAEq 100 g^{-1})	---	(Koolen et al., 2013)
Methanolic extraction from green pulp	281±2.25 (mg of GAEs 100 g^{-1} of FW)	1.55±0.00	(Contreras-Calderón et al., 2011)
Ethanolic extraction from green pulp	461.5 ±32.5 (mg GAE g^{-1} extract)	---	(Tauchen et al., 2016)

---: Not measured; DW: Dry weight; FW: Fresh weight.

Regarding the coffee husk, it is important to remember that coffee is the most important food commodities worldwide. The industrial coffee process (wet or dry) generates waste products such as coffee pulp and peel, which represent 29% and 12%, respectively, of the whole coffee cherry (dry weight) (Mourtzinos & Goula, 2018). In Colombia, these wastes are highly available and slowly degraded; thus, generating environmental problems. Coffee contains flavonoids, chlorogenic acid, caffeine, tannins, sugar, proteins and lipids (Heeger, Kosińska-Cagnazzo, Cantergiani, & Andlauer, 2017), in addition to four classes of polyphenols (flavan-3-ols, hydroxycinnamic acids, flavanols and anthocyanidins) (Esquivel & Jiménez, 2012). It must be indicated that coffee husk and coffee pulp contain important polyphenols such as chlorogenic acid.

1.2.5 Combination of biological treatments with advanced oxidation processes

A useful option, which has been applied to treat diverse wastewaters, is the combination of biological treatments with AOPs. In some researches it have been evaluated the performance of combinations of this type, where biological treatment is the first stage (Merayo, Hermosilla, Blanco, Cortijo, & Blanco, 2013; Nousheen et al., 2014; Oller, Malato, & Sánchez-Pérez, 2011; Trapido et al., 2017; Vidal, Huiliñir, & Salazar, 2016). It is recognized that biological processes partially remove CECs and thus, the AOPs can complete the elimination of that recalcitrant pollutants.

Literature also presents combinations where the AOP is the first stage followed by the biological treatment to deal with real or simulated wastewater, demonstrating applicability of such combination to eliminate both organic matter and persistent compounds. Indeed, combinations of SPF with an anaerobic process to treat coffee pulping wastewater (Kondo et al., 2010), SPF and an aerobic systems to treat pesticides (Ballesteros-Martin, Sanchez-Perez, Casas-López, Oller, & Malato, 2009), photo-Fenton combined with an aerobic treatment to eliminate azo dyes (Jonstrup et al., 2011), among others, are well documented. Therefore, in the context of Florencia-Caquetá, it is possible to think in a combination of processes (as biological-AOP or AOP-biological) as a strategy to treat their MWW.

1.3 Objectives and justification

1.3.1 General objective

To develop a treatment system for the remediation of MWW from Florencia-Caquetá at pilot scale combining a photo-Fenton process at natural pH and a biological treatment.

1.3.2 Specific objectives

1. To determine the global characteristics and representative CECs present in a typical discharge site of MWW from Florencia-Caquetá.

2. To evaluate the performance of aerobic and anaerobic systems to reach both the elimination of CECs and organic matter mineralization of MWW from Florencia-Caquetá.

3. To study the performance of solar photo-Fenton (SPF) process at near neutral pH improved by the presence of amazon fruits extracts for degrading CECs in MWW from Florencia-Caquetá.

4. To assess the elimination of CECs and organic matter mineralization by combination of biological systems (aerobic or anaerobic) with SPF at near neutral pH at lab-scale to treat MWW from Florencia-Caquetá.

5. To develop a system combining a biological step and SPF at near neutral pH for the treatment of MWW from Florencia-Caquetá at pilot-scale.

1.3.3 Justification

This doctoral thesis is justified on the following points:

i) In the Colombian Amazon region, treatments capable of removing both biodegradable components and CECs present in the MWW are urgently needed. Thus, in this doctoral thesis a treatment system for MWW at pilot-scale is proposed. The treatment proposal is framed in the socio-economic conditions of the city and with a sustainable concept where the energy, raw material and requirements of land area are accomplished. Also, the treatment system involves generation of products with a possible economic value such as biogas (methane), fertilizer (sludges) and water for reuse.

ii) Use of autochthonous natural products and renewable resources to improve the performance of treatment system. According to problem statement, it is necessary to implement a sustainable treatment system that allows high efficiency, low energetic requirements and that takes advantage of local resources and conditions. Herein, it is explored the incorporation of renewable and natural resources available in Caquetá to the treatment system. Renewable resources such as solar radiation (which is abundant, free and useable as a direct or indirect input for the SPF) and natural products from agro-industrial wastes (as enhancers of SPF performance) are considered.

iii) Evaluation of combination of SPF with an anaerobic treatment (such combination is little usual). Florencia is located a tropical region with temperature between 23°C and 35°C for all year and high relativity humidity (up to 90%). These climatic conditions can favor methanogenic bacteria growth and anaerobic digestion. Soil characteristics from Florencia are inappropriate for large natural systems such as ponds or wetlands, which suggests the use of treatments with lower area requirements.

1.4 Thesis focus and key contributions

The research activity of this doctoral thesis was focused the development of a combination of biological processes (aerobic and anaerobic) with solar photo-Fenton at near neutral pH) for MWW treatment at pilot-scale under uncontrolled conditions in Florencia-Caquetá. Then, the contributions of this research can be summarized as follows:

i. A First approach to the occurrence of pharmaceuticals in raw MWW from Florencia-Caquetá. This is a primary indicator of pollution of water environment of the region.

ii. A new green solar photo-Fenton process at natural pH promoted by Amazonian natural products as iron complexing agents. Fruit extracts that contained organic acids and polyphenols were employed. This opens future possibilities to evaluate natural products wastes of agroindustry from Amazonian region as SPF enhancers.

iii. A proposal to use anaerobic treatment in combination with SPF for the elimination of CECs and mineralization of organic matter present in MWW, in order to reduce operation and maintenance costs and to generate products as fertilizer with economy value and biogas with energetic value.

iv. A novel strategy to treat MWW by combination of an anaerobic biological configuration with SPF at pilot-scale. This combination consisted of a UASB reactor and a SPF system (by using a CPC reactor) at near neutral pH improved with an Amazonian fruit extract.

1.5 Thesis outline

The results of this doctoral thesis are presented as follows:

In Chapter 2 is shown the occurrence of 38 pharmaceuticals in MWW from Florencia-Caquetá. Likewise, global characterizations of MWW are also showed.

In Chapter 3 is sketched an evaluation of performance of both aerobic and anaerobic biological systems at lab scale for the removal of four representative pharmaceuticals (selected from Chapter 2) and organic matter present in MWW from Florencia.

In Chapter 4 is analyzed the application of solar photo-Fenton process for treating the representative pollutants at lab-scale. Also, the improvement of SPF performance by Amazonian fruit extracts is presented.

In Chapter 5 is described the two strategies of processes combination at laboratory scale: 1) biological (aerobic or anaerobic) treatment as the first stage and SPF as the subsequent process; 2) SPF followed by the biological (aerobic or anaerobic) treatment.

In Chapter 6, it is finally depicted the combination of the SPF process (using a CPC reactor) and an anaerobic treatment (using a UASB reactor) at pilot scale to deal the pharmaceuticals and organic matter present in MWW from Florencia- Caquetá.

References

Alvarino, T., Suarez, S., Lema, J. M., & Omil, F. (2014). Understanding the removal mechanisms of PPCPs and the influence of main technological parameters in anaerobic UASB and aerobic CAS reactors. *Journal of Hazardous Materials*, *278*, 506–513. https://doi.org/10.1016/j.jhazmat.2014.06.031

Armstrong, D. A., Huie, R. E., Lymar, S., Koppenol, W. H., Merényi, G., Neta, P., … Wardman, P. (2013). Standard electrode potentials involving radicals in aqueous solution: inorganic radicals. *Bio Inorganic Reaction Mechanisms*, *9*(1–4), 59–61. https://doi.org/10.1515/irm-2013-0005

Aziz, A., Basheer, F., Sengar, A., Irfanullah, Khan, S. U., & Farooqi, I. H. (2019). Biological wastewater treatment (anaerobic-aerobic) technologies for safe discharge of treated slaughterhouse and meat processing wastewater. *Science of the Total Environment*, *686*, 681–708. https://doi.org/10.1016/j.scitotenv.2019.05.295

Ballesteros-Martin, M. ., Sanchez-Perez, J. A., Casas-López, J. L., Oller, I., & Malato, S. (2009). Degradation of a four-pesticide mixture by combined photo-Fenton and biological oxidation. *Water Research*, *43*, 653–660. https://doi.org/10.1016/j.watres.2008.11.020

Bandala, V. E. E. R., Bautista, P., Mohedano, A. F., Casas, J. A., Zazo, J. A., Rodriguez, J. J., … Wang, Y. (2010). Degradation of fifteen emerging contaminants at microg L(-1) initial concentrations by mild solar photo-Fenton in MWTP effluents. *Water Research*, *44*(2), 545–554. https://doi.org/10.1016/j.watres.2009.09.059

Bandara, W. M. K. R. T. W., Kindaichi, T., Satoh, H., Sasakawa, M., Nakahara, Y., Takahashi, M., & Okabe, S. (2012). Anaerobic treatment of municipal wastewater at ambient temperature: Analysis of archaeal community structure and recovery of dissolved methane. *Water Research*, *46*(17), 5756–5764. https://doi.org/10.1016/j.watres.2012.07.061

Bhatti, Z. A., Maqbool, F., Malik, A. H., & Mehmood, Q. (2014). UASB reactor startup for the treatment of municipal wastewater followed by advanced oxidation process. *Brazilian Journal of Chemical Engineering*, *31*(3), 715–726. https://doi.org/10.1590/0104-6632.20140313s00002786

Botero-Coy, A. M., Martínez-Pachón, D., Boix, C., Rincón, R. J., Castillo, N., Arias-Marín, L. P., … Hernández, F. (2018). An investigation into the occurrence and removal of pharmaceuticals in Colombian wastewater. *Science of the Total Environment*, *642*, 842–853. https://doi.org/10.1016/j.scitotenv.2018.06.088

Bouki, C., Venieri, D., & Diamadopoulos, E. (2013). Detection and fate of antibiotic resistant bacteria in wastewater treatment plants: a review. *Ecotoxicology and Environmental Safety*, *91*, 1–9. https://doi.org/10.1016/j.ecoenv.2013.01.016

Bueno, M. J. M., Gomez, M. J., Herrera, S., Hernando, M. D., Agüera, A., & Fernández-Alba, A. R. (2012). Occurrence and persistence of organic emerging contaminants and priority pollutants in five sewage treatment plants of Spain: Two years pilot survey monitoring. *Environmental Pollution*, *164*, 267–273. https://doi.org/10.1016/j.envpol.2012.01.038

Cantergiani, E., Andlauer, W., Heeger, A., & Kosin, A. (2016). Bioactives of coffee cherry pulp and its utilisation for production of Cascara beverage. https://doi.org/10.1016/j.foodchem.2016.11.067

Chen, J., & Browne, W. R. (2018). Photochemistry of iron complexes. *Coordination Chemistry Reviews*, *374*, 15–35. https://doi.org/10.1016/j.ccr.2018.06.008

Chen, W. H., Wong, Y. T., Huang, T. H., Chen, W. H., & Lin, J. G. (2019). Removals of pharmaceuticals in municipal wastewater using a staged anaerobic fluidized membrane bioreactor. *International Biodeterioration and Biodegradation*, *140*(January), 29–36. https://doi.org/10.1016/j.ibiod.2019.03.008

Chong, M. N., Sharma, A. K., Burn, S., & Saint, C. P. (2012). Feasibility study on the application of advanced oxidation technologies for decentralised wastewater treatment. *Journal of Cleaner Production*, *35*, 230–238. https://doi.org/10.1016/j.jclepro.2012.06.003

Clarizia, L., Russo, D., Somma, I. Di, Marotta, R., & Andreozzi, R. (2017). Homogeneous photo-Fenton processes at near neutral pH : A review. *Applied Catalysis B, Environmental*, *209*, 358–371. https://doi.org/10.1016/j.apcatb.2017.03.011

Contreras-Calderón, J., Calderón-Jaimes, L., Guerra-Hernández, E., & García-Villanova, B. (2011). Antioxidant capacity, phenolic content and vitamin C in pulp, peel and seed from 24 exotic fruits from Colombia. *Food Research International*, *44*(7), 2047–2053. https://doi.org/10.1016/j.foodres.2010.11.003

De la Cruz, N., Giménez, J., Esplugas, S., Grandjean, D., De Alencastro, L. F., & Pulgarín, C. (2012). Degradation of 32 emergent contaminants by UV and neutral photo-fenton in domestic wastewater effluent previously treated by activated sludge. *Water Research*, *46*(6), 1947–1957.

https://doi.org/10.1016/j.watres.2012.01.014

Derlon, N., Wagner, J., da Costa, R. H. R., & Morgenroth, E. (2016). Formation of aerobic granules for the treatment of real and low-strength municipal wastewater using a sequencing batch reactor operated at constant volume. *Water Research*, *105*, 341–350. https://doi.org/10.1016/j.watres.2016.09.007

Díaz, R. O. S., Carrillo, M., Hernandez, M. S., Gutierres, R. H., Lares, M., & Fernandez-Trujillo, J. P. (2017). Development of a microencapsulated Amazonic natural ingredient with potential interest as a functional product. *Acta Hortic*, *1118*, 123–128. https://doi.org/10.17660/ActaHortic.2017.1178.22

Esquivel, P., & Jiménez, V. M. (2012). Functional properties of coffee and coffee by-products. *Food Research International*, *46*(2), 488–495. https://doi.org/10.1016/j.foodres.2011.05.028

European Cooperation in Science and Thecnology. (2017). *Understanding the contribution of biological processes to antibiotic resistance spread into the environment (Report of WG4)*.

Galeano, P. L. (2011, December). Actividad antioxidante y contenido de compuestos fenólicos de diferentes clones de copoazú (Theobroma grandiflorum). *Momentos de Ciencia*, *8*(2), 118–125.

Genaro-Mattos, T. C., Maurício, Â. Q., Rettori, D., Alonso, A., & Hermes-Lima, M. (2015). Antioxidant activity of Caffeic acid against iron-induced free radical generation-A chemical approach. *PLoS ONE*, *10*(6), 1–12. https://doi.org/10.1371/journal.pone.0129963

Gerba, C. P., & Pepper, I. L. (2014). *Municipal Wastewater Treatment*. *Environmental Microbiology: Third Edition* (3rd ed.). Elsevier Inc. https://doi.org/10.1016/B978-0-12-394626-3.00025-9

Geremu, M., Tola, Y. B., & Sualeh, A. (2016). Extraction and determination of total polyphenols and antioxidant capacity of red coffee (Coffea arabica L .) pulp of wet processing plants. *Chemical and Biological Technologies in Agriculture*, 1–6. https://doi.org/10.1186/s40538-016-0077-1

Giannakis, S., Franco, A., Vives, G., & Grandjean, D. (2015). Effect of advanced oxidation processes on the micropollutants and the ef fl uent organic matter contained in municipal wastewater previously treated by three different secondary methods. *Water Research*, *84*, 295–306. https://doi.org/10.1016/j.watres.2015.07.030

Heeger, A., Kosińska-Cagnazzo, A., Cantergiani, E., & Andlauer, W. (2017). Bioactives of coffee cherry pulp and its utilisation for production of Cascara beverage. *Food Chemistry*, *221*, 969–975. https://doi.org/10.1016/j.foodchem.2016.11.067

Huang, Y., Guo, J., Yan, P., Gong, H., & Fang, F. (2019). Sorption-desorption behavior of sulfamethoxazole, carbamazepine, bisphenol A and 17A-

ethinylestradiol in sewage sludge. *Journal of Hazardous Materials*, *368*(January), 739–745. https://doi.org/10.1016/j.jhazmat.2019.01.063

Jonstrup, M., Punzi, M., Mattiasson, B., Serra, A., Brillas, E., Domènech, X., … Li Puma, G. (2011). Comparison of anaerobic pre-treatment and aerobic post-treatment coupled to photo-Fenton oxidation for degradation of azo dyes. *Applied Catalysis B: Environmental*, *224*(January), 761–771. https://doi.org/10.1016/j.jece.2018.11.015

Klamerth, N., Malato, S., Agüera, A., & Fernández-Alba, A. (2013). Photo-Fenton and modified photo-Fenton at neutral pH for the treatment of emerging contaminants in wastewater treatment plant effluents: A comparison. *Water Research*, *47*(2), 833–840. https://doi.org/10.1016/j.watres.2012.11.008

Klamerth, N., Malato, S., Agüera, A., Fernandez-Alba, A., & Mailhot, G. (2012). Treatment of Municipal Wastewater Treatment Plant Effluents with Modified Photo-Fenton As a Tertiary Treatment for the Degradation of Micro Pollutants and Disinfection. *Environmental Science & Technology*, *46*, 2885–2892. https://doi.org/10.1021/es204112d

Klamerth, N., Malato, S., Maldonado, M. I., Agüera, a., & Fernández-Alba, a. (2011). Modified photo-Fenton for degradation of emerging contaminants in municipal wastewater effluents. *Catalysis Today*, *161*(1), 241–246. https://doi.org/10.1016/j.cattod.2010.10.074

Klamerth, N., Rizzo, L., Malato, S., Maldonado, M. I., Agüera, A., & Fernández-Alba, A. R. (2010). Degradation of fifteen emerging contaminants at microg L(-1) initial concentrations by mild solar photo-Fenton in MWTP effluents. *Water Research*, *44*(2), 545–554. https://doi.org/10.1016/j.watres.2009.09.059

Kondo, M. M., Leite, K. U. C. G., Silva, M. R. A., & Reis, A. D. P. (2010). Fenton and Photo-Fenton Processes Coupled to UASB to Treat Coffee Pulping Wastewater. *Separation Science and Technology*, *45:11*, 1506–1511. https://doi.org/10.1080/01496395.2010.487451

Koolen, H. H. F., da Silva, F. M. A., Gozzo, F. C., de Souza, A. Q. L., & de Souza, A. D. L. (2013). Antioxidant, antimicrobial activities and characterization of phenolic compounds from buriti (Mauritia flexuosa L. f.) by UPLC-ESI-MS/MS. *Food Research International*, *51*(2), 467–473. https://doi.org/10.1016/j.foodres.2013.01.039

Kositzi, M., Poulios, I., Malato, S., Caceres, J., & Campos, A. (2004). Solar photocatalytic treatment of synthetic municipal wastewater. *Water Research*, *38*(5), 1147–1154. https://doi.org/10.1016/j.watres.2003.11.024

Krzeminski, P., Concetta, M., Karaolia, P., Langenhoff, A., Almeida, C. M. R., Felis, E., … Fatta-kassinos, D. (2019). Performance of secondary wastewater treatment methods for the removal of contaminants of emerging concern implicated in crop uptake and antibiotic resistance spread : A review. *Science of the Total Environment*, *648*, 1052–1081.

https://doi.org/10.1016/j.scitotenv.2018.08.130

Lazcano-Carreño, C. (2016). *Biotecnología ambiental de aguas y aguas residuales*. (ECOE ediciones, Ed.) (Segunda ed). Bogotá: Universidad Nacional Mayor de San Marcos.

Liu, G., Zheng, S., Xing, X., Li, Y., Yin, D., Ding, Y., & Pang, W. (2010). Fe(III)-oxalate complexes mediated photolysis of aqueous alkylphenol ethoxylates under simulated sunlight conditions. *Chemosphere*, *78*(4), 402–408. https://doi.org/10.1016/j.chemosphere.2009.11.002

Manrique-Losada, L., & Pelaez Rodriguez, M. (2010). Evaluación de la calidad del agua de la quebrada La Perdiz en el área urbana de Florencia (Caquetá, Colombia). *Momentos de Ciencia*, *7*(2), 118–126.

Martínez-Hernández, V., Meffe, R., Herrera López, S., & de Bustamante, I. (2016). The role of sorption and biodegradation in the removal of acetaminophen, carbamazepine, caffeine, naproxen and sulfamethoxazole during soil contact: A kinetics study. *Science of the Total Environment*, *559*, 232–241. https://doi.org/10.1016/j.scitotenv.2016.03.131

Méndez-Arriaga, F., Torres-Palma, R. A., Pétrier, C., Esplugas, S., Gimenez, J., & Pulgarin, C. (2009). Mineralization enhancement of a recalcitrant pharmaceutical pollutant in water by advanced oxidation hybrid processes. *Water Research*, *43*(16), 3984–3991. https://doi.org/10.1016/j.watres.2009.06.059

Mendonca, S. R. (2001). *Sistemas de lagunas de estabilización*. (R. Pertuz Molina, Ed.) (1st ed.). Mc Graw Hill.

Merayo, N., Hermosilla, D., Blanco, L., Cortijo, L., & Blanco, Á. (2013). Assessing the application of advanced oxidation processes, and their combination with biological treatment, to effluents from pulp and paper industry. *Journal of Hazardous Materials*, *262*, 420–427. https://doi.org/10.1016/j.jhazmat.2013.09.005

Miklos, D. B., Remy, C., Jekel, M., Linden, K. G., & Hübner, U. (2018). Evaluation of advanced oxidation processes for water and wastewater treatment- A critical review. *Water Research*, *139*, 118–131. https://doi.org/10.1016/j.watres.2018.03.042

Miralles-Cuevas, S., Oller, I., Sánchez Pérez, J. A., & Malato, S. (2014). Removal of pharmaceuticals from MWTP effluent by nanofiltration and solar photo-Fenton using two different iron complexes at neutral pH. *Water Research*, *64*, 23–31. https://doi.org/10.1016/j.watres.2014.06.032

Moreira, F. C., Soler, J., Alpendurada, M. F., Boaventura, R. A. R., Brillas, E., & Vilar, V. J. P. (2016). Tertiary treatment of a municipal wastewater toward pharmaceuticals removal by chemical and electrochemical advanced oxidation processes. *Water Research*, *105*, 251–263. https://doi.org/10.1016/j.watres.2016.08.036

Mourtzinos, I., & Goula, A. (2018). *Polyphenols in Agricultural Byproducts and Food Waste*. *Polyphenols in Plants* (2nd ed.). Elsevier Inc. https://doi.org/10.1016/b978-0-12-813768-0.00002-5

Mussatto, S. I. (2015). *Generating Biomedical Polyphenolic Compounds from Spent Coffee or Silverskin*. *Coffee in Health and Disease Prevention*. Elsevier Inc. https://doi.org/10.1016/B978-0-12-409517-5.00011-5

Nobre, C. B., Sousa, E. O., Camilo, C. J., Machado, J. F., Silva, J. M. F. L., Filho, J. R., … Costa, J. G. M. (2018). Antioxidative effect and phytochemical profile of natural products from the fruits of "babaçu" (Orbignia speciose) and "buriti" (Mauritia flexuosa). *Food and Chemical Toxicology*, *121*, 423–429. https://doi.org/10.1016/j.fct.2018.08.068

Nogueira, A. A., Souza, B. M., Dezotti, M. W. C., Boaventura, R. A. R., & Vilar, V. J. P. (2017). Ferrioxalate complexes as strategy to drive a photo-Fenton reaction at mild pH conditions: A case study on levofloxacin oxidation. *Journal of Photochemistry and Photobiology A: Chemistry*, *345*, 109–123. https://doi.org/10.1016/j.jphotochem.2017.05.020

Nousheen, R., Batool, A., Rehman, M. S. U., Ghufran, M. A., Hayat, M. T., & Mahmood, T. (2014). Fenton-biological coupled biochemical oxidation of mixed wastewater for color and COD reduction. *Journal of the Taiwan Institute of Chemical Engineers*, *45*(4), 1661–1665. https://doi.org/10.1016/j.jtice.2013.12.008

Novelo, R. M., Velázquez, R. M., René, E., Borges, C., Torres Lozada, P., Rodríguez, J., … Ternes, T. A. (2016). Removal of pharmaceuticals and fragrances in biological wastewater treatment. *Water Research*, *14*(14), 269. https://doi.org/10.1016/S1405-7743(13)72247-9

Oller, I., Malato, S., & Sánchez-Pérez, J. A. (2011). Combination of Advanced Oxidation Processes and biological treatments for wastewater decontamination: A review. *The Science of the Total Environment*, *409*(20), 4141–4166. https://doi.org/10.1016/j.scitotenv.2010.08.061

Orozco-Gaviria, C. A., Triviño-Cabrera, C. C., & Manrique-Losada, L. (2014). Arranque de un reactor UASB para el tratamiento de aguas residuales domésticas en condiciones andino amazónicas. *Revista Facultad de Ciencias Básicas*, *10*(2), 170–185.

Padrón-Páez, J. I., Almaraz, S. D. L., & Román-Martínez, A. (2016). *Design of sustainable municipal wastewater treatment plants*. *Computer Aided Chemical Engineering* (Vol. 38). Elsevier Masson SAS. https://doi.org/10.1016/B978-0-444-63428-3.50256-3

Papoutsakis, S., Miralles-Cuevas, S., Oller, I., Garcia Sanchez, J. L., Pulgarin, C., & Malato, S. (2015). Microcontaminant degradation in municipal wastewater treatment plant secondary effluent by EDDS assisted photo-Fenton at near-neutral pH: An experimental design approach. *Catalysis Today*, *5*.

https://doi.org/10.1016/j.cattod.2015.02.005

Papoutsakis, S., Pulgarin, C., Oller, I., Sánchez-Moreno, R., & Malato, S. (2016). Enhancement of the Fenton and photo-Fenton processes by components found in wastewater from the industrial processing of natural products: The possibilities of cork boiling wastewater reuse. *Chemical Engineering Journal*, *304*, 890–896. https://doi.org/10.1016/j.cej.2016.07.021

Pepper, I. L., & Gerba, C. P. (2015). Municipal Wastewater treatment. In *Environmental Microbiology* (3rd ed., pp. 583–606). Elsevier B.V.

Pérez-Mora, W., Jorrin-Novo, J. V, & Melgarejo, L. M. (2017). Substantial equivalence analysis in fruits from three Theobroma species through chemical composition and protein profiling. *Food Chemistry*. https://doi.org/10.1016/j.foodchem.2017.07.128

Pignatello, J. J., Oliveros, E., & Mackay, A. (2006). Advanced Oxidation Processes for Organic Contaminant Destruction Based on the Fenton Reaction and Related Chemistry. *Critical Reviews in Environmental Science and Technology*, *36*, 1–84. https://doi.org/10.1080/10643380500326564

Polesel, F., Lehnberg, K., Dott, W., Trapp, S., Thomas, K. V., & Plósz, B. G. (2015). Factors influencing sorption of ciprofloxacin onto activated sludge: Experimental assessment and modelling implications. *Chemosphere*, *119*, 105–111. https://doi.org/10.1016/j.chemosphere.2014.05.048

Pouran, S. R., Abdul-Aziz, A. R., & Wan-Daud, W. M. A. (2015). Review on the main advances in photo-Fenton oxidation system for recalcitrant wastewaters. *Journal of Industrial and Engineering Chemistry*, *21*, 53–69. https://doi.org/10.1016/j.jiec.2014.05.005

Ramalho, R. S. (2003). *Tratamiento de aguas residuales*. (Reverté, Ed.) (2nd Editio). Barcelona.

Rizzo, L., Malato, S., Antakyali, D., Beretsou, V. G., Đolić, M. B., Gernjak, W., … Fatta-Kassinos, D. (2019). Consolidated vs new advanced treatment methods for the removal of contaminants of emerging concern from urban wastewater. *Science of the Total Environment*, *655*, 986–1008. https://doi.org/10.1016/j.scitotenv.2018.11.265

Rogez, H., Buxant, R., Mignolet, E., Souza, J. N. S., Silva, E. M., & Larondelle, Y. (2004). Chemical composition of the pulp of three typical Amazonian fruits: Araça-boi (Eugenia stipitata), bacuri (Platonia insignis) and cupuaçu (Theobroma grandiflorum). *European Food Research and Technology*, *218*(4), 380–384. https://doi.org/10.1007/s00217-003-0853-6

Romero-Rojas, J. A. (2001). *Tratamiento de aguas residuales: Teoría y principios de diseño*. (J. A. Romero-Rojas, Ed.) (2nd Editio). Bogotá: Escuela Colombiana de Ingeniería.

Sathishkumar, P., Mangalaraja, R. V., & Anandan, S. (2016). Review on the recent

improvements in sonochemical and combined sonochemical oxidation processes - A powerful tool for destruction of environmental contaminants. *Renewable and Sustainable Energy Reviews*, *55*, 426–454. https://doi.org/10.1016/j.rser.2015.10.139

Serna-Galvis, E. A., Silva-Agredo, J., Botero-Coy, A. M., Moncayo-Lasso, A., Hernández, F., & Torres-Palma, R. A. (2019). Effective elimination of fifteen relevant pharmaceuticals in hospital wastewater from Colombia by combination of a biological system with a sonochemical process. *Science of the Total Environment*, *670*, 623–632. https://doi.org/10.1016/j.scitotenv.2019.03.153

SERVAF, S. A. E. S. P. (2013). *Planes de Saneamiento y Manejo de Vertimientos (PSMV) – Municipio de Florencia- 2013-2024. 2013*.

Show, K., & Lee, D. (2017). Anaerobic Treatment Versus Aerobic Treatment. In *Current Developments in Biotechnology and Bioengineering* (pp. 205–230). Elsevier B.V. https://doi.org/10.1016/B978-0-444-63665-2.00008-4

Sikosana, M. L., Sikhwivhilu, K., Moutloali, R., & Daniel, M. (2019). Municipal wastewater treatment technologies : A review. *Procedia Manufacturing*, *00*, 1–6. https://doi.org/10.1016/j.promfg.2019.06.051

Sirés, I., Brillas, E., Oturan, M. A., Rodrigo, M. A., & Panizza, M. (2014). Electrochemical advanced oxidation processes : today and tomorrow . A review. https://doi.org/10.1007/s11356-014-2783-1

Tauchen, J., Bortl, L., Huml, L., Miksatkova, P., Doskocil, I., Marsik, P., … Kokoska, L. (2016). Phenolic composition, antioxidant and anti-proliferative activities of edible and medicinal plants from the peruvian amazon. *Brazilian Journal of Pharmacognosy*, *26*(6), 728–737. https://doi.org/10.1016/j.bjp.2016.03.016

Torres-Lozada, P. (2012). Perspectivas del tratamiento anaerobio de aguas residuales domésticas en países en desarrollo. *Revista EIA*, *18*, 115–129.

Trapido, M., Tenno, T., Goi, A., Dulova, N., Kattel, E., Klauson, D., … Viisimaa, M. (2017). Bio-recalcitrant pollutants removal from wastewater with combination of the Fenton treatment and biological oxidation. *Journal of Water Process Engineering*, *16*, 277–282. https://doi.org/10.1016/j.jwpe.2017.02.007

Velásquez, R. (2014, January). Las superbacterias más resistentes ya están aquí y exigen cuidado. *El Colombiano*.

Vidal, J., Huiliñir, C., & Salazar, R. (2016). Removal of organic matter contained in slaughterhouse wastewater using a combination of anaerobic digestion and solar photoelectro-Fenton processes. *Electrochimica Acta*, *210*, 163–170. https://doi.org/10.1016/j.electacta.2016.05.064

Villegas- Guzman, P., Giannakis, S., Rtimi, S., Grandjean, D., Bensimon, M., de Alencastro, L. F., … Pulgarin, C. (2017). A green solar photo-Fenton process for the elimination of bacteria and micropollutants in municipal wastewater treatment using mineral iron and natural organic acids. *Applied Catalysis B:*

Environmental, *219*, 538–549. https://doi.org/10.1016/j.apcatb.2017.07.066

Villegas-Guzman, P., Giannakis, S., Torres-palma, R. A., & Pulgarin, C. (2017). Environmental Remarkable enhancement of bacterial inactivation in wastewater through promotion of solar photo-Fenton at near-neutral pH by natural organic acids. *Applied Catalysis B, Environmental*, *205*, 219–227. https://doi.org/10.1016/j.apcatb.2016.12.021

Virkutyte, J. (2017). Aerobic Treatment of Effluents From Pulp and Paper Industries. In *Current Developments in Biotechnology and Bioengineering* (pp. 103–130). Elsevier B.V. https://doi.org/10.1016/B978-0-444-63665-2.00004-7

Wang, Q., Huang, L., Quan, X., & Li Puma, G. (2019). Sequential anaerobic and electro-Fenton processes mediated by W and Mo oxides for degradation/mineralization of azo dye methyl orange in photo assisted microbial fuel cells. *Applied Catalysis B: Environmental*, *245*(January), 672–680. https://doi.org/10.1016/j.apcatb.2019.01.026

CHAPTER 2. APPROACH TOWARDS GLOBAL CHARACTERISTICS AND OCCURRENCE OF PHARMACEUTICALS IN MUNICIPAL WASTEWATER FROM FLORENCIA-CAQUETÁ COLOMBIA

2.1 Introduction

Municipal wastewater (MWW) is a complex mixture of substances that results from the sum of domestic, institutional, hospital, industrial wastewaters, among others. The content of these substances can be defined in terms of global characteristics that allow establishing the quality of the wastewater, the degree of contamination and the treatment that must be applied. Consequently, MWW can be disposed without causing a negative impact on ecosystems and, at the same time, complying with the required legal regulations (Romero-Rojas, 2001, 2009).

The global characteristics of municipal wastewater are mainly of three types: those that account for the content of organic matter, including chemical oxygen demand (COD), biochemical oxygen demand (BOD), total organic carbon (TOC), total suspended solids (TSS), total solids (TS), volatile organic compounds, fats, oils, detergents and so on. A second group that indicates the ionic composition such as alkalinity, sulfates (SO_4^{-2}), hardness, chlorides (Cl^-), conductivity and a third group that demonstrates the distribution of nutrients, such as nitrates (NO_3^-), ammonium (NH_4^+), total nitrogen (TN), organic nitrogen (NKT), orthophosphates (PO_4^{-2}) and total phosphorus (TP) (Lazcano-Carreño, 2016; Manrique-Losada & Pelaez-Rodriguez, 2013). These characteristics do not show which substances (present in MWW) that may generate an invisible impact on the ecosystem. Those substances,

known as CECs, include a wide variety of organic compounds such as phenols, pesticides, phenols among others.

Typically, CECs are present in all municipal wastewater (MWW) around the world. Developed countries have made efforts to determine the occurrence of CECs and the concentration intervals in which they are found (Bueno et al., 2012; Han-Tran, Urase, & Ta, 2014; Jing, Fusi, Chan, Capozzi, & Kjellerup, 2019; Matamoros, Arias, Nguyen, Salvadó, & Brix, 2012; Naidu, Andres, Espana, Liu, & Jit, 2016; Sodré, Locatelli, & Jardim, 2010). Likewise, the removal of these CECs has also been determined and evaluated demonstrating that conventional MWWTPs are not able to remove CECs from treated water.(De la Cruz, Giménez, Esplugas, Grandjean, de Alencastro, et al., 2012; De la Cruz, Giménez, Esplugas, Grandjean, De Alencastro, et al., 2012; Han-Tran et al., 2014; N. Klamerth et al., 2010; Moreira et al., 2016; Novelo et al., 2016; Papoutsakis et al., 2015; Rueda-Márquez, Sillanpää, Pocostales, Acevedo, & Manzano, 2015; Tran, Chen, Reinhard, Mao, & Gin, 2016). The most common CECs are pharmaceuticals and personal care products (PCPs) such as synthetic fragrances and musk's.

Unfortunately, in developing countries there is little information about the presence of CECs in both effluents of MWW and in water bodies (Han-Tran et al., 2014). Colombia is not the exception. Florencia does not have a MWWTP and its MWW are disposed over the bodies of water that cross the urban area of the city. Thus, before starting the tour on the evaluation of strategies for the treatment of MWW from Florencia, it is important to define the global characteristics and occurrence of CECs that allow contextualizing the degree of contamination, biodegradability and presence of persistent pollutants. In this chapter will be showed results about global characterization and occurrence of CECs.

2.2 Materials and methods

2.2.1 Sample collection

Raw MWW samples from Florencia (Caquetá) were taken from representative discharge located in “El Raicero” neighborhood (1° 36’ 53.20” N y 75° 36’ 21.04” W to 264 meters above sea level). Figure 1. shows location of sampling site. The sampling site was selected for the following reasons: it was easily accessible to obtain the samples and guaranteed wastewater constituted primarily by domestic wastewater (8 neighborhoods provide their domestic wastewater) and to a lesser extent hospital wastewater, commercial wastewater and even agro-industrial effluents. In addition, because the discharge is part of the combined sewerage network, rainwater also contributes.

All samples were obtained using a manual composite sampling which consisted of equal volume discrete sample aliquots collected every 1 h during 24 h into one container. The individual sample aliquots had to be preserved at the time of sample collection. The samples for global characterization was taken twice per year for 4 years (May and September 2016, April and September 2017, May and November 2018 and March and September to 2019). Three samples for pharmaceuticals quantification were obtained on august 29th 2016, September 30th 2016 and march 30th 2019. Sept-2016 and march-2019 samples were analyzed both for global characteristics and for pharmaceuticals quantification. The sampling months were defined considering both the rainy season (March - July) and the dry season (August - February) typical in Florencia.

.

2.2.2 Analytical methodology

- **Global characterization of MWW from Florencia**

Physical and Chemical characterization of MWW from Florencia was determined by analytical standardized methods (APHA, AWWA, & WEF, 2012). Table 3 shows analytical methods applied to this target.

The organic matter as total organic carbon (TOC) was monitored by combustion catalytic oxidation method using a TOC-L + ASI –L autosampler Shimadzu. It uses a potassium phthalate solution as calibration standard. Acidification and stripping before analysis were sometimes necessary to keep the solutions free of atmospheric CO_2. The injection volume was 50 µL. The analyzer TOC use non-dispersive infrared detection (NDIR) method, for determination of TC, IC and TOC = TC-IC. Detection limit to TC was 1 mg L^{-1} and to IC was 4 µg L^{-1}, carrier gas was high-purity air with supply pressure in 200±10 kPa. Carrier gas regulator was between 300-600 kPa and gas consumption was kept in 150 mL min^{-1} (230 to 250 mL min^{-1} during sparging).

The biodegradable and oxidizable organic matter present in Florencia MWW were evaluated considering the Biological Oxygen Demand (BOD) and Chemical Oxygen Demand (COD) respectively. The BOD was measured using a WTW Oxytop® IS 12 unit thermostated at 20 °C with the respirometric method (APHA et al., 2012). The COD was measured by the closed reflux method with digestion of sample in thermo-reactor Merck® and quantification in an spectrophotometer UV-Vis at 600 nm (APHA et al., 2012). The pH was directly measured using an OAKTON® pH-meter. Conductivity was determined by direct measurement using an OAKTON® conductimeter. Total phosphorus was determined by spectrophotometry, using ascorbic acid method after persulfate digestion. Total nitrogen was measured by converting all nitrogen forms to nitrate by alkaline persulfate oxidation and

subsequent analysis of nitrate by HCl method using a spectrophotometer (APHA et al., 2012).

Table 3. Analytical methods applied to global characterization of MWW from Florencia

Characteristic	Method	Reference
Nitrates (NO_3^-) (mg L^{-1})	HCl-UV	(APHA et al., 2012) 4500 – NO_3^-
Ammonia Nitrogen (NH_4^+), (mg L^{-1})	Nessler	HACH 8038
Total Nitrogen (TN), (mg L^{-1})	Persulfate oxidation	(APHA et al., 2012) 4500 –N
Orto-phosphates (PO_4^{-3}), (mg L^{-1})	Ascorbic acid	(APHA et al., 2012) 4500-P
Sulfates (SO_4^{-2}) , (mg L^{-1})	Titrimetric	(APHA et al., 2012)
Chlorides (Cl^-), (mg L^{-1})	Argentometric	(APHA et al., 2012)
Alcalinity (mg L^{-1})	Titrimetric	(APHA et al., 2012)
Hardness, (mg L^{-1})	Titrimetric	(APHA et al., 2012)
Conductivity (µS.cm^{-1})	Potentiometric	(APHA et al., 2012)
pH	Potentiometric	(APHA et al., 2012) 4500-pH
Total organic carbon (TOC)	Combustion-IR	(APHA et al., 2012)
Chemical oxygen demand (COD) (mg O_2 L^{-1})	Closed reflux	(APHA et al., 2012) 5220 C
Biochemical oxygen demand(BOD_5) (mg O_2 L^{-1})	Respirometric	(APHA et al., 2012) 5210 B
Total suspend solid (TSS) (mg L^{-1})	Gravimetric	(APHA et al., 2012) 2540 D
Total solid (TS) (mg L^{-1})	Gravimetric	(APHA et al., 2012) 2540B

- **Quantification of pharmaceuticals**

Pharmaceuticals were selected as target compounds in this work. This selection was made due to that those compounds are present commonly in domestic wastewater. They are release from homes because they are not metabolized in human body and they are excreted via urinary and enter to MWW. Several PhAcs (38 compounds) were detected and quantified. The target compounds corresponded to: 1 antiepileptic, 2 analgesics, 17 antibiotics, 1 antidepressant, 2 anticonvulsants, 1 bronchodilator, 1 lipid regulator, 2 anti-inflammatories, 1 antiulcer and 5 antihypertensive pharmaceuticals (Table 5).

Determination of pharmaceuticals was developed by a Waters Acquity UPLC system was interfaced in a triple quadrupole mass spectrometer Xevo TQS (Waters,Milford,MA,USA) equipped with an orthogonal Z-spray electrospray ionization interface (ESI) operated in positive mode. The mobile phase was A = H_2O, B = MeOH, both with 0.01% HCOOH and 1 mM NH_4Ac. The percentage of organic modifier (B) was changed as follows: 0 min, 5%; 7 min, 90%; 8 min, 90%; 8.1 min, 5%; and 10 min, 5%. The flow rate was 0.4 mL min^{-1}. The column was kept at 40 °C, and sample manager was maintained at 5 °C. The analysis run time was 10 min. All data were acquired and processed using Masslynx v 4.1 software.

The wastewater composite samples were unfrozen and filtered under a vacuum through 0.45-µm membrane filters (mixed cellulose ester, Whatman ME 25) (Whatman, Manchester, UK). Then, aliquots of these samples were collected in centrifuge tubes of 50 mL and transported in cool containers to Spain. Once in the laboratory, they were frozen at ≤−18 °C. Water samples were thawed at room temperature the same day of the analysis; an aliquot was transferred to a 2 mL Eppendorf and centrifuged at 12,000 rpm for 3 min. The procedure applied for sample analysis can be review in Botero et al (2018). Quantification of analytes was made using the quantification transition (Q) and external calibration with standards

in solvent. In those cases, in which the analyte ILIS was available (12 out of 20 compounds analyzed), relative areas were used for quantification. In this way, potential matrix effects were corrected, as shown by the acceptable QC recoveries obtained.

2.3 Results

Table 4 shows the results of global characterization of MWW with samples taken in eight different dates from 2016 – 2019 in rainy and dry season each year. It can be observed that MWW had fluctuant concentrations in all parameters. That behavior is according to weather conditions, since rainwater is part of the MWW and ends up being a way to dilute them. Likewise, from table 4, a slightly increase of concentrations of nitrates, ammonium nitrogen, total nitrogen, COD, sulfates and total suspended solids are observed from 2016 to 2019. That changes could be attributed to an increase in use to home products with inorganic forms of nitrogen and sulfates such as cleaning and beauty products. Additionally, an increase in tributaries to the sewerage network has also been recorded by the municipal Mayor's office (Municipal Mayor Office Florencia-Caquetá, 2019).

Typical composition of untreated domestic wastewater reported by Pepper et al., (2015) (Pepper & Gerba, 2015) can be associated with results in table 4 allowing classify the MWW from Florencia as low strength MWW (Pepper & Gerba, 2015; Ramalho, 2003; Romero-Rojas, 2001).

The BOD and COD concentrations shown in Table 4 are consistent with those reported in literature for typical MWW in Colombia (Romero-Rojas, 2001). A BOD_5/COD ratio of around 0.56 to 0.66 was found for the MWW from Florencia, which indicates a high biodegradability character of the effluent. Is worthy to indicate that a higher fraction of organic matter, suspended solids, nitrogen, phosphate and fecal coliforms, in the MWW is due to domestic WW from the city, which is residential

with low industrial development. So, human wastes as urine, feces, washing, bathing, and meal preparation, car washing, are the mainly contributors. It is important to clarify that rainwater carries the polluting load of roofs, streets and other surfaces where it circulates (Romero-Rojas, 2001).

The alkalinity range observed in this type of wastewater demonstrates a moderate alkalinity due mainly to calcium and magnesium bicarbonates. Thus, when an aerobic biological treatment is applied, the moderate alkalinity favors a nitrification process and when an anaerobic process is applied, the moderate alkalinity allows methanogenic oxidation and also favors the anaerobic digestion. The hardness present in MWW from Florencia, indicates moderately soft water and at that concentration the interaction with MWW anions is possible. About sulfates, at the concentrations reported in table 4, it is possible to project a slight influence on an anaerobic process. During anaerobic digestion, the medium is primarily reducing, and the sulfates are reduced to sulfides. In concentrations greater than 200 mg L^{-1}, sulfates would be detrimental to anaerobic oxidation (Crites & Tchobanoglous, 2000) because H_2S increases the acidity in the reaction system. However, at current concentrations, sulfates could complex and cause enzymatic inhibition (Show & Lee, 2017). In addition, during a photo-Fenton based process, it acts as a scavenger and competes for complexing if it has been added to the process (Boshir et al., 2017; Changotra, Rajput, & Dhir, 2019; Duarte, Maldonado-Hódar, & Madeira, 2013)

Concentration of chlorides was between 62 and 103 mg L^{-1} in that sampling site, much lower than reported by literature for low strength MWW (Pepper & Gerba, 2015; Romero-Rojas, 2001). Chlorides are common in MWW and it is known that they are not removed from wastewater by conventional treatments (Bandara et al., 2012; Pepper & Gerba, 2015). These ions do not generate problems in the performance of a biological treatment and only at concentrations above 15000 mg L^{-1} are considered toxic in metabolism. On the other hand, the presence of chlorides can influence the efficiency of the photo-Fenton process because this anion acts as an OH * scavenger, inhibiting the reaction of the latter with contaminants (Serna-Galvis, Silva-Agredo, Giraldo, Flórez-Acosta, & Torres-Palma, 2016).

According to the forms of nitrogen, the predominant specie is the organic nitrogen contributed mainly from domestic waste. Likewise, it is observed that ammonium is in high proportion with respect to nitrate content. This contrast can be due to the presence of fecal matter and urine from domestic waters where organic nitrogen oxidation has not yet occurred. Concentration of ammonium in MWW from Florencia is not a problem into aerobic treatment since only at concentrations above 1600 mg L^{-1} is considered biological oxidation inhibitor. About nitrates in MWW from Florencia, these nitrogen species are electron acceptors in anoxic environment, for this reason, can promote denitrification in anaerobic treatment. Average concentration of TP was according with the expected concentration for medium strength MWW (around 4 mg L^{-1}) reported in literature (Pepper & Gerba, 2015). To selection of a wastewater treatment, it is important to know that orthophosphates favor biological treatment as they are suitable for microbial metabolism. Regularly, organic phosphorus has secondary importance in domestic wastewater.

Table 5 presents a list of pharmaceuticals found in the three samples of MWW taken in the selected discharge named “El Raicero” neighborhood in different date (August 29, 2016, September 30, 2016 and March 29, 2019). According to Table 5, MWW from Florencia contained levels of several pharmaceuticals above 1 µg L^{-1}. To date, this is the first information about occurrence of pharmaceuticals in MWW from Florencia which means that there is no possibility to compare data. Nevertheless, is possible confirm that 19 pharmaceuticals found in MWW from Florencia are typically found in raw MWW from Bogotá and Medellín in Colombia according to Botero et al (Botero-Coy et al., 2018). Of course, these cities have a MWWTP, which removes part of the pharmaceuticals, reducing the concentration in which they are released on the bodies of water.

During the rainy season, the samples from 2016 year was taken. This fact caused a dilution of them. Contrary to those taken in 2019 during the dry period. Contrasting concentrations of pharmaceuticals in the rainy season and the dry season, for the majority of the compounds, there is a dramatic increase in their concentration when only wastewater makes up the MWW (without rainy water).

Likewise, pharmaceuticals such as clindamycin, irbesartan and tetracycline, exceeded the limit of quantification (LOQ) in the dry period sample. This tendency since the target pharmaceuticals are not only used in hospitals but also quite consumed commonly in households.

Table 4. Physicochemical characteristics of the MWW from Florencia (discharge of MWW at Raicero neighborhood) during 8 sampling (2016 – 2019)

Characteristic	May 2016	Oct. 2016	April 2017	Sept. 2017	May 2018	Nov. 2018	May 2019	Sept. 2019	Minimum Value	Maximum Value
NO_3^- (mg L^{-1})	4.62	10.25	5.33	11.17	8.45	14.38	7.89	13.45	4.62	14.38
NH_4^+, (mg L^{-1})	18.34	36.45	19.09	43.34	17.73	42.34	21.34	42.89	17.73	43.34
TN, (mg L^{-1})	140.32	205.67	135.25	187.35	132.56	200	124	210.33	124	210.31
PO_4^{-3}, (mg L^{-1})	1.78	2.87	1.46	3.21	2.06	3.16	1.65	2.85	1.46	3.21
TP, (mg L^{-1})	2.89	5.72	3.56	5.24	2.45	3.32	2.45	4.67	2.45	5.72
COD, (mg L^{-1})	320	520	290	478	277	578	256	580	256	580
BOD_5, (mg L^{-1})	154	285	135	277	128	278	126	302	126	302
TOC (mg L^{-1})	31	88.23	28	66.34	29	72.34	35	89.32	28	89.32
SO_4^{-2} , (mg L^{-1})	65.24	150.58	76.89	178.11	45.60	188.32	58.34	174.67	45.60	188.32
Cl^- (mg L^{-1})	75.45	103.34	62.05	87.34	68.34	90.77	82.54	98.91	62.05	103.34
Alkalinity	53.49	146.76	75.22	120.37	80.13	118.75	84.39	139.04	53.49	146.76

(mg L^{-1})										
Hardness, (mg L^{-1})	58.00	117	84.25	98.34	62	105	57.13	119	57.11	119
Conductivity (µS cm^{-1})	122	220	120	253	145	195	148	250	120	253
pH	6.45	6.75	6.52	6.75	6.54	6.56	6.47	6.61	6.45	6.75
ST (mg L^{-1})	156.59	205.41	140.23	240	128.56	258.78	186	250	128.56	258.78
SST (mg L^{-1})	67.40	120.32	87.34	100.07	76.47	135.86	54.12	147.67	54.12	147.67

The analgesic acetaminophen is presented the highest concentration in the three samples. Acetaminophen is the analgesic of mass use in Florencia and its concentration is due to high consume and consequently after being ingested this compound is excreted in the urine almost 60% (Ahmadzadeh & Dolatabadi, 2018; Bueno et al., 2012). Together with acetaminophen, antibiotics and other pharmaceuticals are absorbed only about 40%. However, the particular structural characteristics and functionality of each compound, generate different interaction during human metabolism and therefore different absorption and excretion rates. This result is according to reported by literature about high occurrence of acetaminophen in raw MWW from Spain, United Kingdom and Germany due to paracetamol is most popular non-opioid analgesic sold in these countries in the last years (Bueno et al., 2012).

In terms of antibiotics, the presence of azithromycin, metronidazole, trimethoprim, sulfamethoxazole, clarithromycin, clindamycin and ciprofloxacin and the presence of anti-inflammatories and analgesics such as diclofenac and naproxen were detected (Botero-Coy et al., 2018). Antibiotics with higher concentrations were azithromycin, metronidazole, trimethoprim, sulfamethoxazole demonstrating its high consumption in Florencia. This trend is similar to reported for MWW from Spain and Hanoi among others (Bueno et al., 2012; Han-Tran et al., 2014). Antibiotics as clarithromycin, clindamycin, erythromycin, lincomycin y tetracycline, are present in low concentrations, this might be due to the lower consumption of this compound compared to other human antibiotics. In lower concentration were found anti-hypertensive as losartan, irbesartan, valsartan y metoprolol and anticonvulsant as carbamazepine. An increment in concentration of anti-hypertensive and anticonvulsant in samples during dry season was observed, however, valsartan suffered a drastic increment. This fact could be attributed to differences in consumption rate between valsartan and the others three compounds.

Table 5. Concentrations of pharmaceuticals (µg L^{-1}) in raw municipal wastewater samples from "*El Raicero*" Florencia, Caquetá

Compound (µg L^{-1})	Family/Function	30/09/16	29/08/16	30/03/2019
Acetaminophen	Analgesic	20.22	12.54	262.52
Alprazolam	Antidepressant	ND	ND	ND
Atorvastatin	Lipid regulator	NM	NM	0.46
Azithromycin	Antibiotic	6.97	6.54	1.23
Carbamazepine	Anticonvulsant	0.012	0.004	1.86
Ciprofloxacin	Antibiotic	0.92	0.573	1.47
Clarithromycin	Antibiotic	0.015	0.027	0.22
Clindamycin	Antibiotic	ND	ND	0.21
Diclofenac	Anti-inflammatory	0.15	0.19	12.77
Doxycycline	Antibiotic	ND	ND	ND
Enalapril	Antihypertensive	NM	NM	0.23
Erythromycin	Antibiotic	0.11	0.009	0.41
Flumequine	Antibiotic	NM	NM	0.41
Furaltadone	Antibiotic	ND	ND	ND
Gabapentin	Antiepileptic	ND	ND	ND
Ioproimide	Contrast agent	NM	NM	0.43
Irbesartan	Antihypertensive	ND	ND	0.07
Levamisole	Anthelmintic	NM	NM	1.89
Lincomycin	Antibiotic	NM	NM	D
Lorazepam	Anxiolytic	ND	ND	ND
Losartan	Antihypertensive	0.49	0.67	1.29
Metoprolol	Antihypertensive	NM	NM	1.13

Metronidazole	Antibiotics	0.97	0.37	27.08
Naproxen	Anti-inflammatory	2.11	3.12	NM
Nalidixic acid	Antibiotic	ND	ND	ND
Norfloxacin	Antibiotic	0.49	0.33	1.29
Oxolinic acid	Antibiotic	NM	NM	2.58
Pantoprazole	Antiulcer	ND	ND	ND
Phenazone	Analgesic	ND	ND	ND
Primidone	Anticonvulsant	NM	NM	D
Roxithromycin	Antibiotic	ND	ND	ND
Salbutamol	Bronchodilator	NM	NM	0.28
Sulfadiazine	Anticonvulsant	NM	NM	0.28
Sulfamethoxazole	Antibiotic	0.28	0.81	6.37
Tetracycline	Antibiotic	ND	ND	0.32
Tramadol	Analgesic	NM	NM	0.20
Trimethoprim	Antibiotic	0.42	0.28	3.19
Valsartan	Anti-hypertensive	0.17	0.11	6.55
Venlafaxine	Anxiolytic	0.017	0.017	0.12

NM: Not measured
ND: Not detected
D: LOD (Limit of detection)

2.4 Conclusion of this chapter

The raw MWW of Florencia-Caquetá presented a high biodegradability (BOD/COD = 0.56 - 0.66) and the content of organic and inorganic matter makes it possible to assume that a biological treatment will make biotransformation of organic matter. Likewise, pharmaceuticals such as analgesics, antibiotics, anti-inflammatories and

anti-hypertensive among others were detected and quantified in raw MWW from Florencia, evidencing the high consumption of acetaminophen by the population, as well as antibiotics such as metronidazole, sulfamethoxazole and trimethoprim among others.

The fact that raw wastewater is directly discharged to surface waters (La Perdiz, La Sardina and Hacha Rivers) may suppose a risk for the aquatic environment, causing bacterial resistance, among other effects. Therefore, there is an urgent need to implement efficient treatments that are able of removing organic matter as well as to remove pharmaceuticals in MWW. The research about MWW from Florencia should be directed at the degradation of pharmaceuticals, selected in light of the data reported in this chapter and the literature (Botero-Coy et al., 2018), using advanced oxidation systems, such as photo-Fenton, photo-electro-Fenton which have demonstrated high removal percentages at the laboratory scale and under controlled conditions (see references chapter 3 and 4).

References

Ahmadzadeh, S., & Dolatabadi, M. (2018). Removal of acetaminophen from hospital wastewater using electro-Fenton process. *Environmental Earth Sciences*, 1–11. https://doi.org/10.1007/s12665-017-7203-7

APHA, AWWA, & WEF. (2012). *Standard Methods for the Examination of Water and Wastewater*. (E. W. Rice, R. B. Baird, A. D. Eaton, & L. S. Clesceri, Eds.) (22nd ed.). Washington D.C.

Bandara, W. M. K. R. T. W., Kindaichi, T., Satoh, H., Sasakawa, M., Nakahara, Y., Takahashi, M., & Okabe, S. (2012). Anaerobic treatment of municipal wastewater at ambient temperature: Analysis of archaeal community structure and recovery of dissolved methane. *Water Research*, *46*(17), 5756–5764. https://doi.org/10.1016/j.watres.2012.07.061

Boshir, M., Zhou, J. L., Hao, H., Guo, W., Thomaidis, N. S., & Xu, J. (2017). Progress in the biological and chemical treatment technologies for emerging contaminant removal from wastewater : A critical review. *Journal of Hazardous Materials*, *323*, 274–298. https://doi.org/10.1016/j.jhazmat.2016.04.045

Botero-Coy, A. M., Martínez-Pachón, D., Boix, C., Rincón, R. J., Castillo, N., Arias-Marín, L. P., … Hernández, F. (2018). An investigation into the occurrence and

removal of pharmaceuticals in Colombian wastewater. *Science of the Total Environment*, *642*, 842–853. https://doi.org/10.1016/j.scitotenv.2018.06.088

Bueno, M. J. M., Gomez, M. J., Herrera, S., Hernando, M. D., Agüera, A., & Fernández-Alba, A. R. (2012). Occurrence and persistence of organic emerging contaminants and priority pollutants in five sewage treatment plants of Spain: Two years pilot survey monitoring. *Environmental Pollution*, *164*, 267–273. https://doi.org/10.1016/j.envpol.2012.01.038

Changotra, R., Rajput, H., & Dhir, A. (2019). Treatment of real pharmaceutical wastewater using combined approach of Fenton applications and aerobic biological treatment. *Journal of Photochemistry and Photobiology A: Chemistry*, *376*(December 2018), 175–184. https://doi.org/10.1016/j.jphotochem.2019.02.029

Crites, R., & Tchobanoglous, G. (2000). *Sistemas de manejo de aguas residuales: para pequeños núcleos y descentralizados*. (E. Ariza H., Ed.) (First Edit). Mc Graw Hill.

De la Cruz, N., Giménez, J., Esplugas, S., Grandjean, D., de Alencastro, L. F., & Pulgarín, C. (2012). Degradation of 32 emergent contaminants by UV and neutral photo-fenton in domestic wastewater effluent previously treated by activated sludge. *Water Research*, *46*(6), 1947–1957. https://doi.org/10.1016/j.watres.2012.01.014

Duarte, F. M., Maldonado-Hódar, F. J., & Madeira, L. M. (2013). Influence of the iron precursor in the preparation of heterogeneous Fe/activated carbon Fenton-like catalysts. *Applied Catalysis A: General*, *458*, 39–47. https://doi.org/10.1016/j.apcata.2013.03.030

Han-Tran, N., Urase, T., & Ta, T. T. (2014). A Preliminary Study on the Occurrence of Pharmaceutically Active Compounds in Hospital Wastewater and Surface Water in Hanoi , Vietnam. *Clean - Soil Air Water*, *42*(3), 267–275. https://doi.org/10.1002/clen.201300021

Jing, R., Fusi, S., Chan, A., Capozzi, S., & Kjellerup, B. V. (2019). Distribution of polychlorinated biphenyls in effluent from a large municipal wastewater treatment plant: Potential for bioremediation? *Journal of Environmental Sciences (China)*, *78*(3), 42–52. https://doi.org/https://doi.org/10.1016/j.scitotenv.2018.06.088

Klamerth, N., Rizzo, L., Malato, S., Maldonado, M. I., Agüera, A., & Fernández-Alba, A. R. (2010). Degradation of fifteen emerging contaminants at µg L-1 initial concentrations by mild solar photo-Fenton in MWTP effluents. *Water Research*, *44*(2), 545–554. https://doi.org/10.1016/j.watres.2009.09.059

Lazcano-Carreño, C. (2016). *Biotecnología ambiental de aguas y aguas residuales*. (ECOE ediciones, Ed.) (Segunda ed). Bogotá: Universidad Nacional Mayor de San Marcos.

Manrique-Losada, L., & Pelaez-Rodriguez, M. (2013). *Manual de análisis de calidad*

de aguas en ecosistemas acuáticos andino amazónicos: Análisis físicos y químicos. (Universidad de la Amazonia, Ed.). Florencia-Caquetá Colombia.

Matamoros, V., Arias, C. A., Nguyen, L. X., Salvadó, V., & Brix, H. (2012). Occurrence and behavior of emerging contaminants in surface water and a restored wetland. *Chemosphere*, *88*(9), 1083–1089. https://doi.org/10.1016/j.chemosphere.2012.04.048

Moreira, F. C., Soler, J., Alpendurada, M. F., Boaventura, R. A. R., Brillas, E., & Vilar, V. J. P. (2016). Tertiary treatment of a municipal wastewater toward pharmaceuticals removal by chemical and electrochemical advanced oxidation processes. *Water Research*, *105*, 251–263. https://doi.org/10.1016/j.watres.2016.08.036

Naidu, R., Andres, V., Espana, A., Liu, Y., & Jit, J. (2016). Emerging contaminants in the environment : Risk-based analysis for better management. *Chemosphere*, *154*, 350–357. https://doi.org/10.1016/j.chemosphere.2016.03.068

Novelo, R. M., Velázquez, R. M., René, E., Borges, C., Torres Lozada, P., Rodríguez, J., … Ternes, T. A. (2016). Removal of pharmaceuticals and fragrances in biological wastewater treatment. *Water Research*, *14*(14), 269. https://doi.org/10.1016/S1405-7743(13)72247-9

Papoutsakis, S., Miralles-Cuevas, S., Oller, I., Garcia Sanchez, J. L., Pulgarin, C., & Malato, S. (2015). Microcontaminant degradation in municipal wastewater treatment plant secondary effluent by EDDS assisted photo-Fenton at near-neutral pH: An experimental design approach. *Catalysis Today*. https://doi.org/10.1016/j.cattod.2015.02.005

Pepper, I. L., & Gerba, C. P. (2015). Municipal Wastewater treatment. In *Environmental Microbiology* (3rd ed., pp. 583–606). Elsevier B.V.

Ramalho, R. S. (2003). *Tratamiento de aguas residuales*. (Reverté, Ed.) (2nd Editio). Barcelona.

Romero-Rojas, J. A. (2001). *Tratamiento de aguas residuales: Teoría y principios de diseño*. (J. A. Romero-Rojas, Ed.) (2nd Editio). Bogotá: Escuela Colombiana de Ingeniería.

Romero-Rojas, J. A. (2009). *Calidad del agua*. (Escuela Colombiana de Ingeniería, Ed.) (3rd Editio). Bogotá: Escuela Colombiana de Ingeniería.

Rueda-Márquez, J. J., Sillanpää, M., Pocostales, P., Acevedo, A., & Manzano, M. A. (2015). Post-treatment of biologically treated wastewater containing organic contaminants using a sequence of H2O2 based advanced oxidation processes: photolysis and catalytic wet oxidation. *Water Research*, *71*, 85–96. https://doi.org/10.1016/j.watres.2014.12.054

Serna-Galvis, E. A., Silva-Agredo, J., Giraldo, A. L., Flórez-Acosta, O. A., & Torres-Palma, R. A. (2016). Comparative study of the effect of pharmaceutical additives

on the elimination of antibiotic activity during the treatment of oxacillin in water by the photo-Fenton, TiO2-photocatalysis and electrochemical processes. *Science of the Total Environment*, *541*, 1431–1438. https://doi.org/10.1016/j.scitotenv.2015.10.029

Show, K., & Lee, D. (2017). Anaerobic Treatment Versus Aerobic Treatment. In *Current Developments in Biotechnology and Bioengineering* (pp. 205–230). Elsevier B.V. https://doi.org/10.1016/B978-0-444-63665-2.00008-4

Sodré, F., Locatelli, M. A., & Jardim, W. F. (2010). Occurrence of emerging contaminants in Brazilian drinking waters: A sewage-to-tap issue. *Water, Air, and Soil Pollution*, *206*(1–4), 57–67. https://doi.org/10.1007/s11270-009-0086-9

Tran, N. H., Chen, H., Reinhard, M., Mao, F., & Gin, K. Y. H. (2016). Occurrence and removal of multiple classes of antibiotics and antimicrobial agents in biological wastewater treatment processes. *Water Research*, *104*, 461–472. https://doi.org/10.1016/j.watres.2016.08.040

CHAPTER 3. TREATMENT OF WASTEWATERS FROM FLORENCIA BY TWO BIOLOGICAL PROCESSES AT LAB-SCALE

3.1 Introduction

In this chapter is presented the treatment of MWW from Florencia-Caquetá by two biological processes (an aerobic and other anaerobic) at lab-scale. Initially, the acclimatization of the sludges is considered. Then, variations of the relationship between the total volume of system and the volume of sludge were tested to define the proper sludge amount to reach a higher efficiency of bio-treatment action toward MWW loaded with four representative pharmaceuticals. Afterwards, the removal of macro-components (organic carbon and nitrogen species) from MWW was assessed. Finally, the biodegradation of the target pollutants (acetaminophen, sulfamethoxazole, carbamazepine and diclofenac) by both aerobic and anaerobic systems is discussed. The selected compounds represent different classes of pharmaceuticals with varied chemical structure and therefore it is expected to find differences in reactivity or mechanisms of elimination, during the biological process and the photo-Fenton solar process which will be applied in this thesis too, as mentioned before.

3.2 Materials and methods

3.2.1 Chemicals

Acetaminophen (ACT), sulfamethoxazole (SMX), carbamazepine (CBZ) and diclofenac (DCF) were supplied by Sigma-Aldrich®. Sodium bicarbonate from

Merck® was used. Chemical structures of four pharmaceuticals used in this thesis are shown in figure 3B. The selection of pharmaceuticals, was based considering the most representative pharmaceuticals according to the results of Chapter 2. ACT had a higher concentration in MWW from Florencia, the other three represent antibiotics, antihypertensive and anti-inflammatory pharmaceuticals, which are highly consumed in Florencia.

MWW was sampled from a specific discharge located in the neighborhood "El Raicero" selected in the Chapter 2 (global characterization shown in the Table 2.2). The raw MWW was spiked with four representative pharmaceuticals mentioned before, at a concentration of 0.0066 mM each one.

3.2.2 Bioreaction systems

*- Laboratory scale **aerobic** bioreactor*

Activated sludge for aerobic treatment was derived from raw MWW from Florencia-Caquetá and cultivated in a lab-scale Sequencing Batch Reactor (SBR). The SBR was filled with MWW plus an inoculum consisting of human feces and MWW sediment and after the sludge settling the MWW was draw. Every 2 days the MWW was replaced to maintain the concentration of organic matter and nutrients available for biomass growth. Constant stirring and aeration were provided to the SBR.

The laboratory scale SBR reactor is an efficient alternative for evaluating the performance of the aerobic process. The operation of the SBR reactor was in batch mode and consisted of mixing and periodic feeding and discharge. This allows to simulate the behavior of a secondary aerobic treatment system on a real scale.

The aerobic treatment was carried out in a glass reactor (500 mL) under constant aeration and agitation (500 rpm) (Fig. 3). The reactor was charged with 200 mL of activated sludge and a sample containing 0.0066 mM of each pharmaceutical (SMX, DCF, CBZ and ACT) spiked in real municipal wastewater (MWW). In experiments to select V_T/V_S ratio (V_T/V_S, where V_T is total reaction volume and V_S is sludge volume)

(section 3.3.2) were evaluated three ratios 2, 4 y 10. Each treatment lasted 48 hours and it was done in duplicate. To experiments of section 3.3.3 and 3.3.4 was used the same V_s selected in section 3.3.2. Although the concentration of 0.0066 mM (around 1 mgL^{-1}) for each compound is quite high compared to the real concentration of these ECs present into raw MWW from Florencia (ug L^{-1} range), it is still low enough to simulate real conditions and compare the different approaches under measurable conditions with the equipment available for this work.

The organic matter was monitored daily by TOC, as well as the conversion efficiency of ammonium and nitrate.

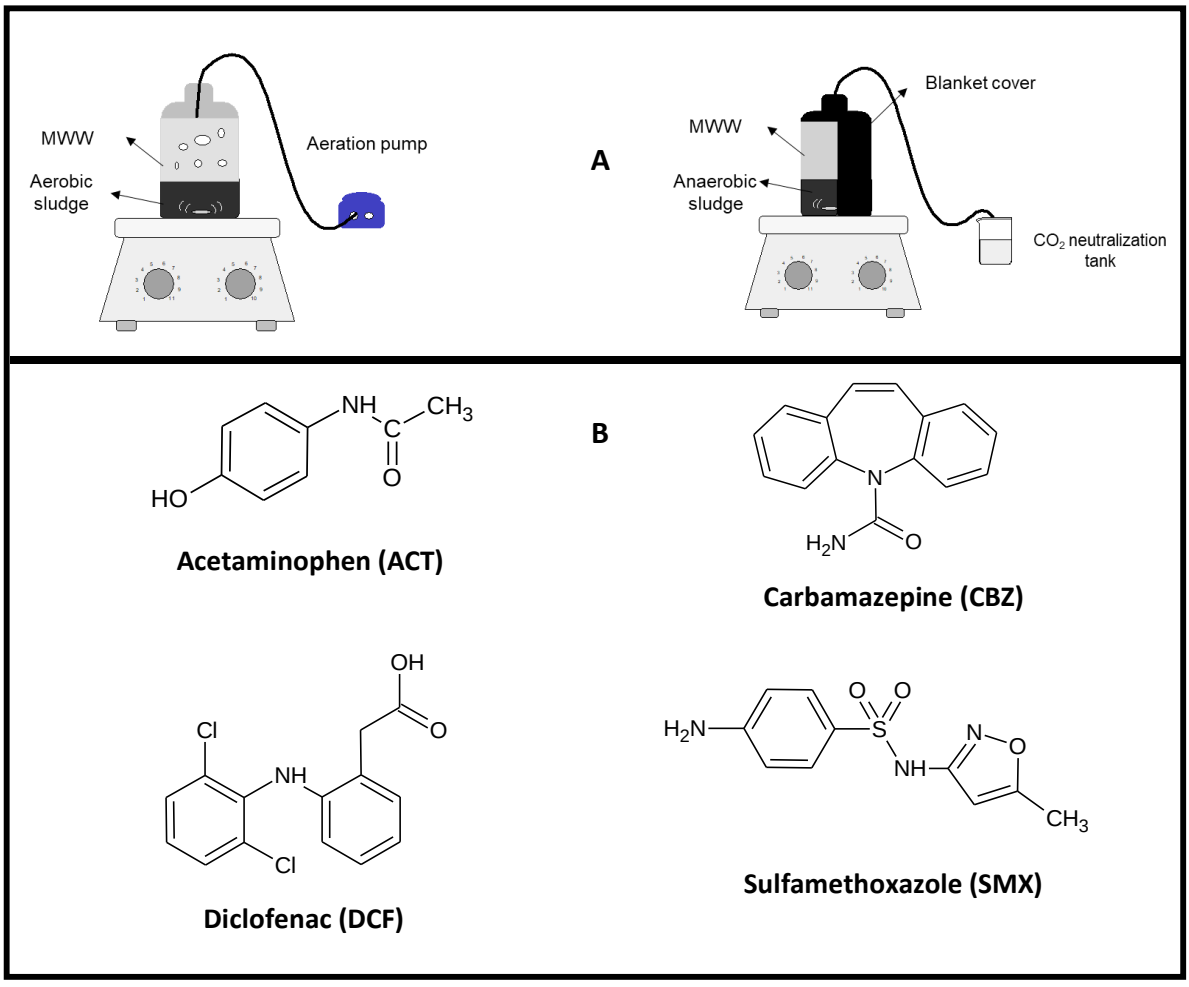


Figure 3. A. Experimental setup for aerobic (left) and anaerobic (right) treatments at laboratory scale. **B**. Chemical structures of model pharmaceuticals of this work.

*- Laboratory scale **anaerobic** bioreactor*

Anaerobic sludge was taken from a septic tank used in the treatment of domestic wastewater from a local farm (Florencia-Caquetá-Colombia). The anaerobic treatments were developed using a glass batch reactor covered with a black blanket to avoid contact with light. The reactor was charged with 200 mL of anaerobic sludge and a sample containing 0.0066 mM of each pharmaceutical (SMX, DCF, CBZ and ACT) spiked in real municipal wastewater (MWW). Slow stirring was applied during the experiments (50 rpm). The reactor was hermetically sealed to prevent gas leakage or contact with air and the gas mixture produced was led to a 10% NaOH solution (Fig. 3). The experiments lasted 48 hours. In experiments to select V_T/V_S ratio (section 3.3.2) were evaluated three ratios 2, 4 y 10, as for the laboratory scale aerobic reactor. Each treatment lasted 48 hours and it was done in duplicate. To experiments of section 3.3.3 and 3.3.4 was used the same V_s selected in section 3.3.2.

3.2.3 Analytical methods

- Quantification of pharmaceuticals in MWW samples

The concentration of the four pharmaceuticals was analyzed using an HPLC Shimadzu with UV detector at 254 and 267 nm with a C18 column (5 µm, 4.6 x 150 mm), with a flow of 0.5 mL min^{-1}. The injection volume was 100 µL.

The method consists in a gradient flow with phase A: 25 mmol L^{-1} formic acid and phase B: acetonitrile where: at 0 min 90%A, 3 min 90%A and 13 min 20%A, 13.1 min 0%A, 20 min 0%A, 20.1 min 90% and 25 min 90%A.

- Quantification of pharmaceuticals in sludge samples

Sludge samples were taken in glass bottles and immediately transferred to the laboratory. Then, they were centrifuged during 20 min at 7000 rpm and separated in two phases. The solid phase was frozen at − 50 °C and then lyophilized for 48 h, homogenized by crushing in a mortar, sieved to 0.5 mm, and stored at − 20 °C until

analysis. The supernatant, liquid phase separated during the centrifugation step (sludge aqueous phase onwards) was filtered through 0.45 µm cellulose nitrate filter and keep at 4 °C until analysis. Extraction method was QuEChERS + Clean-up: $MgSO_4$ + C18+ PSA (with different cleanup sorbents: PSA-C18, Z-Sep, and Z-Sep+) for solid sewage sludge, according to methodology used by Ponce-Robles et al. (Ponce-Robles, Rivas, et al., 2017).

Quantification of pharmaceuticals concentration present in initial and final sludge was developed in the "Centro de Investigación en Energía Solar" – CIESOL at Almería University. A HPLC Series 1200 of Agilent (Agilent Technologies, Palo Alto, CA, USA), coupled to a hybrid Triple Quadrupole-Linear Ion Trap-Mass Spectrometer 5500 QTRAP®LC/MS/MS system (Sciex Instruments, Foster city, CA, USA) was used. Equipped with two analytical columns: one column to detect acetaminophen, carbamazepine and sulfamethoxazole in positive ionization mode and another to detect diclofenac in negative ionization mode. The first one was Kinetex C18 100A, 150x4.6mm, 2.6um, Phenomenex®. The method in this column consists in a gradient flow with phase A: water at 0.1% of formic acid and phase B: Methanol where: at 0 min 80%A, 0.5 min 80%A, 3 min 50%A and 7 min 10%A, 9.5 min 0%A, 14 min 0%A, 14.1 min 80% and 21 min 80%A. An injection volume of 10 µL, flow of 0.5 mL min^{-1}, Ion Source: Turbo Spray, Curtain gas: 25, Ion Spray Voltage: 5000 V, Temperature: 500 °C, Gas 1: 50, Gas 2: 40. The second analytical column was a Zorb ax Eclipse Plus C18, 150x4.6 mm, 5um from Agilent®. The method in this column consists in a gradient flow with phase A: water 5mM sodic acetate and phase B: Acetonitrile where: at 0 min 90%A, 1 min 90%A, 9 min 0%A, 12 min 0%A, 12.1 min 90%A, 17 min 90%A. An injection volume of 10 µL, flow of 0.5 mL min^{-1}, Ion Source: Turbo Spray, Curtain gas: 25, Ion Spray Voltage: -4500 V, Temperature: 500 °C, Gas 1: 50, Gas 2: 40 and N_2 was used as the nebulizer gas, curtain gas, and collision gas.

- *TOC, ammonium and nitrate*

Analyses for TOC, ammonium and nitrate were carried out as described in chapter 2. When the results reported during analysis of results in this thesis are presented or expressed as removal percentage, this affirmation was calculated by the Equation 3.1:

$$\% \text{ Removal percentage} = \frac{C_{initial}-C_{final}}{C_{initial}} \times 100 \qquad \text{Eq. (3.1)}$$

-Prediction of aerobic biodegradation pathways

To support some interpretations of the aerobic transformation mechanisms for the representative pharmaceuticals, it was utilized free online Pathway Prediction System (PPS) application from EAWAG (http://eawag-bbd.ethz.ch/index.html), which provides predictions about biotransformation rules, based on reactions found in the EAWAG-BBD database and the scientific literature.

3.3 Results

3.3.1 Acclimatization of aerobic and anaerobic sludges.

In the implementation of biological treatments, acclimatization of the inoculum to the MWW is an initial necessary step (Gonzalez-Gil et al., 2019; Huang et al., 2019; Jonstrup et al., 2011; Min et al., 2018; Sikosana et al., 2019). The acclimatization can be followed through TOC, ammonia and nitrates measurements. Figure 4 shows the evolution of TOC, ammonia and nitrates for acclimatization of the aerobic system. It can be noted that both the TOC consumption and ammonia decreasing were slow at the first 40 days. This indicates that in the first phase occurs the growth of microorganisms, such behavior is typical because the biomass is adapting to the wastewater environment. After 40 days, TOC consumption by microorganism reached up to 95%, the removal of ammonia was up to 70% and an increase of up to 15 times the concentration of nitrates was observed, which reveals that a sufficient sludge amount was available for the further experimentation.

As indicated in Chapter 1, in the aerobic system organic carbon is transformed into carbon dioxide and biomass by means oxidative and biosynthetic mechanisms. Meanwhile, the mechanism of nitrogen removal is a nitrification process. This process includes transformation of ammonia into nitrite and then to nitrate through nitrifying bacteria. This process is favored due to high ammonia solubility in water. Additionally, direct relationship between nitrate and ammonia nitrogen concentrations (Figure 4B-C) indicates a good nitrification in the aerobic reactor (Zhang et al., 2019).

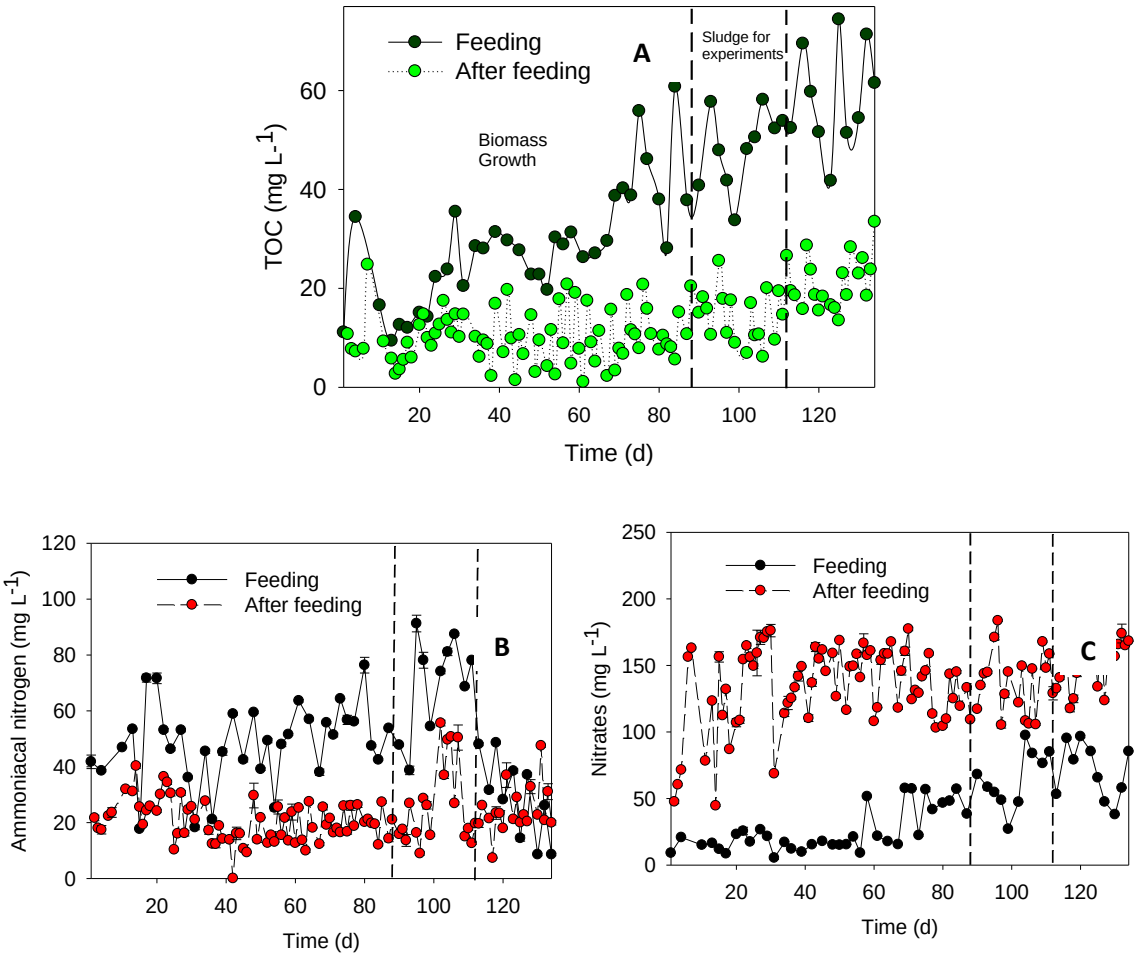


Figure 4. Evolution of organic matter (TOC (A)) and nitrogen species (ammonia nitrogen (B) and nitrate(C)) during acclimatization of aerobic reactor at laboratory scale.

Figure 5 presents the evolution of TOC and nitrogen species during acclimatization of the anaerobic reactor at lab-scale. In this case, the nutritional requirements (COD:N:P of 350:5:1) were guaranteed (Cajacuri, Behling, Rincón, Colina, & Marín, 2013; Fernández & Seghezzo, 2015). Thus, considering the MWW characterization (Table 2.2), proper amounts of $K_2HPO_3.3H_2O$ were added. From Figure 5 can be noted that TOC had fluctuation during start-up and the organic carbon consumption was high, which was between 40% and 86%. The mineralization can be associated to hydrolysis, acidogenesis, acetogenesis and methanogenesis by anaerobic microorganisms (with predominance of methanogenic bacteria) (Aziz et al., 2019; Show & Lee, 2017). The alkalinity during start-up step was controlled by addition of sodium bicarbonate to guarantee an acidity index under 0.3 all time (data not shown). Thus, pH always was between 6.9 and 7.5, to limit sulfate reducing bacteria growth. Accordingly, the transformation of acetate and H_2 towards methane is favored. It should be mentioned that the interaction of acetate and H_2 with sulfate reducing bacteria has more negative values of Gibbs free energy ($\Delta G°$) than methanogenesis (Eqs. 3.2-3.5). For this reason, the control of alkalinity and pH in the anaerobic reactor is definitive to favor methanogenic bacteria action (Fernández & Seghezzo, 2015).

Acetate

$$CH_3COO^- + H_2O \rightarrow CH_4 + HCO_3^- \; ; \quad \Delta G^\circ = -28.0 \text{ kJ mol}^{-1} \quad \text{Eq. 3.2}$$

$$CH_3COO^- + SO_4^{-2} \rightarrow HS^- + 2HCO_3^- \; ; \Delta G^\circ = -71.7 \text{ kJ mol}^{-1} \quad \text{Eq. 3.3}$$

Hydrogen

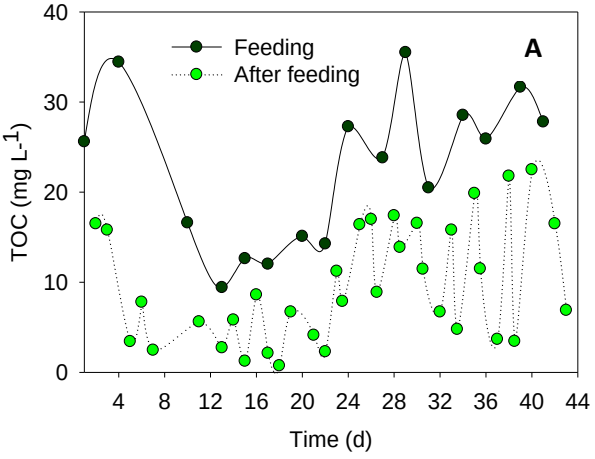
$$4H_2 + H^+ + HCO_3^- \rightarrow CH_4 + 3H_2O; \quad \Delta G^\circ = -135.6 \text{ kJ mol}^{-1} \quad \text{Eq. 3.4}$$

$$4H_2 + H^+ + SO_4^{-2} \rightarrow HS^- + 4H_2O \; ; \quad \Delta G^\circ = -151.9 \text{ kJ mol}^{-1} \quad \text{Eq. 3.5}$$

Denitrification was small considering that nitrate removal did not exceed 25% during the whole stages (Figure 5C). This is coherent with literature, which reports

moderated denitrifications (~53%) for anaerobic reactors (Aziz et al., 2019; W. H. Chen et al., 2019; Fernández & Seghezzo, 2015). It should be mentioned that such transformation does not interfere with the methanogenesis (Cajacuri et al., 2013). Regarding ammonia, after the first 12 days of start-up, a high increment in its concentration was observed (3 times the initial concentration). Ammonia nitrogen production can be attributed to hydrolysis of proteins into amino acids followed by formation of volatile fatty acids (VFAs) and finally to NH_4^+. Also, the reducing environment in the anaerobic reactor could help transform NO_3^- into NH_4^+ (W. H. Chen et al., 2019).

From Figures 4 and 5 it can be deduced that the aerobic and anaerobic reactors were acclimatized after 88 and 36 days, respectively. When the best mineralization was reached in this stage, the spiking of pharmaceuticals in MWW was done and such water was added to the reactors.



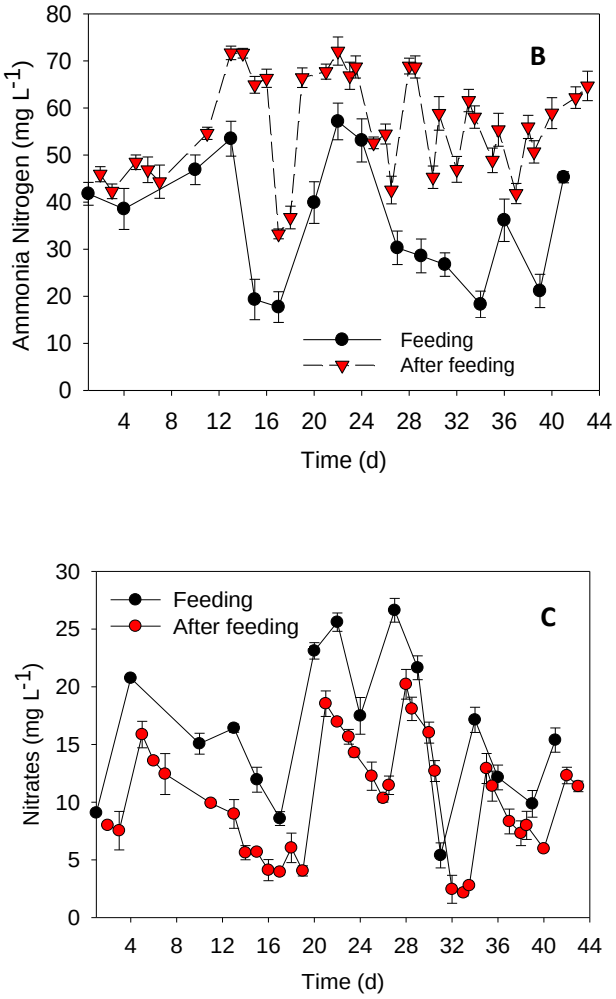


Figure 5. Evolution of organic matter (TOC (A)) and nitrogen species (ammonia (B) and nitrate(C)) during acclimatization of anaerobic reactor at laboratory scale.

3.3.2. Effect of sludge volume on bio-treatments performance

To define the proper sludge amount to reach a higher efficiency of bio-treatment action toward MWW loaded with the representative pharmaceuticals, variations of the relationship between total volume of system and volume of sludge (i.e., V_T/V_S) were tested for both biological processes. Thus, percentage of TOC removal, evolutions of nitrate and ammonia nitrogen were followed in addition to

pharmaceuticals removal. Moreover, an ANOVA to determine differences between the biological treatments and V_T/V_S ratios was applied (data not shown).

The V_T/V_S ratio did not influence the organic matter removal when the aerobic treatment was used, achieving an average of about 64% of TOC elimination (Figure 6). In contrast, in the anaerobic system, the mineralization decreased significantly when the V_T/V_S ratio increased from 2 to 10. Furthermore, at the V_T/V_S ratio = 10, according to Tukey test, significant differences in mineralization reached by both treatments were observed (aerobic system removed 63% of TOC, whereas the anaerobic achieved 52% of mineralization, Figure 6). Under the volumes of sludge worked here, the continuous and efficient mixing between the sludge and the MWW in the aerobic treatment, allows to maintain an intimate contact between them, favoring the mineralization. However, for anaerobic biodegradation, the mixing of the substrate and the sludge is difficult, because the sludge has a high concentration of suspended solids and the mixture reached by them is lower limiting the contact and interaction between biomass and wastewater and therefore biodegradation. Thus, with an increase in the volume of sludge, the available area of biomass to take the organic matter of the MWW is increased.

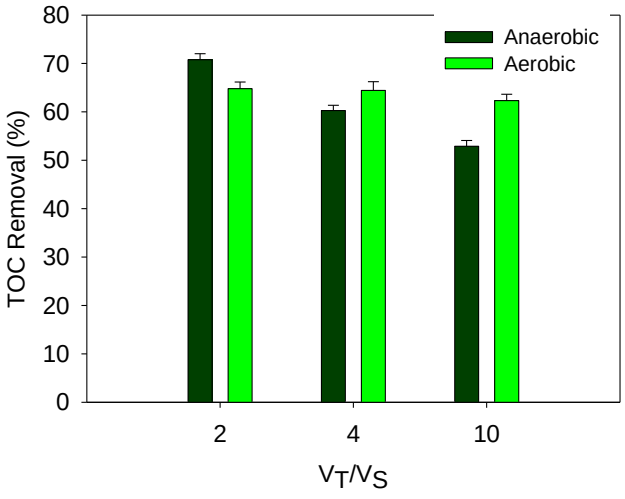


Figure 6. Percentage of organic matter at different V_T / V_S ratios for both aerobic or anaerobic treatments. V_T = 200 mL, V_S = 100, 50 and 20 mL. $V_{MWW} = V_T - V_S$.

According to Figure 7, for the aerobic treatment, it was observed that nitrification is favored at the highest V_T/V_S value (i.e., when V_S decreased, the nitrate concentrations increased). In turn, the concentrations of ammonia nitrogen are reduced on average up to 82% but there were not significant differences among the V_T/V_S ratios. Taking into account that these results, it could be indicated that the aerobic system promotes the formation of nitrates mainly from the organic nitrogen in the MWW (Show & Lee, 2017).

In the anaerobic treatment, a nitrate removal up to 25% was observed for any V_T/V_S ratio. This reduction is associated with a typical denitrification by anaerobic microorganisms. Ammonia nitrogen increased markedly when V_T/V_s changed from 2 to 4. This behavior is consistent with the expected for an anaerobic process (Aziz et al., 2019; Bhatti et al., 2014; Lazcano-Carreño, 2016), showing an optimum sludge volume to kept maximum ammonia production.

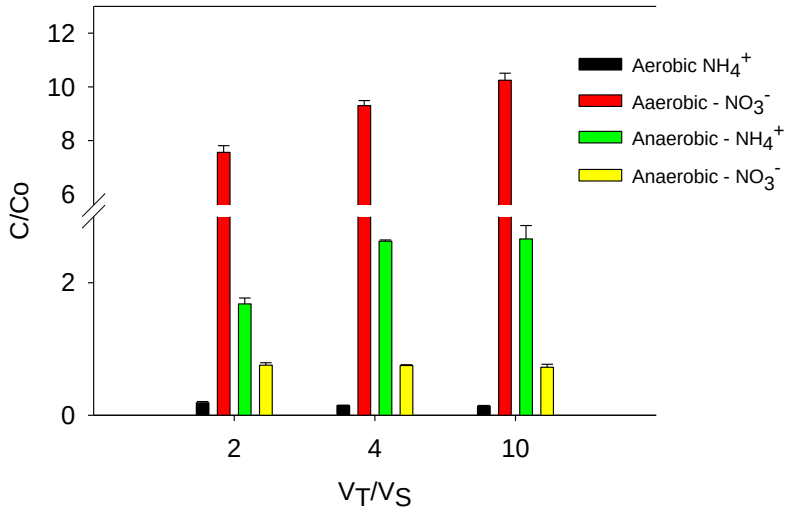


Figure 7. Nitrate and ammonium removal achieved at different V_T / V_S ratios and aerobic or anaerobic treatment. V_T = 200 mL, V_S = 100, 50 and 20 mL.

Regarding bio-treatments action on the representative pharmaceuticals, their removal by the aerobic process is not influenced by V_T/V_S ratio (Figure 8). On contrary, in the anaerobic treatment, the percentage of pharmaceutical removal was

increased with the increasing the V_T/V_S ratio. This response could be attributed to a higher sludge volume (lower V_T/V_s) since the reducing environment is increased too, keeping dissolved reduced species where the oxidation of pharmaceuticals is not favored. Moreover, its known that anaerobic bioprocesses require plentiful electron donors (far exceeds stoichiometric requirements) for microbial metabolism such as organic matter from MWW (Cui, Cui, Gao, Wang, & Cheng, 2017). So, when less sludge volume more MWW volume is added to the reactor which cause an increment in electron donors and thus a higher extent of removal pharmaceuticals is observed too. Additionally, through aerobic treatment reached higher removal of the four pharmaceuticals than the obtained by anaerobic system (Figure 8).

Based on the results in this section, the appropriate water sample/ sludge ratio for aerobic and anaerobic treatments was V_T/V_S = 10. Such ratio led to the highest removal of pharmaceuticals and elevated bio-transformation of organic carbon and nitrogen species by both aerobic and anaerobic processes. Then, the subsequent experiments were developed by using a V_T/V_S = 10.

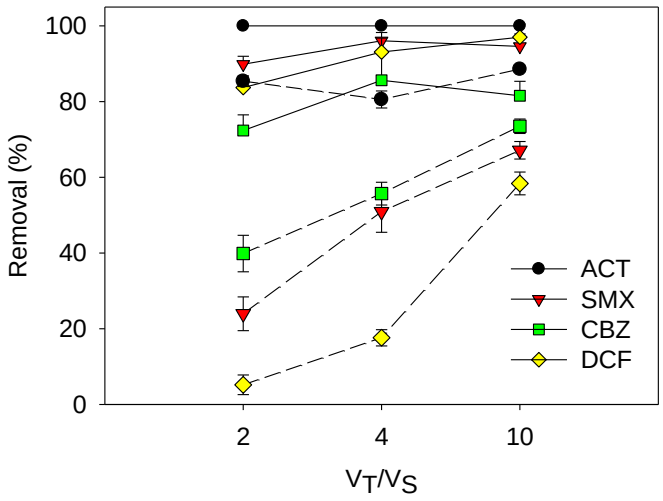
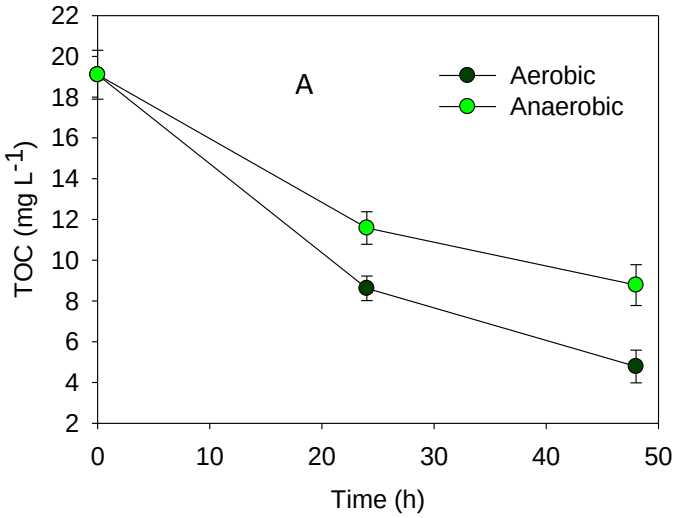


Figure 8. Pharmaceuticals removal at different V_T / V_S ratios and (—) aerobic or (---) anaerobic treatment. V_T = 200 mL, V_S = 100, 50 and 20 mL. $[Pharmaceutical]_o$= 0.0066 mM.

3.3.3 Removal of macro-components in MWW from Florencia under favorable conditions of bio-treatment at lab-scale

The MWW with the pharmaceuticals was submitted to aerobic and anaerobic treatments (individually) using a V_T/V_S ratio equal to 10, during 48 h. Then, the macro-components evolution was followed. Figure 9 depicts the consumption/formation of TOC, nitrate and ammonia nitrogen during the biological treatments. It can be observed that in the aerobic treatment a mineralization up to 79.4% was reached (Figure 9A). Meanwhile, the ammonium decreased up to 55.7% and the nitrates increased 13.1 times (Figure 9B). This indicates an effective oxidation of macro-components through microbial metabolism, which demands organic carbon and ammonium nitrogen (as a nutrient source) for the biomass growth (Show & Lee, 2017).



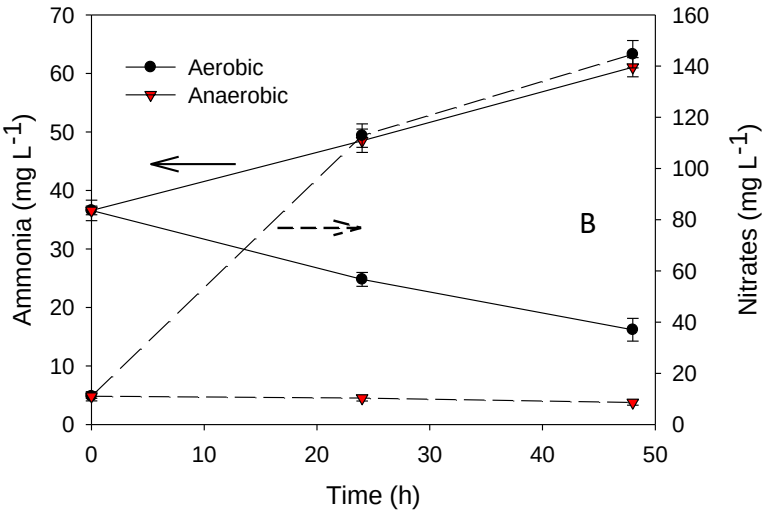


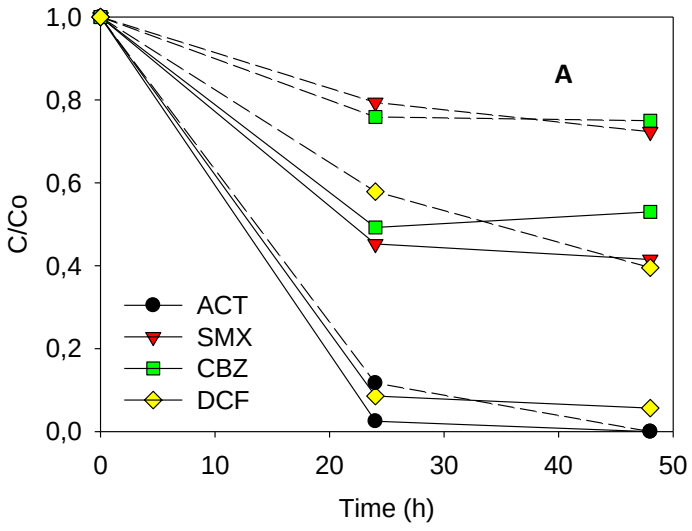
Figure 9. Evolution of macro-components of MWW during the biological treatments. A. TOC. B. (—) Ammonium and (---) Nitrate.

In the anaerobic conditions, 54.1% of TOC was removed, in addition to an increment of the ammonium concentration from 36.6 mg L^{-1} to 61.1 mg L^{-1}. As expected to this biological system, organic nitrogen and nitrate anion were reduced toward ammonium (Figure 9B) (Suarez, Lema, & Omil, 2010). The nitrogen species decreasing was associated to the reducing/anoxic environment in the reactor (W. H. Chen et al., 2019). However, considering the low initial TOC concentration (~19 mg L^{-1}), the growth of heterotrophic reducing bacteria in bioreactor is expected to be limited (W. H. Chen et al., 2019). On the other hand, it is well known that in aerobic treatments the microbial growth rate is much higher than the anaerobic treatment, which allow us to support the higher TOC consumption by the aerobic system (Figure 9A) (Phan et al., 2014).

After establishment the action of the biological processes on the macro-components, it must be considered their efficiency for eliminating the relevant pharmaceuticals. This aspect is discussed in the subsequent section.

3.3.4 Removal of pharmaceuticals in MWW from Florencia under favorable conditions of bio-treatment at lab-scale

The MWW spiked with the four representative pharmaceuticals was treated under aerobic and anaerobic treatments (individually) using a V_T/V_S ratio equal to 10, during 48 h. Evolutions of the pharmaceuticals was evaluated (Figure 10A). For all four pharmaceuticals, the total removal efficiencies observed between the aerobic and anaerobic treatment was significantly different ($p > 0.05$). These systems partially removed SMX, CBZ and DCF. However, the aerobic treatment demonstrated greater efficiency for total pharmaceutical removal (up to 88.5%) than anaerobic treatment (up to 51.4%) (Figure 10B). On the other hand, the trends of degradation are different among the four pharmaceuticals (ACT> DCF> SMX~ CBZ). Thus, to understand the removal of each pharmaceutical from the MWW, it is important to remember that the decreasing of concentration in a biological system depends on two mechanisms: biodegradation and sorption on the sludge (Lin, Lin, Tung, & Chary, 2010; Martínez-Hernández et al., 2016; Min et al., 2018).



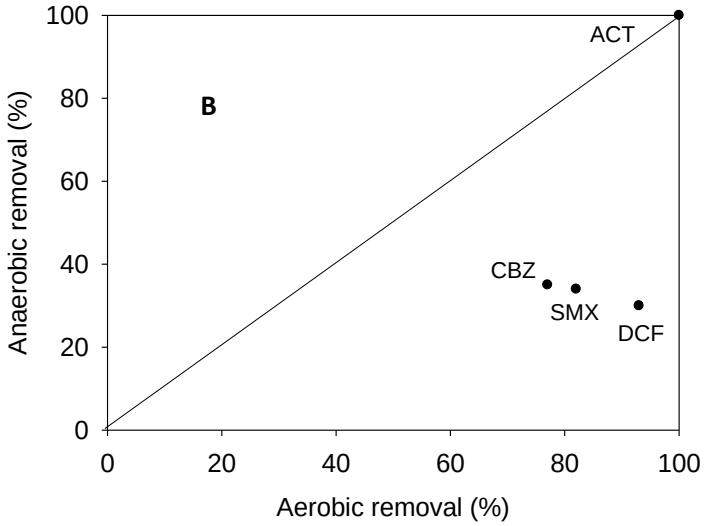


Figure 10. Evolution of degradation and mineralization of pharmaceuticals spiked in MWW by biological treatment and mineralization. A. Elimination of pharmaceuticals (—) Aerobic treatment and (---)anaerobic treatment. B. Comparison of the total pharmaceutical removals in aerobic and anaerobic treatment after 48 h of operation.

To establish contribution of sorption on sludges to pollutants removal, retention of the pharmaceuticals on the biomass was measured (Table 6). It can be noted that aerobic sludge retained ~ 71% and ~1.0 % of CBZ and DCF, respectively. Meanwhile, the anaerobic sludge sorbed ~50% and 5.3 % of CBZ and DCF, respectively. CBZ shown the highest concentration into sludge at final of both biological treatments. CBZ and DCF have octanol–water partition coefficients (log K_{ow}) of 2.45 and 4.51 respectively. CBZ is moderately hydrophobic, which could be favored sorption on sludge surface (W. H. Chen et al., 2019; Hyland, Dickenson, Drewes, & Higgins, 2012; Luo et al., 2014; Martínez-Hernández et al., 2016; Phan et al., 2014; Suarez et al., 2010). Although molecular form of diclofenac is more hydrophobic than carbamazepine at the experimental pH (which was 6.6-7.0), DCF is ionized (DCF has a pK_a 4.15) and consequently its interaction with sludges is disfavored (Hyland et al., 2012; Luo et al., 2014; Suarez et al., 2010). On the other

hand, the percentage of sorption of CBZ on aerobic sludge is higher than on the anaerobic one. This result could be explained considering that in the anaerobic treatment, the contact area between the sludge and this pharmaceutical is smaller than the exposed to aerobic sludge (Gupta, Sreekrishnan, & Ahammad, 2016).

Table 6. Pharmaceutical concentration in aerobic and anaerobic sludges

SLUDGE	**AEROBIC**				**ANAEROBIC**			
PHARMACEUTICAL	**ACT**	**SMX**	**CBZ**	**DCF**	**ACT**	**SMX**	**CBZ**	**DCF**
In initial sludge (μg L^{-1})	0	0	28.66±7	0.43±1	0.11±1	0	0.24±1	0
In final sludge (μg L^{-1})	0	0	424.82±8	11.02±3	0	1.32±1	148.32±6	51.55±7
Total removal from MWW (μg L^{-1})	965.00±12	928±23	561±5	1505±7	965±10	439±8	298±7	965±12

SMX and ACT exhibited a very low sorption on sludges (Table 6) because their hydrophilic nature (as suggested by their log K_{ow} values, 0.89 and 0.49 for sulfamethoxazole and acetaminophen, respectively). Additionally, under the pH of this work, SMX was mainly as an anionic species (pK_a = 5.60), which makes it more hydrophilic. Therefore, it is possible to indicate that the removals of SMX and ACT by the biological processes are mainly due to biotransformations (Luo et al., 2014; Suarez et al., 2010; Tran et al., 2016; Lin et al., 2010; Martínez-Hernández et al., 2016). Also, it should be mentioned that as the CBZ was mainly removed by sorption on the sludges (Table 6), the discussion about bio-transformations was focused on the other three pharmaceuticals (i.e., DCF, SMX and ACT).

From Figure 10A, it is remarkable that ACT was completely degraded by both biological processes after 48h of treatment. This result is consistent with previous works. For example, ACT was removed up to 95% by the biological processes of the MWWTP in Medellin-Colombia (Botero-Coy et al., 2018). Bueno *et al*. reported 99% of removal efficiency for ACT in five MWWTP from Spain (Bueno et al., 2012). Indeed, ACT has been classified as a highly bio-removable compound (Luo et al.,

2014), and it has been demonstrated that in commonly used aerobic reactors at lab-scale (such as membrane biological reactor–MBR and conventional activated sludge–CAS) achieve acetaminophen removals around 80% (Luo et al., 2014). Moreover, according measurements done by Lin *et al*., ACT biodegradation can be approximated to a pseudo-first order kinetics (R^2 = 0.97) with half-lives ($t_{1/2}$) around 2.1 days (Lin et al., 2010).

According to Figure 10A, DCF transformation was up to 92% and 60% in aerobic and anaerobic reactors at 48 h of treatment, respectively. The literature also reports that DCF presents a greater elimination by aerobic treatment than by the anaerobic process (W. H. Chen et al., 2019; Long et al., 2019; Suarez et al., 2010). Here, it can be mentioned that the differences between both biological processes is related to the biotransformation involved in each system.

Biotransformation mechanisms are dependent on the atoms needed for the bacterial metabolism; additionally, the presence of electron donating groups (EDG) or electron withdrawing groups (EWG) has a critical role in the pathway of biodegradation of pharmaceuticals (Poirier-Larabie, Segura, & Gagnon, 2016). ACT, DCF and SMX elimination was favored through oxidative action (aerobic metabolism) thanks presence of phenolic, carboxyl and amine/amide groups, which are susceptible to biological oxidation because they are electron-rich regions (i.e., EDG). In contrast, the reductive action (anaerobic metabolism) requires EWG, but the considered pharmaceuticals have low presence of such moieties; consequently, anaerobic biodegradation was less favored (Ghattas, Fischer, Wick, & Ternes, 2017; Phan et al., 2014). This could explain the differences in bio-degradation (Figure 3.7A-B).

ACT has the simplest structure among the four tested pharmaceuticals and its phenolic and nitrogen groups are very susceptible to biological oxidation. In fact, aerobic metabolism can promote a deacetylation followed by a deamination of aniline generating a hydroquinone, such compound could suffer an oxidative cleavage forming maleylacetate. Besides the maleylacetate can experiment a decarboxylation oxidative to form succinate according to the PSS analysis (EAWAG,

2018). Regarding anaerobic transformation, it can be indicated that ACT could experiment a deacetylation/hydrolysis of secondary amide as primary mechanism steps of this bio-degradation (Gonzalez-Gil et al., 2019).

In the case of DCF, three biodegradation products by aerobic via have been reported. The first product comes from hydroxylation of the phenyl containing no chlorine ($C_{13}H_9Cl_2NO$). The second product corresponds to a decarboxylation ($C_{14}H_{11}Cl_2NO_3$) and the third one is a microbial metabolite ($C_{14}H_{10}Cl_2NO_2$) (Poirier-Larabie et al., 2016). Also, from PSS, it was found a similar mechanism, where the first DCF oxidation lead to formation of 1,5-dichloro an di-hydroxylated compound, which after several oxidation reactions form chloroacetate, hydroxypiruvate, amine-carboxylate and imine-dicarboxylate (EAWAG, 2018). Meanwhile, biodegradation of DCF under anaerobic conditions produces $C_{14}H_{10}Cl_2NO_2$ (Poirier-Larabie et al., 2016). Likewise, from PSS, it was found a reductive dehalogenation from a muconate derivative, which is according to literature. However, dechlorination only occurred after oxygenation of the chlorinated benzene ring, which might explain why DCF is more recalcitrant under strictly anaerobic conditions, where a hydroxylation of the benzene ring is less likely (Ghattas et al., 2017).

Regarding SMX, it can be indicated that its aerobic biotransformation is able to mainly form two products: an hydroxylamine of SMX through an addition of an oxygen to SMX and an acetylated aromatic amine of SMX by losing of the NH group (Poirier-Larabie et al., 2016). Also, the PPS showed an initial hydrolysis of SMX in C-NH bond to generate a 3-amine,5-metilisoxazole and 4-aminobenzenesulfonate, followed by an oxidation of the primary alcohol to aldehyde, oxidation of that aldehyde to carboxylate and finally a decarboxylation to form an amino-isoxazole (EAWAG, 2018). In turn, in the anaerobic biodegradation of SMX, it has been suggested a reductive transformation on the aromatic ring due to the EWG sulfonyl group (Alvarino et al., 2014). In contrast, it is reported that the SMX can be transformed by cleavage of isoxazole ring, while the sulfonamide group of SMX is not altered. The mechanism was proposed to be an abiotic reduction of the N-O bond in the isoxazole ring by the Fe(II) generated during microbial Fe(III) reduction

(Ghattas et al., 2017; Mohatt, Hu, Finneran, & Strathmann, 2011). Finally, two mainly biodegradation products were proposed in a anaerobic membrane reactor: Butylbenzene-sulfonamide without antibiotic functions and sulfanilamide with much lower antibiotic toxicity than SMX (Wei et al., 2019).

At this point, it is important to indicate that for biotransformation, the structural complexity of the pharmaceuticals can limit enzymatic degradation (a main action route of microorganisms) due to steric interferences or negative effects on active sites (Ghattas et al., 2017). Then, it is normal the low/moderate elimination observed for CBZ, SMX and DCF in Figure 10. Consequently, effective elimination of the pharmaceuticals requires other complementary processes such as advanced oxidation technologies.

3.4 Conclusions of the chapter

It is to known that the extent of biodegradation of an organic compound depends of water matrix. Therefore, it was important to define the performance of this process on the degradation of pharmaceuticals (ACT, SMX, CBZ and DCF) present in Florencia's MWW to describe the differences in the elimination mechanism of them.

Biological processes acclimatization to MWW sample allowed a good performance of microorganism for degrading macro-components (Organic carbon and nitrogen species). It can be indicated that the type of biological oxidation (i.e., aerobic or anaerobic) and the volume of sludge in the reactors strongly influence the extent of mineralization, nitrogen consumption and elimination of pharmaceuticals in the MWW (being favorable at a V_T/V_S ratio equal to 10). The chemical structure and properties of pharmaceuticals defined the mechanism of elimination: sorption or biotransformation. The compound with simplest chemical structure (ACT) experimented a faster biotransformation regardless of the type of bio-treatment, while hydrophobic compounds (as CBZ) were sorbed on both type of sludges.

Although, the biological systems showed moderated ability to eliminate the indicator pharmaceuticals, there were significant differences between these systems in removal percentages of pharmaceuticals. In fact, the aerobic treatment exhibited higher biotransformation than the anaerobic one. This, thanks to the presence of electron-rich moieties on the target pollutants susceptible to biological oxidation. Considering the complexity of aerobic and anaerobic biodegradation mechanisms, future studies may be focused on the identification of degradation products that provide more light about the transformation pathways under our experimental conditions of bio-treatment.

Finally, it must be indicated that as in the case of SMX and CBZ (even DCF) more than 50% remained even after 48h of biotreatment, the application of complementary/alternative processes (for example AOP) are needed to achieve a complete degradation of the bio-recalcitrant pharmaceuticals.

References

Alvarino, T., Suarez, S., Lema, J. M., & Omil, F. (2014). Understanding the removal mechanisms of PPCPs and the influence of main technological parameters in anaerobic UASB and aerobic CAS reactors. *Journal of Hazardous Materials*, *278*, 506–513. https://doi.org/10.1016/j.jhazmat.2014.06.031

Aziz, A., Basheer, F., Sengar, A., Irfanullah, Khan, S. U., & Farooqi, I. H. (2019). Biological wastewater treatment (anaerobic-aerobic) technologies for safe discharge of treated slaughterhouse and meat processing wastewater. *Science of the Total Environment*, *686*, 681–708. https://doi.org/10.1016/j.scitotenv.2019.05.295

Bhatti, Z. A., Maqbool, F., Malik, A. H., & Mehmood, Q. (2014). UASB reactor startup for the treatment of municipal wastewater followed by advanced oxidation process. *Brazilian Journal of Chemical Engineering*, *31*(3), 715–726. https://doi.org/10.1590/0104-6632.20140313s00002786

Botero-Coy, A. M., Martínez-Pachón, D., Boix, C., Rincón, R. J., Castillo, N., Arias-Marín, L. P., … Hernández, F. (2018). An investigation into the occurrence and removal of pharmaceuticals in Colombian wastewater. *Science of the Total Environment*, *642*, 842–853. https://doi.org/10.1016/j.scitotenv.2018.06.088

Bueno, M. J. M., Gomez, M. J., Herrera, S., Hernando, M. D., Agüera, A., & Fernández-Alba, A. R. (2012). Occurrence and persistence of organic emerging

contaminants and priority pollutants in five sewage treatment plants of Spain: Two years pilot survey monitoring. *Environmental Pollution*, *164*, 267–273. https://doi.org/10.1016/j.envpol.2012.01.038

Cajacuri, M. P., Behling, E., Rincón, N., Colina, G., & Marín, J. C. (2013). Microbiological diversity of the anaerobic sludge during treatment. *Ingeniería Investigación y Tecnología*, *14*(3), 325–334. https://doi.org/10.1016/S1405-7743(13)72247-9

Chen, W. H., Wong, Y. T., Huang, T. H., Chen, W. H., & Lin, J. G. (2019). Removals of pharmaceuticals in municipal wastewater using a staged anaerobic fluidized membrane bioreactor. *International Biodeterioration and Biodegradation*, *140*(January), 29–36. https://doi.org/10.1016/j.ibiod.2019.03.008

Cui, M. H., Cui, D., Gao, L., Wang, A. J., & Cheng, H. Y. (2017). Evaluation of anaerobic sludge volume for improving azo dye decolorization in a hybrid anaerobic reactor with built-in bioelectrochemical system. *Chemosphere*, *169*, 18–22. https://doi.org/10.1016/j.chemosphere.2016.11.034

EAWAG. (2018). Biocatalysis/Biodegradation database: Pathway Prediction System. http://eawag-bbd.ethz.ch/predict/

Fernández, F., & Seghezzo, L. (2015). *Diseño De Reactores Upflow Anaerobic Sludge Blanket (UASB)*. (Proyecto Mejora De Las Economías Regionales Y Desarrollo Local, Ed.). Retrieved from www.ue-inti.gob.ar

Ghattas, A. K., Fischer, F., Wick, A., & Ternes, T. A. (2017). Anaerobic biodegradation of (emerging) organic contaminants in the aquatic environment. *Water Research*, *116*, 268–295. https://doi.org/10.1016/j.watres.2017.02.001

Gonzalez-Gil, L., Krah, D., Ghattas, A.-K., Carballa, M., Wick, A., Helmholz, L., … Ternes, T. A. (2019). Biotransformation of organic micropollutants by anaerobic sludge enzymes. *Water Research*, *152*, 202–214. https://doi.org/https://doi.org/10.1016/j.watres.2018.12.064

Gupta, P., Sreekrishnan, T. R., & Ahammad, S. Z. (2016). Role of sludge volume index in anaerobic sludge granulation in a hybrid anaerobic reactor. *Chemical Engineering Journal*, *283*, 338–350. https://doi.org/10.1016/j.cej.2015.07.058

Huang, Y., Guo, J., Yan, P., Gong, H., & Fang, F. (2019). Sorption-desorption behavior of sulfamethoxazole, carbamazepine, bisphenol A and 17A-ethinylestradiol in sewage sludge. *Journal of Hazardous Materials*, *368*(January), 739–745. https://doi.org/10.1016/j.jhazmat.2019.01.063

Hyland, K. C., Dickenson, E. R. V., Drewes, J. E., & Higgins, C. P. (2012). Sorption of ionized and neutral emerging trace organic compounds onto activated sludge from different wastewater treatment configurations. *Water Research*, *46*(6), 1958–1968. https://doi.org/10.1016/j.watres.2012.01.012

Jonstrup, M., Punzi, M., Mattiasson, B., Serra, A., Brillas, E., Domènech, X., … Li Puma, G. (2011). Comparison of anaerobic pre-treatment and aerobic post-

treatment coupled to photo-Fenton oxidation for degradation of azo dyes. *Applied Catalysis B: Environmental*, *224*(January), 761–771. https://doi.org/10.1016/j.jece.2018.11.015

Lazcano-Carreño, C. (2016). *Biotecnología ambiental de aguas y aguas residuales*. (ECOE ediciones, Ed.) (Segunda ed). Bogotá: Universidad Nacional Mayor de San Marcos.

Lin, A. Y. C., Lin, C. A., Tung, H. H., & Chary, N. S. (2010). Potential for biodegradation and sorption of acetaminophen, caffeine, propranolol and acebutolol in lab-scale aqueous environments. *Journal of Hazardous Materials*, *183*(1–3), 242–250. https://doi.org/10.1016/j.jhazmat.2010.07.017

Long, Y., Feng, Y., Li, X., Suo, N., Chen, H., Wang, Z., & Yu, Y. (2019). Removal of diclofenac by three-dimensional electro-Fenton-persulfate (3D electro-Fenton-PS). *Chemosphere*, *219*, 1024–1031. https://doi.org/10.1016/j.chemosphere.2018.12.054

Luo, Y., Guo, W., Ngo, H. H., Nghiem, L. D., Hai, F. I., Zhang, J., … Wang, X. C. (2014). A review on the occurrence of micropollutants in the aquatic environment and their fate and removal during wastewater treatment. *Science of the Total Environment*, *473–474*, 619–641. https://doi.org/10.1016/j.scitotenv.2013.12.065

Martínez-Hernández, V., Meffe, R., Herrera López, S., & de Bustamante, I. (2016). The role of sorption and biodegradation in the removal of acetaminophen, carbamazepine, caffeine, naproxen and sulfamethoxazole during soil contact: A kinetics study. *Science of the Total Environment*, *559*, 232–241. https://doi.org/10.1016/j.scitotenv.2016.03.131

Min, X., Li, W., Wei, Z., Spinney, R., Dionysiou, D. D., Seo, Y., … Xiao, R. (2018). Sorption and biodegradation of pharmaceuticals in aerobic activated sludge system: A combined experimental and theoretical mechanistic study. *Chemical Engineering Journal*, *342*(December 2017), 211–219. https://doi.org/10.1016/j.cej.2018.01.012

Mohatt, J. L., Hu, L., Finneran, K. T., & Strathmann, T. J. (2011). Microbially mediated abiotic transformation of the antimicrobial agent sulfamethoxazole under iron-reducing soil conditions. *Environmental Science & Technology*, *45*(11), 4793–4801. https://doi.org/10.1021/es200413g

Phan, H. V., Hai, F. I., Kang, J., Dam, H. K., Zhang, R., Price, W. E., … Nghiem, L. D. (2014). Simultaneous nitrification/denitrification and trace organic contaminant (TrOC) removal by an anoxic-aerobic membrane bioreactor (MBR). *Bioresource Technology*, *165*(1), 96–104. https://doi.org/10.1016/j.biortech.2014.03.094

Poirier-Larabie, S., Segura, P. A., & Gagnon, C. (2016). Degradation of the pharmaceuticals diclofenac and sulfamethoxazole and their transformation products under controlled environmental conditions. *Science of the Total*

Environment, *557–558*, 257–267. https://doi.org/10.1016/j.scitotenv.2016.03.057

Ponce-Robles, L., Rivas, G., Esteban, B., Oller, I., Malato, S., & Agüera, A. (2017). Determination of pesticides in sewage sludge from an agro-food industry using QuEChERS extraction followed by analysis with liquid chromatography-tandem mass spectrometry. *Analytical and Bioanalytical Chemistry*, *409*(26), 6181–6193. https://doi.org/10.1007/s00216-017-0558-5

Shoukat, R., Khan, S. J., & Jamal, Y. (2019). Hybrid anaerobic-aerobic biological treatment for real textile wastewater. *Journal of Water Process Engineering*, *29*(July 2018), 100804. https://doi.org/10.1016/j.jwpe.2019.100804

Show, K., & Lee, D. (2017). Anaerobic Treatment Versus Aerobic Treatment. In *Current Developments in Biotechnology and Bioengineering* (pp. 205–230). Elsevier B.V. https://doi.org/10.1016/B978-0-444-63665-2.00008-4

Sikosana, M. L., Sikhwivhilu, K., Moutloali, R., & Daniel, M. (2019). Municipal wastewater treatment technologies : A review. *Procedia Manufacturing*, *00*, 1–6. https://doi.org/10.1016/j.promfg.2019.06.051

Suarez, S., Lema, J. M., & Omil, F. (2010). Removal of Pharmaceutical and Personal Care Products (PPCPs) under nitrifying and denitrifying conditions. *Water Research*, *44*(10), 3214–3224. https://doi.org/10.1016/j.watres.2010.02.040

Wei, C. H., Sanchez-Huerta, C., Leiknes, T. O., Amy, G., Zhou, H., Hu, X., … Rong, H. (2019). Removal and biotransformation pathway of antibiotic sulfamethoxazole from municipal wastewater treatment by anaerobic membrane bioreactor. *Journal of Hazardous Materials*, *380*(July), 120894. https://doi.org/10.1016/j.jhazmat.2019.120894

Zhang, H., Zhao, Z., Li, S., Chen, S., Huang, T., Li, N., … Zhang, X. (2019). Nitrogen removal by mix-cultured aerobic denitrifying bacteria isolated by ultrasound: Performance, co-occurrence pattern and wastewater treatment. *Chemical Engineering Journal*, *372*(April), 26–36. https://doi.org/10.1016/j.cej.2019.04.114

CHAPTER 4. ENHANCING SOLAR PHOTO-FENTON AT NATURAL pH FOR DEGRADING REPRESENTATIVE PHARMACEUTICALS IN MUNICIPAL WASTEWATER

4.1 Introduction

This chapter deals about the degradation of representative pharmaceuticals by photo-Fenton process. Firstly, it is studied the treatment of ACT, DFC, SMX and CBZ in distilled water by solar photo-Fenton (SPF). Secondly, the performance of SPF at near neutral pH in presence of extracts from three Amazonian fruits (as a strategy to improve the iron availability and pollutants degradation) is discussed. Afterwards, a deeper exploration of the best extract for pharmaceuticals degradation is offered.

4.2 Materials and methods

4.2.1 Chemicals

Iron (III) sulfate heptahydrate and hydrogen peroxide were purchased from Panreac®. Iron (III) was used in photo Fenton solar experiments because the Fe^{+3} ion and organic acids produce highly soluble organo-iron complexes, which increases the amount of dissolved iron in the system (Miralles-Cuevas, Oller, Sánchez Pérez, & Malato, 2014; Villegas-Guzman, P., Giannakis, Torres-Palma, & Pulgarin, 2017). Sulfuric acid, acetonitrile (HPLC grade), sodium bisulfite, and sodium hydroxide were supplied by Merck®. All solutions were prepared using deionized water or municipal wastewater from Florencia-Caquetá. The characterization of the MWW is reported in Table 4.

4.2.2 Analytical measurements

The concentration of the four pharmaceuticals and the total organic carbon (TOC) was analyzed using analytical methods described in chapter 3 and 2 respectively. Dissolved iron was determined by 1-10-orthophenanthroline with filtered and unfiltered samples according to Standard Methods for the Examination of Water and Wastewater (method 3500-Fe B) (APHA et al., 2012), the hydrogen peroxide concentration was followed by the meta-vanadate method based on the reaction of H_2O_2 with ammonium metavanadate in acidic medium, which results in the formation of a red-orange color peroxovanadium cation, with maximum absorbance at 450nm (R. Nogueira, Oliveira, & Paterlini, 2005). Concentration of total poly-phenols present in fruit extracts was done using the total polyphenols method with Folin-Ciocalteu reagent as described by Horszwald and Andlauer (2011) with some modifications. The latter method is based on an electron transfer reaction in which phenolic and nonphenolic substances are reduced; however, the obtained result is traditionally called total polyphenols content. The result is given as mg gallic acid equivalent per litre (mg GAE L^{-1}) (Heeger et al., 2017). Citric and ascorbic acids were determined by UHPLC using ultimate 3000 thermo scientific, with UV detector at 210 and 220 nm and a Hi-plex H 8um column, with a flow of 0.6 mL min^{-1}, H_2SO_4 1% as mobile phase.

4.2.3 Experimental procedure

SPF experiments were carried out at natural pH (pH 6.2) using 0.0066 mM of each pharmaceutical (SMX, DCF, CBZ and ACT) spiked in 1 L of distilled water or real municipal wastewater (MWW) in a 1L beaker. 5 mg L^{-1} of Fe (III) and 68 to 120 mg L^{-1} of H_2O_2 were added to reactor. Fe (III) and H_2O_2 concentrations were selected considering both the literature and some previous experiments in our research group (not shown here). The degradation was done with a solar simulator (Suntest CPS+,

Atlas) equipped with an air-cooled xenon lamp having an illumination surface of 560 cm^2 and 250 - 750 W m^{-2} of solar intensity (global irradiance). In this section, the irradiance used was 250 W m^{-2}, which according to the data taken by the radiometer, was close to the typical irradiance on sunny days in Florencia-Caquetá.

4.2.4 Extracts characterization

Three Amazonian fruits (canangucha "*Maurita Flexuosa*", coffee "*coffe arábica*" and copoazu "*Theobroma gramdiflorum*") were considered. Copoazu fruits were collected when it was in a 50% of maturity degree and the pulp juice (COPE) was obtained by mechanical extraction. The canangucha fruit was taken from the palm, the pulp and part of the shell was used and an aqueous extract (CANE) through maceration was made. As for the coffee extract (COFE), the fruits of a coffee tree were taken, the seed was extracted and the shell was used to obtain its aqueous extract by maceration too. The content of total phenols, total organic carbon and presence of citric and ascorbic acids was also assessed (Table 7 Extract fruits were added to the sample in SPF experiments according to the following molar ratios between iron and total phenols, Fe:Extract = 0.07, 0.16 or 0.25. These molar ratios were selected according to previous results. That tests were made to establish the range of extract dose at which the iron was kept on solution as part of the organo-complex compound.

Table 7. Content of total phenols, TOC and some organic acids in the extracts from Amazonian fruits evaluated.

Extract	Extraction technique	Total phenols (mg GAE L^{-1})	Ascorbic acid	TOC
Canangucha extract CANE	Squeezed fruit pulp	297.03±10.31	---	32±3
Coffee extract COFE	Maceration of husk	454.40±32.45	---	162±11
Copoazú extract COPE	Squeezed fruit pulp	481.43±21.18	Presence	92±5

4.3 Results and discussion

4.3.1 Treatment of the representative pharmaceuticals by solar photo-Fenton (SPF)

As indicated in Chapter 3, since to bio-treatments were not able to completely degrade pharmaceutical compounds, complementary processes are required. Considering that Florencia-Caquetá is located in the Amazonian zone (Colombia), a region with a high solar irradiation, and that photo-Fenton process has shown high efficiencies for eliminating recalcitrant organic pollutants, the capability of SPF process to degrade a mix of the representative pharmaceuticals from distilled water (at pH adjusted to 6) was initially tested. The results are contained in Figure 11.

It was found that the SPF process degraded 18% of both CBZ and ACT, 35% of SMX and 68% of DCF. SMX and DCF can undergo photolysis under sunlight irradiation. DCF is the main responsible of this achievement. In fact, 70% of this compound was eliminated in 90 min, which is due to its ability to absorbs light between 254 and 290 nm (Figure 13). According to literature, DCF photolysis yields carbazole structures from elimination of a chloro-substituent with the subsequent

cyclization (Pinto, Da Silva, Spadoto, Botta, & Azevedo, 2019; Salaeh et al., 2016). Meanwhile, SMX begins its photolytic degradation with the breaking of the sulfonamide bond and rearranging the isoxazole ring (Alharbi et al., 2017; Martínez-costa, Rivera-utrilla, Leyva-ramos, & Sánchez-polo, 2018). In contrast, CBZ and ACT are quite resistant to photolysis, but the H_2O_2/light subsystem is able to improve their degradation such as it is shown by Figure 13 (below) where H_2O_2 improves significantly (from 22% to 42%) the action of the sunlight (H_2O_2/light) due to its oxidant effect (Alharbi et al., 2017).

On the other hand, SPF at pH 6 is not able to degrade more than 34% of the total of pharmaceuticals concentration (Fig. 11), which is probably due to the iron precipitation. Iron particles can avoid the light penetration and decrease the efficiency of light action on the pharmaceuticals. Analysis of dissolved iron in the SPF system indicated that iron is not available in solution (Figure 11), and at this time ~3 mg L^{-1} of H_2O_2 were consumed (which supports the slightly oxidative action of peroxide) and $OH^{\cdot}$ radicals couldn't be generate.

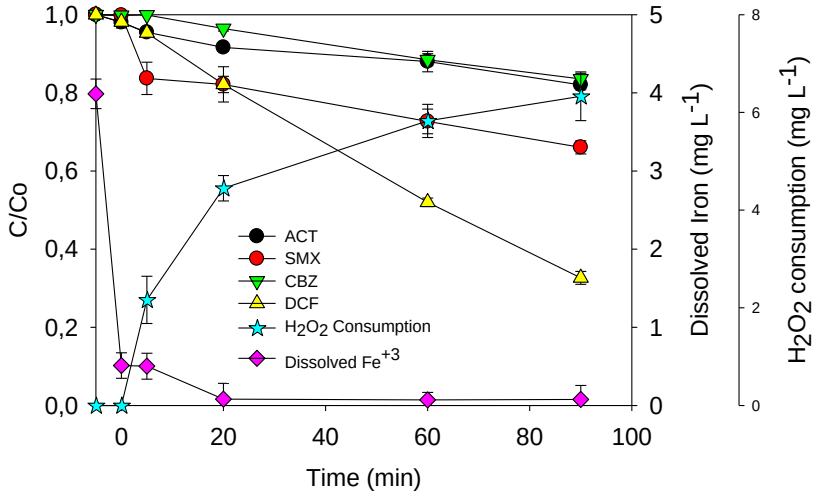


Figure 11. SPF at natural pH for treatment of pharmaceuticals mix in distilled water. $[Fe^{+3}]_o$ = 5 mg L^{-1} (90 µmol L^{-1}). $[Pharm]_o$ = 0.0066 mM. $[H_2O_2]_o$ = 100 mg L^{-1}. pH = 6.1

Due to limitation of iron availability in solution at pH around 6 (during SPF, pH had slightly changes from 6.03 to 5.9), the average removal of the pharmaceuticals was low (34.4%). Then, to obtain a higher removal of the target pollutants, it should be applied strategies to maintain the iron in solution (and increase the hydroxyl radical production). Such topic is developed in the next subsection.

4.3.2 Performance of SPF in presence of COFE, CANE and COPE

With the purpose of increasing the amount of iron in solution, extracts of Amazonian fruits were added to the SPF system at pH around 6. Figure 12 presents the treatment of a mix of the four target pharmaceuticals with individual addition of COFE, CANE or COPE. Interestingly, in the presence of all extracts, the dissolved iron was higher than in their absence (Figure 11). However, for the addition of COFE, a detrimental effect on the process performance was observed (Figure 11 and 12A).

The COFE addition provided coloration to the reaction system (probably due to the content of tannins and chlorogenic acid,(Genaro-Mattos et al., 2015)), which prevents light penetration, avoiding the photolysis and oxidation by hydroxyl radical from Fenton process. Also, the COFE has the highest content of TOC (it is twice that contributed by COPE and five times that of CANE, see Table 7), this implies that organic matter could also compete by the radicals, inhibiting the pharmaceuticals elimination.

In the case of CANE, both SMX and CBZ maintained almost similar degradation to the achieved by the SPF process without extract, but DCF only reached 40% of degradation (Figure 12B). On the contrary, ACT elimination was enhanced (~82% was eliminated). The results for SMZ, CBZ and DFC with CANE can be rationalized in analogous way (competence by organic matter) to the indicated in the COFE case. Meanwhile, the selective elimination of ACT may be attributed to an interaction between this pharmaceutical and specific polyphenols of CANE (Abdel-Daim et al.,

2018; Pang et al., 2016; Sentkowska & Pyrzynska, 2018); although, this particularity result should be studied in depth in subsequent investigations.

Interestingly, when COPE was added, an acceleration of the pharmaceutics degradation and an increasing of H_2O_2 consumption was observed (Figure 12C). This fact can be attributed to the high presence of total phenols in COPE. Also, it can be mentioned that COPE has presence of ascorbic acid (Table 7). Phenolic and acid compounds can complex ferric ions (Eq. 1.7-1.9) keeping the iron in soluble forms (Fazary, Taha, & Ju, 2009; Papoutsakis et al., 2016). Besides, many of such complexes are photo-active and promote the catalytic cycle of iron at near neutral pH. It is necessary to mention that pH did not have relevant changes during experiments with COPE staying in from 6 to 5.6-6.2. This favors the generation of radicals for the degradation of pollutants (Eq. 1.7-1.9), which is supported by a highest consumption of hydrogen peroxide. Considering these results for COPE, to better understand its enhancing effect new sets of experiments were performed and their outcomes are presented and discussed in the next subsection.

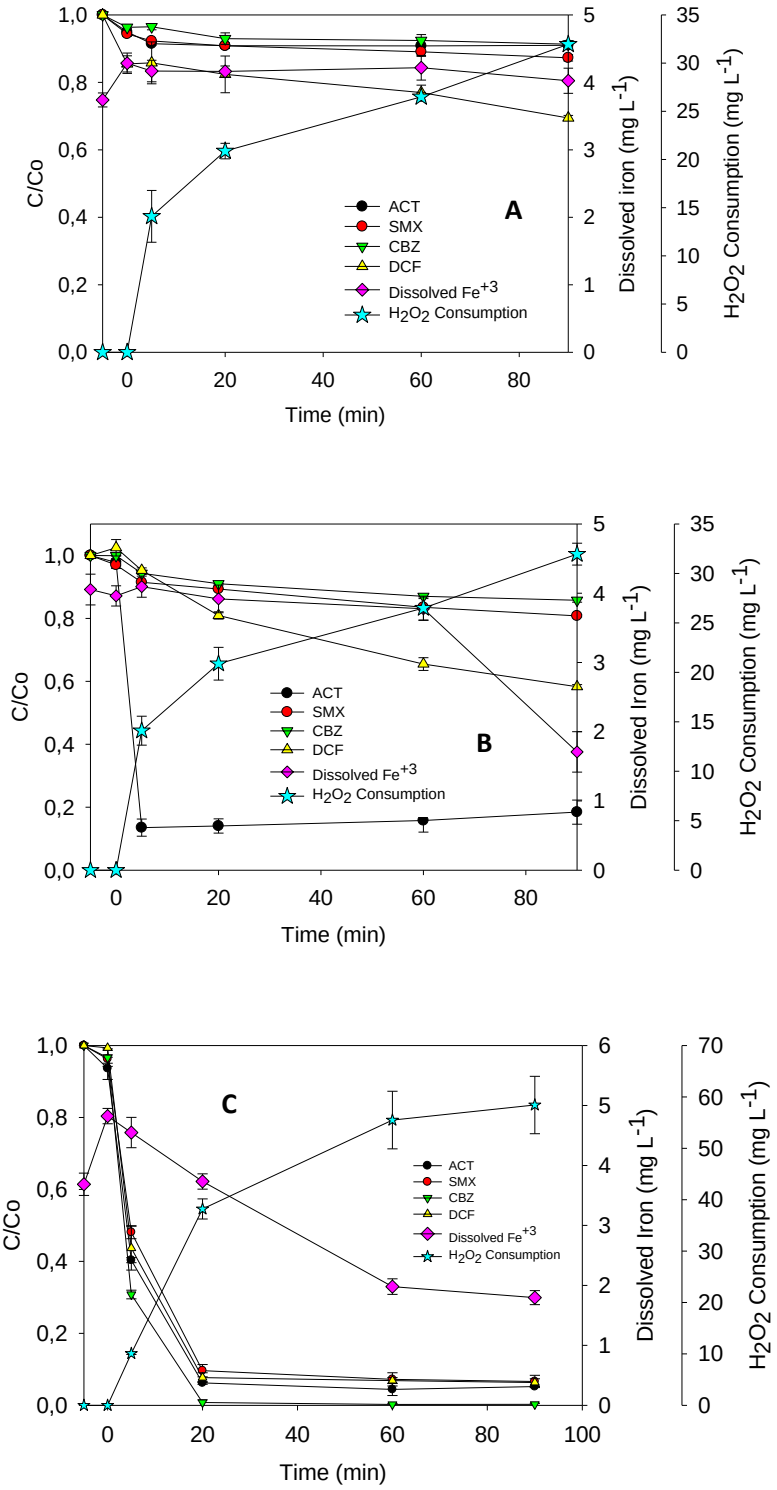


Figure 12. Treatment of the pharmaceuticals mix in distilled water by SPF at natural pH in presence of extracts. A. COFE. B. CANE. C. COPE. Molar ratio Fe:extract = 1:0.16. $[Fe^{+3}]_o$ = 5 mg L^{-1}. $[Pharm]_o$ = 0.0066 mM. $[H_2O_2]_o$ = 100 mg L^{-1}. pH ≅ 6.2

4.3.3 Pharmaceuticals degradation enhancement by COPE during SPF at natural pH

To better understand the enhancing role, initially, it was evaluated the individual degradation of ACT, DFC, SMX and CBZ at a fixed concentration of COPE (Fe:COPE = 1:0.16). The pharmaceuticals degradation followed a pseud-first order kinetics and their corresponding rate constants (k) were established. Furthermore, the ratio (ρ) between k values with and without COPE was calculated (Table 8). It can be noted that for the four pharmaceuticals ρ is much higher than one, indicating that COPE presence is a big accelerator factor.

Table 8. Pseudo-first order kinetic constants - *k* - (s^{-1}) for individual degradation of the pharmaceuticals by SPF at natural pH with or without COPE.

Pharmaceutical	SPF with individual pharmaceuticals				
	k With COPE	**R^2**	**k Without COPE**	**R^2**	**$\rho = \left(\frac{k_{with}}{k_{without}}\right)$**
ACT	0.88	0.99	0.0060	0.99	146.67
SMX	0.49	0.99	0.0080	0.99	61,25
CBZ	0.84	0.99	0.0091	0.99	92,31
DCF	0.81	0.99	0.0239	0.99	33,89

Conditions: $[Fe^{+3}]_o$ = 5 mg L^{-1}. $[Pharm]_o$ = 0.0066 mM. $[H_2O_2]_o$ = 100 mg L^{-1}. Fe:COPE = 1:0.16.

COPE showed that it is capable of maintaining dissolved iron and therefore the SPF process can be carried out at pH = 6, generating $OH^{\cdot}$ radicals. Specifically, as indicated in Chapter 1, photo-Fenton process generates the non-selective hydroxyl radicals ($OH^{\cdot}$, Eqs. 1.5-1.6). Hence, the principal route of degradation for CBZ and ACT is associated to action of $OH^{\cdot}$. In fact, for CBZ, it is reported a by-product (9-formylacridine-10(9H)-carboxamide) formed from a hydroxylation in the non-

aromatic double bond of carbamazepine (Alharbi et al., 2017). Interestingly, according to table 8, SMX is the pharmaceutical with the slowest kinetics when SPF with COPE is applied. This behavior can be attributed to the SMX degradation by-products (generated when OH radicals attack by-products formed from breaking of sulfonamide bond) also compete for these radicals (Alharbi et al., 2017).

After individual degradation, the pharmaceuticals mix in distilled water was subjected to SPF at natural pH with different amounts of COPE (Figure 13). In addition to SPF, photolysis and light plus COPE were tested. As seen, the sunlight action removed ~22% of initial pharmaceuticals load at 90 min. In this case, degradation of DCF is the main responsible of this achievement (according to the following of individual concentration results do not showed in this thesis), DCF is easily photolyzable thanks its ability to absorbs light between 254 and 290 nm (Alharbi et al., 2017; De la Cruz et al., 2013; Gonzalez-Gil et al., 2019).

To investigate the possible formation of reactive oxygen species (ROS) from COPE photolysis, the experiment in presence of the fruit extract and solar light was carried out. When the sunlight is combined with COPE, after 90 min of treatment, the pharmaceuticals removal was the same than obtained by photolysis with sunlight alone. This suggests that COPE did not act as a photosensitizer for pharmaceuticals degradation (Porras et al., 2016). From Figure 13 it can be also noted that SPF efficiency for degradation of the pharmaceuticals increased as the COPE amount rose up.

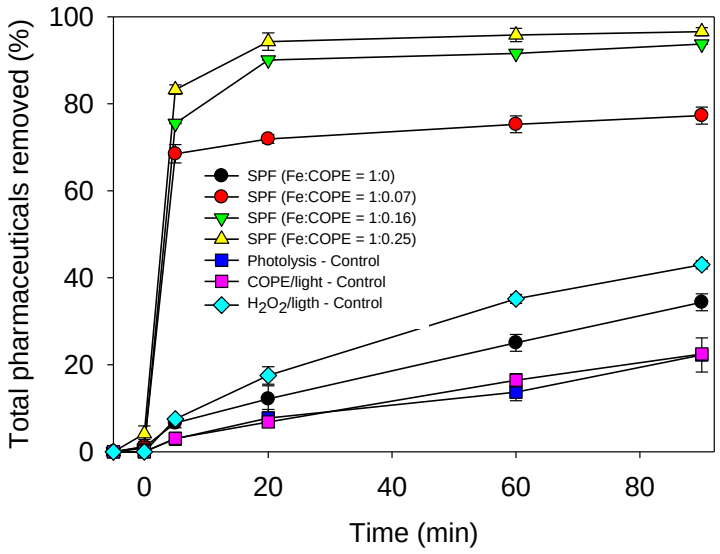


Figure 13. SPF at natural pH applied to elimination of pharmaceuticals mix in distilled water. $[Fe^{+3}]_o$ = 5 mg L^{-1}. $[Pharm]_o$ = 0.0066 mM. $[H_2O_2]_o$ = 100 mg L^{-1}, pH near to 6.2.

The positive effect of extract concentration was related to the ability of COPE to act as complexing agent of iron, allowing to the process occurs at pH 6. To demonstrate this hypothesis, the dissolved iron and H_2O_2 consumption were measured during the SPF processes. Figure 14 shows that both the iron in solution and hydrogen peroxide consumption were higher as COPE amount increased. In fact, in presence of the highest COPE, 80% of the initial iron remained in solution during the whole experiment. On the contrary, in absence of COPE more than 95% of iron was quickly precipitated. Regarding H_2O_2 consumption increasing when COPE was increased, this is caused by the higher availability of iron species, which react with H_2O_2 and produce more hydroxyl radicals.

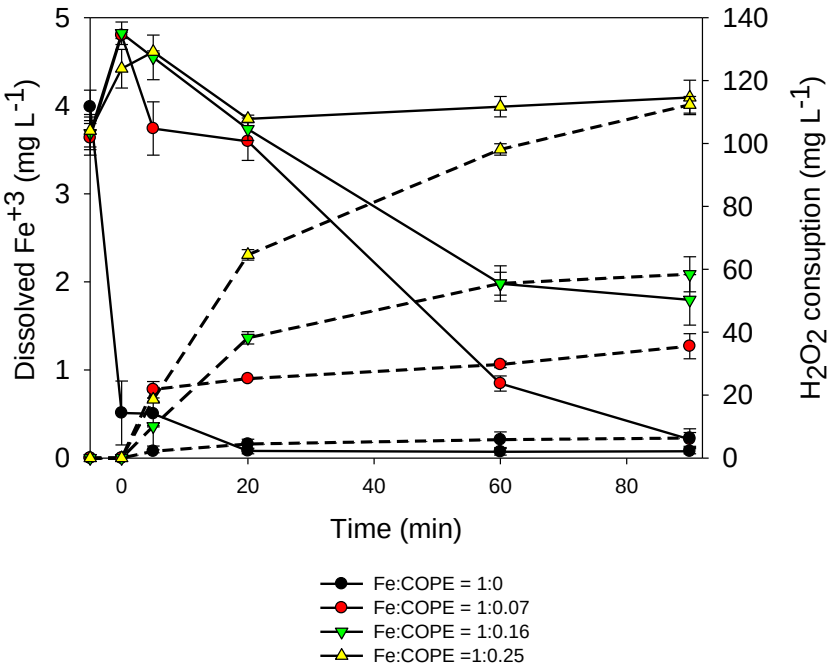


Figure 14. Behavior of dissolved iron and H_2O_2 consumption during SPF at natural pH with COPE in different molar relations Fe^{+3} : COPE. (–): Dissolved Fe^{+3} and (----): H_2O_2 consumption. $[Fe^{+3}]_o$ = 5 mg L^{-1}. $[Pharm]_o$ = 0.0066 mM. $[H_2O_2]_o$ = 100 mg L^{-1}

Finally, the SPF process in presence of COPE was evaluated for the treatment of raw municipal wastewater spiked with the representative pharmaceuticals. In this case, the initial concentration of iron (III) was 5 or 8 mg L^{-1}. Total removal of pharmaceuticals and consumption of hydrogen peroxide plus iron evolution were followed (Figure 15). With the increasing of the initial concentration of iron the percentage of pharmaceuticals removal as well as peroxide consumption increased. Remarkably, high pollutants removals (>75%) were achieved during the first 20 min of treatment, when more iron remained dissolved.

Naturally, the presence of other organic and inorganic components in MWW competed by the radicals decreasing the pharmaceuticals elimination compared to degradation in distilled water (Figures 15 and 13 respectively). However, the

pollutants removal higher than 75% by SPF in presence of COPE, evidenced the high potentiality of this process to treat pharmaceuticals in raw MWW.

Likewise, an increase in the initial TOC concentration of MWW causes a decrease in the extent of the degradation. This result, which was expected, is relevant when considering a real application of the photo Fenton process improved with COPE for the MWW from Florencia. This is important considering the permanent fluctuations in the TOC concentration, which occurs in the MWW that flows through the city sewer system.

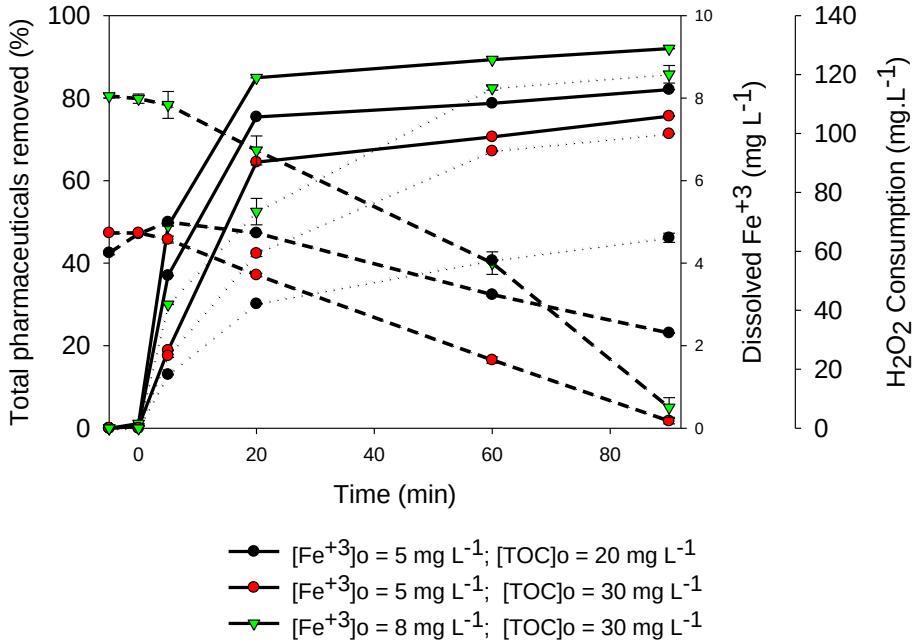


Figure 15. SPF at natural pH of MWW with the four pharmaceuticals mix with COPE with different initial TOC. (–) Total pharmaceuticals removal; (---) Dissolved Fe^{+3} and (….) H_2O_2 consumption. [Pharm]o = 0.0066 mM. Fe^{+3}:COPE = 1:0.16 and $[H_2O_2]_o$ = 120 mg L^{-1}

4.4 Conclusions of this Chapter

The application of SPF to degrade the representative pharmaceuticals in distilled water led to a moderate removal of pollutants due to limitations in the iron availability. The addition of Amazonian fruit extracts (COFE, CANE and COPE) increased the dissolved iron, although only COPE improved significantly the degradation of the pharmaceuticals by SPF at natural pH (~6.0). This as result of the COPE ability to keep iron in solution (possibly by complexation with organic acids and phenolic compounds present in the extract). Interestingly, the treatment of the target pollutants in MWW reached degradations > 75%. It can be remarked that this work shows for the first time, the use of Amazonian fruits to improve the efficiency of photo-Fenton at near neutral pH to remove pharmaceuticals in MWW.

The potential of this process and future applications in MWWTP of Florencia were also evidenced in this chapter. Therefore, further studies considering all aspects of the full-scale application of the technology should be carried out. The use of Amazonian fruit extracts, as a promising way to improve the photo-Fenton efficiency, is of particular interest for the Caquetá region because of the new opportunities that it opens toward the valorization of the agro-industrial wastes.

References

Abdel-Daim, M., Abushouk, A. I., Reggi, R., Yarla, N. S., Palmery, M., & Peluso, I. (2018). Association of antioxidant nutraceuticals and acetaminophen (paracetamol): Friend or foe? *Journal of Food and Drug Analysis*, *26*(2), S78–S87. https://doi.org/10.1016/j.jfda.2017.11.004

Alharbi, S. K., Kang, J., Nghiem, L. D., van de Merwe, J. P., Leusch, F. D. L., & Price, W. E. (2017). Photolysis and UV/H_2O_2 of diclofenac, sulfamethoxazole, carbamazepine, and trimethoprim: Identification of their major degradation products by ESI–LC–MS and assessment of the toxicity of reaction mixtures. *Process Safety and Environmental Protection*, *112*, 222–234.

https://doi.org/10.1016/j.psep.2017.07.015

APHA, AWWA, & WEF. (2012). *Standard Methods for the Examination of Water and Wastewater*. (E. W. Rice, R. B. Baird, A. D. Eaton, & L. S. Clesceri, Eds.) (22nd ed.). Washington D.C.

De la Cruz, N., Esquius, L., Grandjean, D., Magnet, A., Tungler, A., de Alencastro, L. F., & Pulgarín, C. (2013). Degradation of emergent contaminants by UV, UV/H_2O_2 and neutral photo-Fenton at pilot scale in a domestic wastewater treatment plant. *Water Research*, *47*(15), 5836–5845. https://doi.org/10.1016/j.watres.2013.07.005

Fazary, A. E., Taha, M., & Ju, Y. H. (2009). Iron complexation studies of gallic acid. *Journal of Chemical and Engineering Data*, *54*(1), 35–42. https://doi.org/10.1021/je800441u

Genaro-Mattos, T. C., Maurício, Â. Q., Rettori, D., Alonso, A., & Hermes-Lima, M. (2015). Antioxidant activity of Caffeic acid against iron-induced free radical generation-A chemical approach. *PLoS ONE*, *10*(6), 1–12. https://doi.org/10.1371/journal.pone.0129963

Gonzalez-Gil, L., Krah, D., Ghattas, A.-K., Carballa, M., Wick, A., Helmholz, L., … Ternes, T. A. (2019). Biotransformation of organic micropollutants by anaerobic sludge enzymes. *Water Research*, *152*, 202–214. https://doi.org/https://doi.org/10.1016/j.watres.2018.12.064

Heeger, A., Kosińska-Cagnazzo, A., Cantergiani, E., & Andlauer, W. (2017). Bioactives of coffee cherry pulp and its utilisation for production of Cascara beverage. *Food Chemistry*, *221*, 969–975. https://doi.org/10.1016/j.foodchem.2016.11.067

Martínez-costa, J. I., Rivera-utrilla, J., Leyva-ramos, R., & Sánchez-polo, M. (2018). Journal of Photochemistry and Photobiology A : Chemistry Individual and simultaneous degradation of the antibiotics sulfamethoxazole and trimethoprim in aqueous solutions by Fenton , Fenton-like and photo-Fenton processes using solar and UV radiations. *"Journal of Photochemistry & Photobiology, A: Chemistry," 360*, 95–108. https://doi.org/10.1016/j.jphotochem.2018.04.014

Miralles-Cuevas, S., Oller, I., Sánchez Pérez, J. A., & Malato, S. (2014). Removal of pharmaceuticals from MWTP effluent by nanofiltration and solar photo-Fenton using two different iron complexes at neutral pH. *Water Research*, *64*, 23–31. https://doi.org/10.1016/j.watres.2014.06.032

Nogueira, R., Oliveira, M., & Paterlini, W. (2005). Simple and fast spectrophotometric determination of H2O2 in photo-Fenton reactions using metavanadate. *Talanta*, *66*(1), 86–91. https://doi.org/10.1016/j.talanta.2004.10.001

Pang, C., Zheng, Z., Shi, L., Sheng, Y., Wei, H., Wang, Z., & Ji, L. (2016). Caffeic acid prevents acetaminophen-induced liver injury by activating the Keap1-Nrf2 antioxidative defense system. *Free Radical Biology and Medicine*, *91*, 236–246. https://doi.org/10.1016/j.freeradbiomed.2015.12.024

Papoutsakis, S., Pulgarin, C., Oller, I., Sánchez-Moreno, R., & Malato, S. (2016). Enhancement of the Fenton and photo-Fenton processes by components found in wastewater from the industrial processing of natural products: The possibilities of cork boiling wastewater reuse. *Chemical Engineering Journal*, *304*, 890–896. https://doi.org/10.1016/j.cej.2016.07.021

Pinto, L. K. A., Da Silva, B. F., Spadoto, M., Botta, C. M. R., & Azevedo, E. B. (2019). Which route to take for diclofenac removal from water: Hydroxylation or direct photolysis? *Journal of Photochemistry and Photobiology A: Chemistry*, *382*(April), 111879. https://doi.org/10.1016/j.jphotochem.2019.111879

Porras, J., Bedoya, C., Silva-Agredo, J., Santamaría, A., Fernández, J. J., & Torres-Palma, R. A. (2016). Role of humic substances in the degradation pathways and residual antibacterial activity during the photodecomposition of the antibiotic ciprofloxacin in water. *Water Research*, *94*, 1–9. https://doi.org/10.1016/j.watres.2016.02.024

Salaeh, S., Juretic Perisic, D., Biosic, M., Kusic, H., Babic, S., Lavrencic Stangar, U., … Loncaric Bozic, A. (2016). Diclofenac removal by simulated solar assisted photocatalysis using TiO_2-based zeolite catalyst; mechanisms, pathways and environmental aspects. *Chemical Engineering Journal*, *304*, 289–302. https://doi.org/10.1016/j.cej.2016.06.083

Sentkowska, A., & Pyrzynska, K. (2018). Investigation of antioxidant interaction between Green tea polyphenols and acetaminophen using isobolographic analysis. *Journal of Pharmaceutical and Biomedical Analysis*, *159*, 393–397. https://doi.org/10.1016/j.jpba.2018.07.029

Villegas-Guzman, P., Giannakis, S., Torres-Palma, R. A., & Pulgarin, C. (2017). Remarkable enhancement of bacterial inactivation in wastewater through promotion of solar photo-Fenton at near-neutral pH by natural organic acids. *Applied Catalysis B: Environmental*, *205*, 219–227. https://doi.org/https://doi.org/10.1016/j.apcatb.2016.12.021

CHAPTER 5. SEQUENTIAL COMBINATION OF BIOLOGICAL PROCESSES WITH SPF AT NATURAL pH: LAB-SCALE TREATMENT OF RAW MWW FROM FLORENCIA

5.1 Introduction

In the previous chapter the viability of the enhancement of SPF performance by COPE was demonstrated. Also, in the Chapter 3, the ability of the biological processes to remove biodegradable organic matter was shown. Then, in this chapter the action of both systems (SPF with COPE plus biological treatments) was conjugated. Herein, it was evaluated the combination of processes for treating a raw MWW (which intrinsically contains ACT, CBZ, SMX and DFC) from Florencia-Caquetá. Initially, the two strategies of processes combination at laboratory scale were tested: 1) biological (aerobic or anaerobic) treatment as the first stage and SPF as the subsequent process; 2) SPF followed by the biological (aerobic or anaerobic) treatment. Afterwards, the most convenient configurations were identified.

5.2 Materials and methods

5.2.1 Chemicals

The information about pharmaceuticals, iron, hydrogen peroxide, solvents for HPLC analyses is the same provided in Chapter 2. The COPE (copoazu extract) was obtained as indicated in Chapter 4.

In this part of the thesis, it was used raw MWW (which intrinsically contained the representative pharmaceuticals, ACT, SMX, CBZ and DCF at 262.52, 6.37, 1.86 and 12.77 µg L^{-1}, respectively). This MWW was used to all experiments with different combination of processes (aerobic/SPF, SPF/aerobic, anaerobic/SPF and SPF/anaerobic).

5.2.2 Experimental set up

For solar photo-Fenton in presence of COPE (SPF process), a solar box (characteristics previously detailed in the Chapter 4) was used as light source. The iron and COPE solutions were added to photo-reactor (a glass beaker containing a 1.0 L of water sample) and homogenized during 5 min. Then, H_2O_2 was added to the reactor and the light was switched on. The degradation conditions were: $[Fe^{3+}]$ = 5 mg L^{-1}; Fe:COPE = 1:0.16; $[H_2O_2]$ = 68 mg L^{-1}. Reaction time was 3 h.

Biological processes were applied during 48 h to water samples (0.5 L), under the experimental conditions detailed in the Chapter 3.

5.2.3 Analyses

Evolution of the pharmaceuticals during the treatments was followed by HPLC-MS technique as it is reported in chapter 2.

The changes in the content of organic matter (TOC) were determined by measure through a TOC analyzer following the methodology described in the Chapter 2.

5.3 Results and discussion

5.3.1 Sequential combination of aerobic biological process with SPF (aerobic/SPF)

To establish the best order of the process combinations for treating the raw MWW from Florencia-Caquetá, the configurations: biological process followed by the AOP and the AOP followed by biological process were evaluated. Tables 9-10 present the removed amount (in µg) by the two configurations for the aerobic system. From aerobic process/SPF combination, it was found that the biological process initially removed part ACT, SMX and DFC (which represents removals of 99,95%, 98.67% and 81.72%, respectively), but in the case of CBZ, this pharmaceutical was not bio-degraded; instead of this, its amount was increased after the aerobic treatment (as indicated by the negative value of the removed amount, Table 9).

The pharmaceuticals removal is according to the results presented in Chapter 3 and literature (Giannakis et al., 2015), where it was indicated that ACT, SMX and DFC are susceptible to biotransformations. In the case of CBZ, its response could be attributed to desorption of such compound from sludge. CBZ has demonstrated a high adsorption on sludges as reported in Chapter 3 and previous works (Delgado, Marino, & Ronco, 2018; Huang et al., 2019; Kårelid, Larsson, & Björlenius, 2017; Martínez-Hernández et al., 2016; Wang & Wang, 2016). Also, it should be considered that aerobic sludge was cultivated with raw MWW, this implies an initial CBZ concentration in the sludge before to experiments, thus, an adsorption during acclimatization of microorganism and a posterior desorption (during treatment) could explain the results for carbamazepine. After aerobic treatment, the SPF process caused the degradation of all the remaining target pharmaceuticals present in MWW.

When the AOP was performed previous the aerobic process (i.e., SPF/Aerobic process configuration), the SPF system induced degradations of the four representative pollutants higher than 93% of the initial charge of them (ACT: 98.6%, SMX: 98.1%, CBZ: 93% and DCF: 99.9%) (Table 10). Then, it could be affirmed that

the biological processes completed removal of the small amounts of the pharmaceuticals remaining in the resultant MWW from the AOP.

A comparison between aerobic/SPF and SPF/aerobic configurations for treatment of raw MWW from Florencia-Caquetá reveals that both combinations favored a higher total removal of the target combination of pollutants (see Tables 9-10). Indeed, if the SPF is first in the combination, pharmaceuticals degradation is increased to more than biodegradation by the microorganisms in aerobic process and additionally, the sorption of some pharmaceuticals as CBZ on sludge is avoid.

Table 9. Removal of the representative pharmaceuticals by the *aerobic process/SPF* configuration.

Initial amount (µg)				
	ACT	**SMX**	**CBZ**	**DCF**
Raw MWW	131.26	3.19	0.93	6.4
Removed amount (µg)				
Processes order	**ACT**	**SMX**	**CBZ**	**DCF**
Aerobic	131.19	3.14	-3.38	5.21
SPF	0.12	0.01	5.55	1.77
Total removal	**131.31**	**3.15**	**2.17**	**6.98**

Table 10. Removal of the representative pharmaceuticals by the *SPF/aerobic and SPF/anaerobic process* configuration.

Initial amount (µg)				
	ACT	**SMX**	**CBZ**	**DCF**
Raw MWW	262.52	6.37	1.86	12.77
Removed amount (µg)				
Processes order	**ACT**	**SMX**	**CBZ**	**DCF**

SPF	258.73	6.25	1.73	12.65
Aerobic/Anaerobic	NM	NM	NM	NM
Total removal	**--**	**--**	**--**	**--**

NM : Not measured

5.3.2 Sequential combination of anaerobic biological process with SPF

In an analogous way to the developed in section 5.3.1, the effect of the order of the sequential combination was tested for the anaerobic process. Tables 11-12 show the removed amount (in µg) by the two configurations. For the anaerobic/SPF configuration, the biological component partially removed the pharmaceuticals. In contrast to the observed for the aerobic process, CBZ was removed by anaerobic treatment. This response was related to characteristics of sludge (this was taken from septic tank used to treat domestic wastewater from a farm), which did not reach CBZ adsorption-desorption equilibrium since the sludge did not have CBZ before acclimatization (Gonzalez-Gil et al., 2019; Martínez-Hernández et al., 2016). On the other hand, SPF complemented the degrading action (specially for ACT and SMX).

It was observed an increment of concentration to CBZ during SPF process in spite of kept dissolved iron at least to first 20 min of reaction (data not shown). This behavior could be associated with a destabilization of sludge granules and subsequent pharmaceutical release. Then, an elimination of the compound by SPF is difficult due to the competition generated by COPE and organic matter from sludge granules by the radicals produced in this process. Regarding, the SPF/anaerobic system configuration, as mentioned in the previous section, that SPF led to a high pollutants degradation, achieving removals >93%. Then, it could be expected the biological system was able to remove the few µg of the pollutants remaining after the SPF application.

Similar to the observed for combinations with the aerobic process, for the anaerobic process, the configuration where the AOP is in the first place, favors slightly more the target pharmaceuticals elimination. This could be associated to the high ability

of the applied SPF to produce radicals, which is reflected in a high degradation of the pharmaceuticals even in a complex matrix as raw MWW. Here, it is interesting to note that the biological processes worked well with the resultant solution from SPF, suggesting the AOP did not generate toxic products for the microorganisms (Oller, Malato, & Sánchez-pérez, 2011; Ponce-Robles, Millares-Cuevas, et al., 2017)
.

Table 11. Removal of the representative pharmaceuticals by the *anaerobic process/SPF* configuration.

Initial amount (µg)				
	ACT	**SMX**	**CBZ**	**DCF**
Raw MWW	131.26	3.19	0.93	6.4
Removed amount (µg)				
Processes order	**ACT**	**SMX**	**CBZ**	**DCF**
Anaerobic	116.51	1.94	0.81	5.23
SPF	27.02	2.20	-0.56	0.0
Total removal	**143.53**	**4.14**	**0.25**	**5.23**

In addition to the removal of the target pollutants, the TOC elimination by the four configurations was determined (Table 12). It can be noted that when the SPF is applied after biological process there was not mineralization; indeed, the content of organic matter is increased (as indicated by the negative value for TOC removal percentage). This is associated to the addition of COPE in SPF system, which increased the TOC content. In the opposite case, when the AOP was initially placed in the combinations, an effective removal of the organic matter was found, and the biological processes also removed some portion of TOC. As the main components of COPE are biodegradable substances (Pereira, Abreu, & Rodrigues, 2018; Rogez et al., 2004), the water initially treated by SPF has organic matter from COPE susceptible to biotransformation. These results also support the convenience of the AOP/biological process configurations for treating the MWW from Florencia-Caquetá.

Table 12. TOC removal for the combination of processes.

Process combination	Systems	TOC removal (%)	Total removal (%)
Aerobic/SPF	Aerobic	80.06	**16.72**
	SPF	-335.16	
SPF/aerobic	SPF	-41.38	**56.12**
	Aerobic	77.27	
Anaerobic/SPF	Anaerobic	61.11	**-26.25**
	SPF	-225.03	
SPF/anaerobic	SPF	-41.38	**-8.38**
	Anaerobic	60.54	

5.4 Conclusions of this chapter

The combination of SPF (in presence of COPE) with biological processes in different orders of application for the treatment of raw MWW showed that the combinations where the AOP was in the first stage, showed higher efficiencies for elimination of the pharmaceuticals and TOC removal. In general, the SPF as a second stage provides extra organic matter from COPE which increases TOC at the final of the processes; hence, it is recommended in future works to optimize the dose of COPE in order to have an enhanced efficiency of the AOP with a limited contribution to TOC. Thus, a combination at pilot-scale involving SPF followed by the anaerobic process could be a favorable configuration to treat the MWW of Florencia (Colombia).

References

Chavaco, L. C., Arcos, C. A., & Prato-Garcia, D. (2017). Decolorization of reactive dyes in solar pond reactors : Perspectives and challenges for the textile industry. *Journal of Environmental Management*, *198*, 203–212. https://doi.org/10.1016/j.jenvman.2017.04.077

Delgado, N., Marino, A. N. D., & Ronco, G. A. P. A. (2018). Removal of pharmaceuticals and personal care products from domestic wastewater using rotating biological contactors. *International Journal of Environmental Science and Technology*, (0123456789). https://doi.org/10.1007/s13762-018-1658-2

Giannakis, S., Franco, A., Vives, G., & Grandjean, D. (2015). Effect of advanced oxidation processes on the micropollutants and the ef fl uent organic matter contained in municipal wastewater previously treated by three different secondary methods. *Water Research*, *84*, 295–306. https://doi.org/10.1016/j.watres.2015.07.030

Giménez, J., Bayarri, B., González, Ó., Malato, S., Peral, J., & Esplugas, S. (2015). Advanced Oxidation Processes at Laboratory Scale: Environmental and Economic Impacts. *ACS Sustainable Chemistry and Engineering*, *3*(12), 3188–3196. https://doi.org/10.1021/acssuschemeng.5b00778

Gonzalez-Gil, L., Krah, D., Ghattas, A.-K., Carballa, M., Wick, A., Helmholz, L., … Ternes, T. A. (2019). Biotransformation of organic micropollutants by anaerobic sludge enzymes. *Water Research*, *152*, 202–214. https://doi.org/https://doi.org/10.1016/j.watres.2018.12.064

Grisales, C. M., Salazar, L. M., & Garcia, D. P. (2018). Treatment of synthetic dye baths by Fenton processes: evaluation of their environmental footprint through life cycle assessment. *Environmental Science and Pollution Research*. https://doi.org/10.1007/s11356-018-2757-9

Guinée, J., Gorree, M., Heijungs, R., Huppes, G., Kleijn, R., Haes, H., & Voet, E. (2001). *Life cycle assessment An operational guide to the ISO standards*.

Huang, Y., Guo, J., Yan, P., Gong, H., & Fang, F. (2019). Sorption-desorption behavior of sulfamethoxazole, carbamazepine, bisphenol A and 17A-ethinylestradiol in sewage sludge. *Journal of Hazardous Materials*, *368*(January), 739–745. https://doi.org/10.1016/j.jhazmat.2019.01.063

Ioannou-Ttofa, L., Foteinis, S., Chatzisymeon, E., Michael-Kordatou, I., & Fatta-Kassinos, D. (2017). Life cycle assessment of solar-driven oxidation as a polishing step of secondary-treated urban effluents. *Journal of Chemical Technology and Biotechnology*, *92*(6), 1315–1327.

https://doi.org/10.1002/jctb.5126

Kårelid, V., Larsson, G., & Björlenius, B. (2017). Pilot-scale removal of pharmaceuticals in municipal wastewater: Comparison of granular and powdered activated carbon treatment at three wastewater treatment plants. *Journal of Environmental Management*, *193*, 491–502. https://doi.org/10.1016/j.jenvman.2017.02.042

Martínez-Hernández, V., Meffe, R., Herrera López, S., & de Bustamante, I. (2016). The role of sorption and biodegradation in the removal of acetaminophen, carbamazepine, caffeine, naproxen and sulfamethoxazole during soil contact: A kinetics study. *Science of the Total Environment*, *559*, 232–241. https://doi.org/10.1016/j.scitotenv.2016.03.131

Oller, I., Malato, S., & Sánchez-pérez, J. A. (2011). Combination of Advanced Oxidation Processes and biological treatments for wastewater decontamination — A review. *Science of the Total Environment, The*, *409*(20), 4141–4166. https://doi.org/10.1016/j.scitotenv.2010.08.061

Pereira, A. L. F., Abreu, V. K. G., & Rodrigues, S. (2018). Cupuassu— Theobroma grandiflorum. *Exotic Fruits*, *2010*, 159–162. https://doi.org/10.1016/b978-0-12-803138-4.00021-6

Ponce-Robles, L., Millares-Cuevas, S., Oller, I., Aguera, A., Trinidad-Lozano, M. J., Yuste, F. J., & Malato, S. (2017). Cork boiling wastewater treatment and reuse through combination of advanced oxidation technologies. *Environment Science Pollutant Research*, *24*, 6317–6328. https://doi.org/10.1007/s11356-016-7274-0

Rogez, H., Buxant, R., Mignolet, E., Souza, J. N. S., Silva, E. M., & Larondelle, Y. (2004). Chemical composition of the pulp of three typical Amazonian fruits: Araça-boi (Eugenia stipitata), bacuri (Platonia insignis) and cupuaçu (Theobroma grandiflorum). *European Food Research and Technology*, *218*(4), 380–384. https://doi.org/10.1007/s00217-003-0853-6

Wang, S., & Wang, J. (2016). Carbamazepine degradation by coupled to biological treatment. *Journal of Hazardous Materials*. https://doi.org/10.1016/j.jhazmat.2016.09.053

CHAPTER 6. COMBINATION OF SPF AND BIOLOGICAL PROCESS FOR THE TREATMENT OF MWW FROM FLORENCIA-CAQUETÁ AT PILOT SCALE

6.1 Introduction

In the previous chapter, it was shown the advantages of the combination of anaerobic process with SPF at lab-scale. In this one, the same combination but at pilot scale was studied. According to the above results, it was considered the order: solar-photo-Fenton (in presence of COPE, at near neutral pH) followed by the anaerobic process. For the AOP, a compound parabolic concentrator (CPC) reactor and direct solar irradiation were used, whereas for the biological process an up-flow anaerobic sludge blanket (UASB) reactor was employed. In the first part of this chapter, the starting-up and acclimatization of the anaerobic system are presented, and in the second part the treatment of MWW from Florencia-Caquetá by the combination of SPF/anaerobic process is discussed.

6.2 Material and methods

6.2.1 Chemicals and MWW sample

Target pharmaceuticals (i.e., Sulfamethoxazole, diclofenac, acetaminophen and carbamazepine) analytical grade, $Fe_2(SO_4)_3xH_2O$ (75%) and hydrogen peroxide (30% w/v) were provided by Sigma-Aldrich. Experiments were done with real MWW. Global characteristics of the MWW are presented in Table 13.

Table 13. **Global characterization of MWW used for experiments at pilot scale.**

Characteristic	Average
NO_3^- (mg L^{-1})	8.74 ± 1.23
NH_4^+ (mg L^{-1})	28.62 ± 5.67
TN (mg L^{-1})	113.35 ± 17.65
PO_4^{-3} (mg L^{-1})	0.87 ± 0.02
COD, (mg L^{-1})	287.04 ± 6.89
BOD_5 (mg L^{-1})	190.11 ± 17.89
TOC (mg L^{-1})	34.12 ± 2.56
SO_4^{-2} (mg L^{-1})	185.33 ± 3.87
Cl^- (mg L^{-1})	83.34 ± 4.23
Alkalinity (mg L^{-1})	86.56 ± 4.34
Hardness, (mg L^{-1})	119.12 ± 3.45
Conductivity (µS cm^{-1})	138.07 ± 8.67
pH	6.75 ± 0.34

6.2.2 Analytical measurements

For the pharmaceuticals, the concentration evolution was determined by the method presented in Chapter 3. Characterization of the MWW was done by applying the methodologies indicated in Chapter 2. Total organic carbon (TOC), nitrate and ammonium evolutions were measured according to the procedures mentioned in Chapter 3. Dissolved iron was measured using the ortho-phenanthroline method presented in Chapter 4. Meanwhile, hydrogen peroxide evolution was followed according to the methodology based on utilization of metavanadate proposed by Pupo-Nogueira et al. (Pupo-Nogueira, Oliveira, & Paterlini, 2005).

6.2.3 Experimental set-up

- Anaerobic biological treatment

For the anaerobic treatment an up-flow anaerobic sludge blanket (UASB) reactor was used. Such reactor had cylindric geometry (height, 165 cm; diameter 6.35 cm; working volume, 5.23 L) and was built in acrylic material. The reactor was inoculated with 1.74 L of anaerobic microorganisms (same microorganism used in Chapter 3). The UASB reactor was fed with raw MWW from Florencia-Caquetá (Colombia). The reactor had a total and volatile solid concentration of 22.5 g L^{-1} and 12.4 g L^{-1}, respectively. The specific methanogenic activity (SMA) of anaerobic sludge was determinated by Chernicharo *et al.* (Torres-Lozada & Perez, 2010) and remained between 0.043 and 0.05 g COD/g VSS d (Volatile suspended solids – VSS), a value typical for domestic wastewater digested sludge. The objective was to operate the UASB reactor in uncontrolled environmental conditions. Temperature and pH were not controlled and varied from 25 °C to 40 °C and 6.3 to 6.7, respectively. Likewise, the relative humidity during start-up and operation was no controlled and it was ranged between 70 and 84%. It must be indicated that for the utilization of the anaerobic treatment, oxygen supply was not required, small infrastructural area was needed (1 m^2) and it only requires the acidity index control to favors the production of biogas. Besides, taking into account the successful experiences regarding the use of anaerobic treatment application using UASB at real-scale for the treatment of MWW in tropical countries such as Brazil (Bhatti et al., 2014; Orozco Gaviria & Triviño Cabrera, 2014; Torres-Lozada, 2012), it is expected that this kind of reactor has good opportunities in Florencia-Caquetá.

It must be mentioned that the UASB reactor was equipped with a Gas-Liquid-Solid (GLS) separator baffle and with a gas collection funnel attached to a CO_2 neutralization tank containing a 10% NaOH solution. Methane volume is quantified with measure of displaced volume of NaOH solution when gas produced enter to neutralization tank. The MWW was fed by pumping with a peristaltic pump (Dolphin

Series model 10-brand Pulse feeder) from the bottom of the reactor as shown in Figure 16.

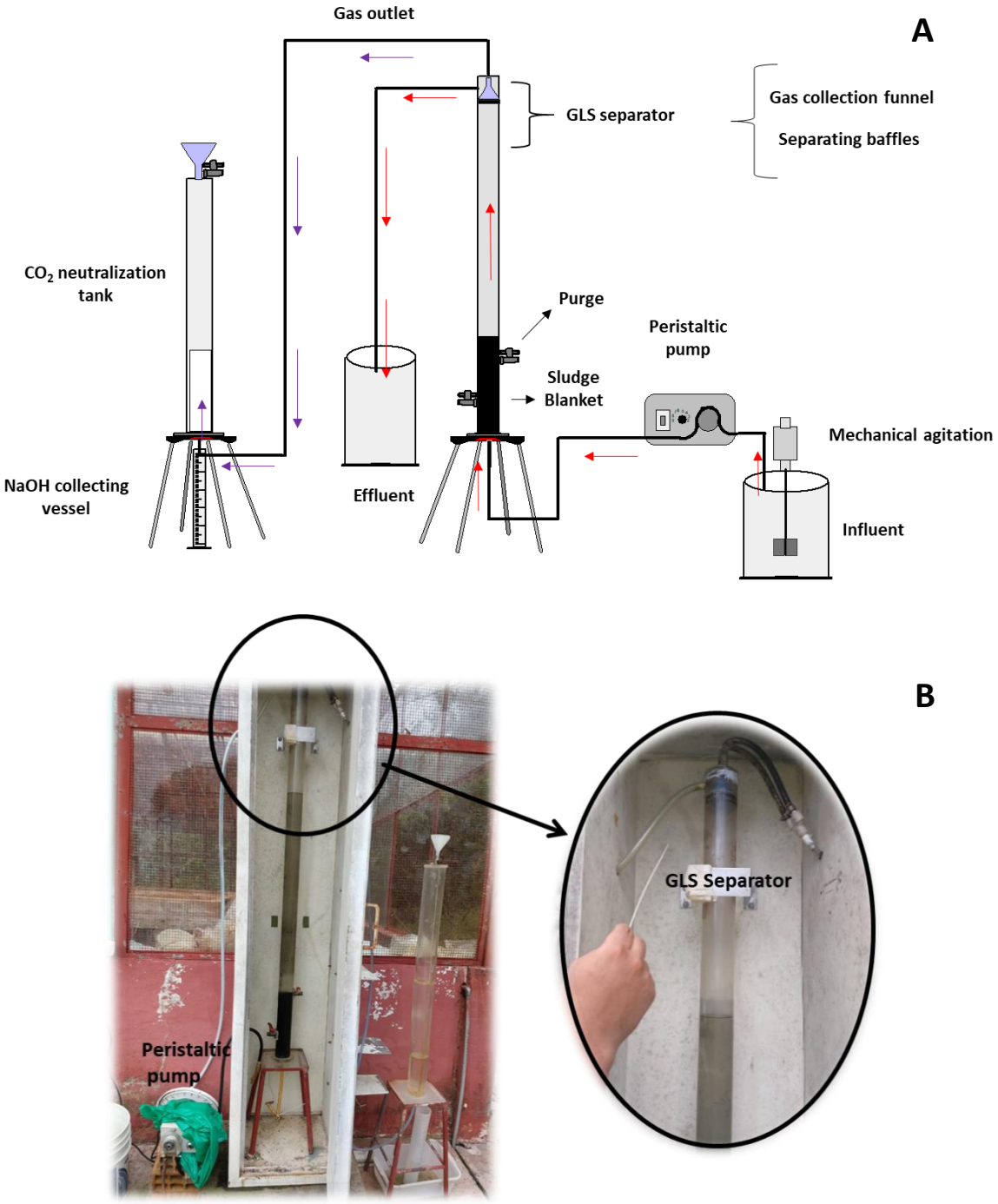


Figure 16. A. Scheme of the UASB reactor at pilot scale. **B.** Photographic record of the UASB reactor located in the Environmental Chemistry Laboratory of the Universidad de la Amazonia

- Solar pilot plant

Figure 17 schematizes the reaction system for the solar photo-Fenton process at pilot scale. The experiments of solar photo-Fenton (in presence of COPE) at near neutral pH were developed in a compound parabolic collector (CPC) reactor from Laboratory of Environmental Chemistry in Florencia-Caquetá (Colombia) (Longitude: O75°34'0.48", Latitude: N6°18'32.69") and by using direct solar radiation. The CPC reactor was composed by two modules with aluminum reflectors. Each module had 5 tubes (length 1 m and inner diameter 2.54 cm) of borosilicate placed on reflectors at center of each semi-parabola. The reactor structure was inclined with an angle equal to local latitude (<10°) and facing west. The modules were connected in series to a cylindrical recirculation tank of stainless steel (20 L of capacity). An electric pump (Pedrollo®, PK60, ½ HP) was used to recirculate at constant flow (18 L min^{-1}, the flow was turbulent) the water sample. The operation conditions of the CPC reactor were selected based on our previous works (Ramón, Amaya, & Manrique-Losada, 2013).

The reactor was operated in global batch mode by recirculation loop (figure 17A). This had a total volume of 15 L (V_T) and an illuminated volume of 10 L. Raw MWW was added to recirculation tank of the CPC unit. Then, MWW was spiked with the pharmaceuticals and homogenized during 15 min. Afterwards, Fe^{3+} and COPE were added to the tank and homogenization was performed in darkness by turbulent recirculation during 15 min. Finally, hydrogen peroxide (30% w/v) was added in excess (at 150 mg L^{-1}) and the CPC was uncovered to start the process. Solar ultraviolet radiation (UV) was measured by using a PMA2100 Dual-Input Data Logging Radiometer and accumulated energy per volume unit for the experiment was calculated trough Eq. 6.1.

$$Q_{UV,\,n} = Q_{UV,n-1} + \Delta t_n . UV_{G,n} . \frac{A_r}{V_T} \;;\quad \Delta t_n = t_n - t_{n-1} \qquad (6.1)$$

Where, $UV_{G,n}$ is the average incident UVA intensity (in W m^{-2}), Δt_n (in seconds) is the experimental time of sample, A_r (in m^2) is the illuminated area (1 m^2 in this case) and V_T (L) is the total volume of water treated (15 L in our experimental conditions).

$Q_{UV,n}$ and $Q_{UV,n-1}$ is the UV accumulated energy per volume unit (in kJ L^{-1}) at times n and n-1, respectively.

6.3 Results and discussion

6.3.1 Start-up of the anaerobic reactor at pilot scale for the treatment of MWW from Florencia

For an effective operation of the UASB reactor, a preliminary start-up stage is necessary (Bhatti et al., 2014; Cajacuri et al., 2013; Manrique-Losada et al., 2012). In this case, the initial inoculum was acclimatized because the microorganism must be adapted to the operating conditions and MWW to be treated. For this investigation, a hydraulic residence time (HRT) of 1 d was used and the evolution of the TOC at the influent and outlet of the reactor was followed. The HRT was selected according to previous results reported in literature (Orozco-Gaviria et al., 2014) and those made in this experimentation (not showed). The initial TOC of the MWW fed into the reactor fluctuated between 28 and 61 mg L^{-1} (Figure 18). This can be associated to fluctuating nature of the raw MWW. Indeed, the raw MWW results from a mixture of MWW with rainwater. Therefore, the reactor start-up stage was used to define the time where the percentage of TOC removal became stable.

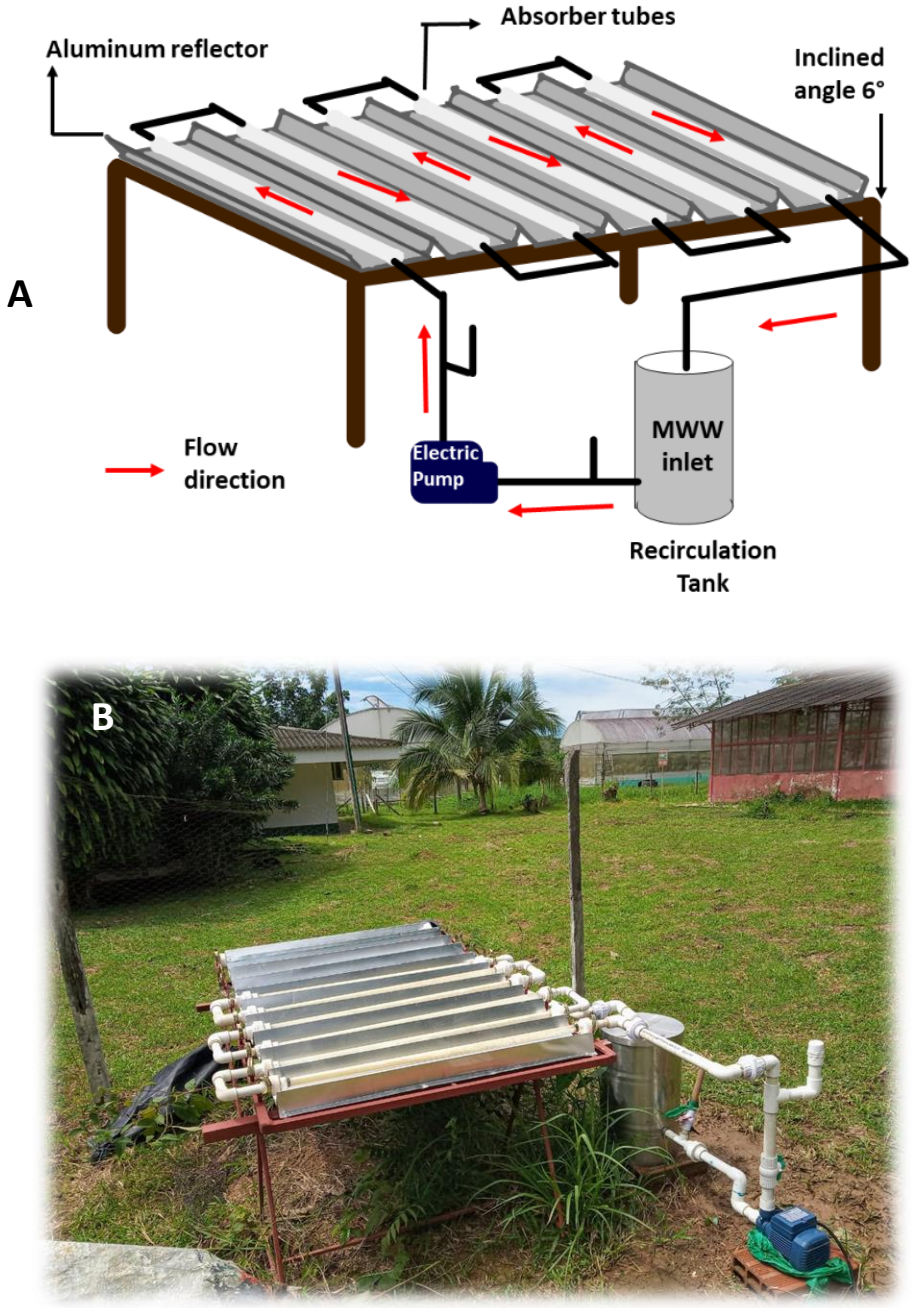


Figure 17. A. Scheme of the reactor used in the experiments at pilot-scale for the SPF process. **B.** Photographic record of the CPC reactor located in the Environmental Chemistry Laboratory of the Universidad de la Amazonia.

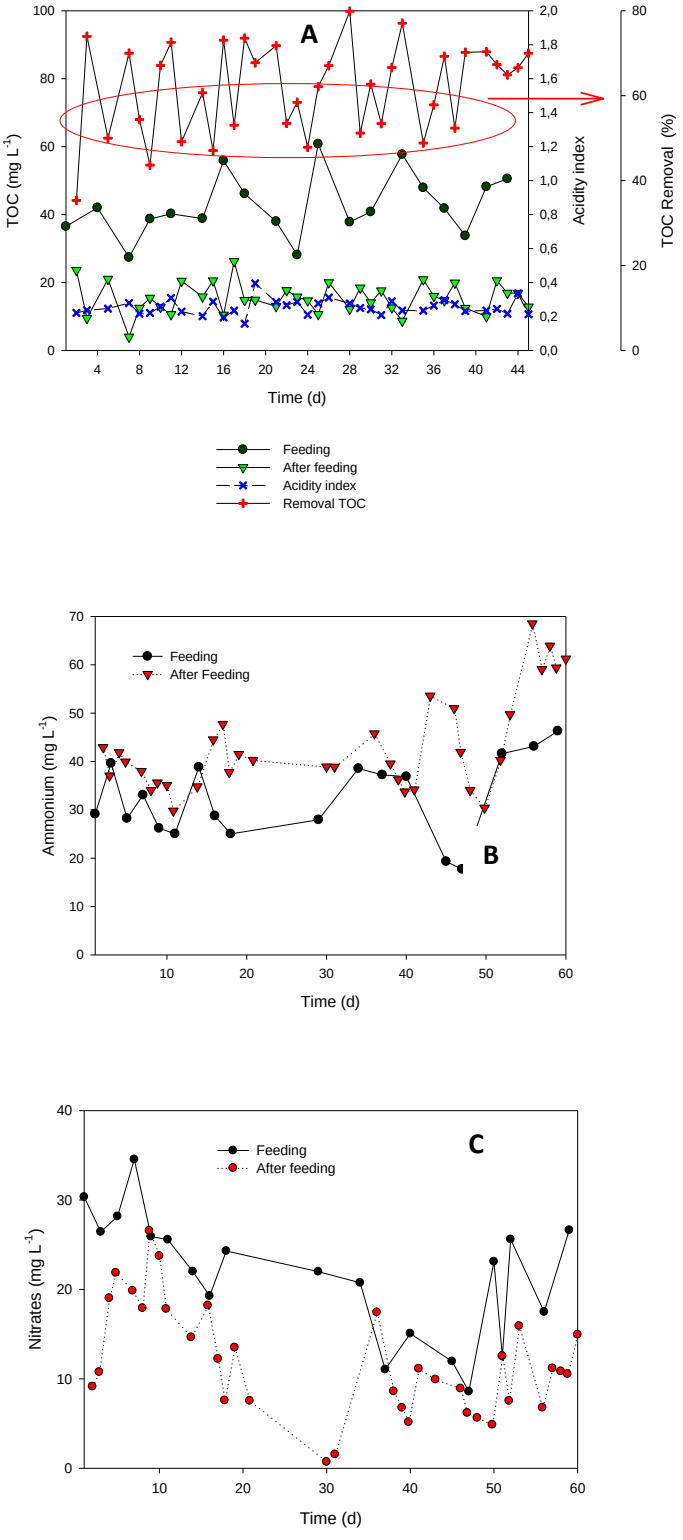


Figure 18. Evolution of TOC and acidity index (**A**), ammonium (**B**) and nitrates (**C**) during start-up of the UASB reactor.

It can be noted that throughout the reactor start-up stage, the percentage of TOC removal oscillated between 43 and 66% (percentages measured between feed and one day after feed). After 39 days, a stable removal percentage (between 65 and 70%) was observed (Figure 18A). During the start-up and course of the reactor operation acidity level was controlled with the addition of $NaHCO_3$ to favor methane production in the anoxic environment. In this way, the addition of bicarbonate maintains suitable conditions for growth of methanogenic bacteria and an acidity index <0.3 (Intermediate Alkalinity / Total Alkalinity) (Figure 18A). This limits the sulfate-reductive bacteria activity, avoiding the formation of sulfides, which tend to acidify the medium by affecting the normal buffer effect of the reactor (Lei et al., 2018).

From Figure 18B, it is observed that the concentration of ammonium increased throughout the start-up stage, suggesting that anaerobic digestion of proteins present in the raw MWW was effectively carried out. Denitrification was also present during the reactor start-up, which was evidenced by the permanent reduction of nitrates (Figure 18C). Nitrate removal is favored when C/N is high (less initial nitrate amount); then, it is likely that part of the organic matter (e.g., acetic acid) has been used as an electron donor in denitrification and the other organic carbon was occupied in the anaerobic digestion (Chong, Sen, Kayaalp, & Ang, 2012). Under the tested conditions, anaerobic digestion and denitrification were carried out.

Generation of biogas during start-up from anaerobic reactor had an average rate of 1.3 L d^{-1}, which is consistent with similar studies (Shoukat, Khan, & Jamal, 2019). The biogas production was slow because the organic matter degradation involves many steps (e.g., hydrolysis, acidogenesis) prior to methanogenesis. Additionally, the sludge acclimatization for biogas production is influenced drastically by temperature (Shoukat et al., 2019), and in the present work this parameter was not controlled (temperature intrinsically varied between 27°C and 40°C), thereby, this also determined the initial low biogas production.

Then, the next step was the evaluation of the anaerobic reactor action on MWW spiked with the four representative pharmaceuticals. Figure 19 shows the elimination of the four pharmaceuticals and mineralization during the treatment in the UASB reactor. In general, the pharmaceuticals had the same elimination trend found at the laboratory scale. Indeed, ACT is the pharmaceutical with the highest removal (88% after 72 h) and SMX, CBZ and DCF achieved removals of 51%, 33% and 27%, respectively. Likewise, the CBZ suffered mainly sorption. According to analysis made in this work of the content of pharmaceuticals in sludge, from 465.84 µg L^{-1} of CBZ removed by the process, 441 µg L^{-1} were retained in the sludge.

The main differences observed between the biological process at lab-scale and pilot-scale are due to the type of reactor. At the lab-scale, a batch reactor was implemented, in which the sludge was in contact with the MWW for 24 or 48 h under low agitation. At the pilot-scale, the UASB reactor had a continuous operation with 24 h of HRT, in which, it was guaranteed, an adequate contact between the phases and a proper feed of the MWW at the bottom of the reactor. Despite the mentioned efforts, it was difficult to reach two aspects: (i) to improve the mass transfer at lab-scale and (ii) to keep the same height:width ratio at pilot scale than the used at lab-scale. In fact, the geometry of the reaction vessel is a key element of the process, which affects the agitation patterns and the mass transfer, and its design is facilitated when the height:width ratio is the same at both scales (Stitt & Simmons, 2011). These aspects affect the kinetics of the process and consequently, longer reaction times, lower yield and lower quality of the effluent at pilot scale experiments could occur (Wood-Black, 2014).

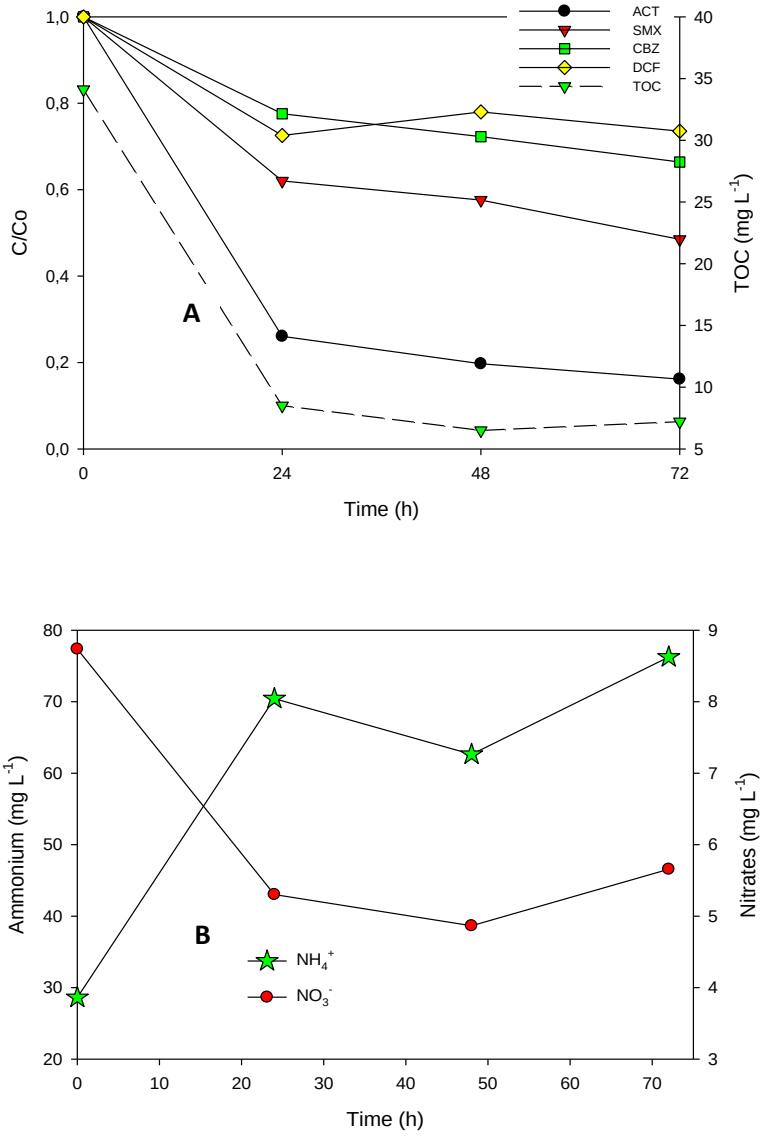


Figure 19. Treatment of MWW spiked with the pharmaceuticals in the UASB reactor. Evolution of the pharmaceuticals and TOC (A). Evolution of Ammonium and nitrate (B).

The monitoring of TOC (Figure 19A) during the three days showed that the bio-treatment always eliminated up to 79% of its initial value, despite the reactor worked at not controlled temperature (25–36°C). The effective anaerobic digestion was also demonstrated by the high increasing of ammonium concentration (from 28.6 to 76.2

mg L^{-1}) (Figure 19B). The denitrifying bacteria present in the medium also reduced nitrate to ammonium (Figure 19B). Additionally, methane production rate was approximately of 1.31 L d^{-1} (methane produced during operation of UASB was quantified by displaced NaOH solution volume in neutralization tank). Besides, the acidity index was also controlled and was kept below 0.3 guaranteeing a pH range of 6.5-7.1 to favor methanogenic environment.

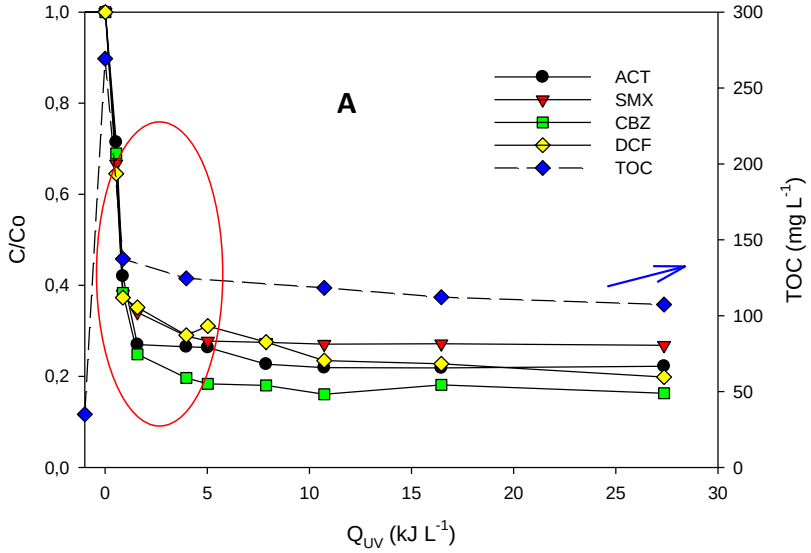
Once the UASB reactor was on operation, it was combined with the pilot-scale reactor of the SPF process (CPC). This combination was named UASB+CPC. A degradation up to 99.15%, 82.18%, 77.00%, and 81,41% of ACT, SMX, CBZ, and DCF was achieved by the combined process. Unfortunately, there was no global mineralization. The dose of H_2O_2 must be determined and Fe:COPE ratio adequate to increase removal percentages of organic matter. These results are not showed in this thesis in order to kept the attention in the final purpose of this research.

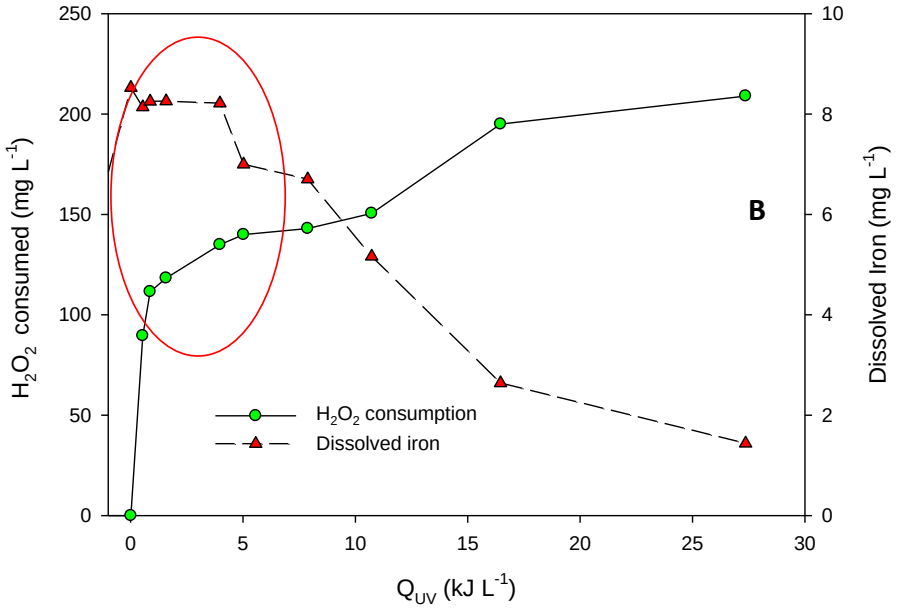
Thus, the final purpose in this thesis is a combination CPC+UASB and is developed in the next section, in which the results obtained for that combination are reported.

6.3.2 Combination of SPF with Biological treatment

Combination of SPF in presence of COPE followed by the anaerobic treatment (CPC+UASB) for treating the MWW was considered. The four pharmaceuticals SMX, ACT, DCF and CBZ were degraded up to 72%, 77%, 76% and 82%, respectively (Figure 20A). There were no significant differences between degradation of pharmaceuticals. This behavior agreed with the reported in Chapter 4. It can be noted that the SPF process required 5 kJ L^{-1} to achieve the maximum degradation of pharmaceuticals. In such level of accumulated energy also occurred the maximum consumption of H_2O_2 and a high amount of iron remained in soluble form (Figure 20B). Regarding mineralization at this first stage (i.e., in the AOP), despite the high TOC initial concentration due to COPE addition and original TOC in raw MWW (~ 34 mg L^{-1}), at the final of SPF process in the CPC reactor this parameter reached 60.16% of elimination at 8 kJ L^{-1} (during first 60 min of treatment).

COPE represented ~84% of initial TOC, which was susceptible to be attacked by hydroxyl radicals.





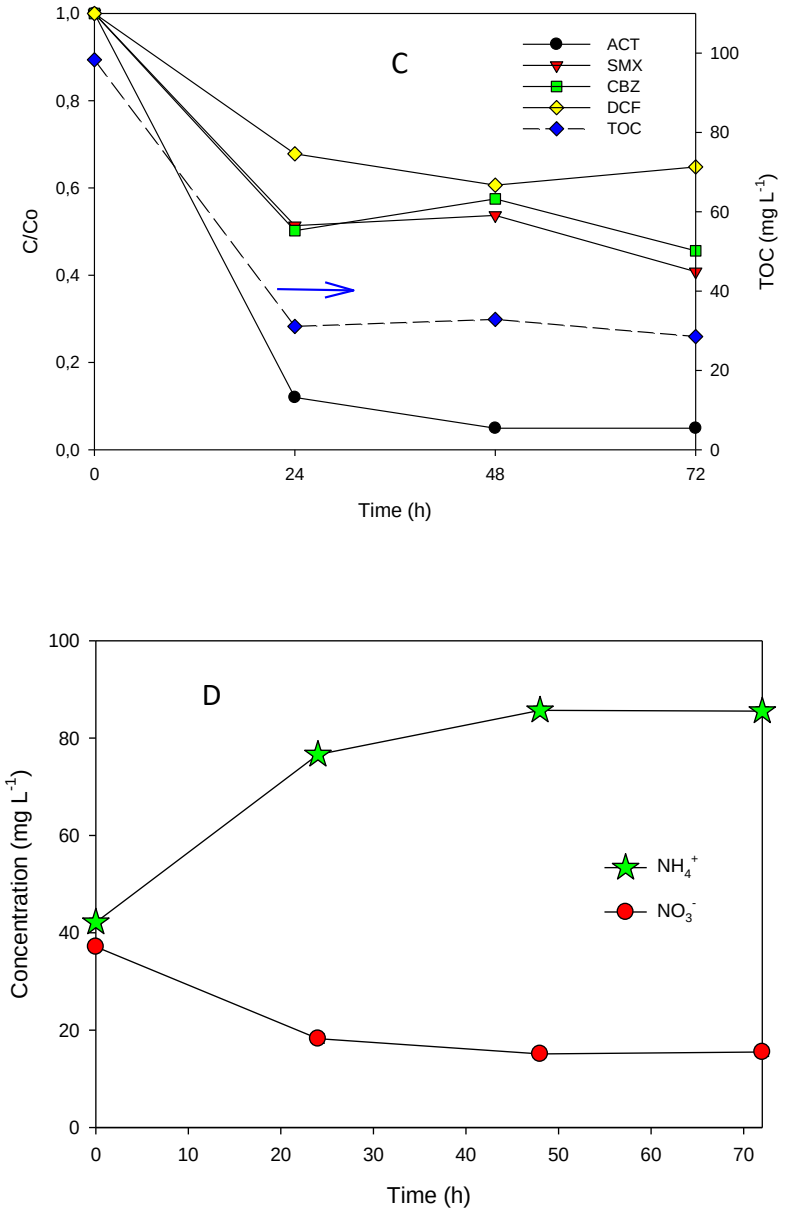


Figure 20. Combination CPC + UASB applied to MWW from Florencia-Caquetá. **A.** *First stage:* Evolution of pharmaceuticals and TOC in the CPC reactor. **B.** Evolution dissolved iron and H_2O_2 consumed during SPF with COPE in the CPC reactor. **C**. *Second stage:* Evolution of pharmaceuticals and TOC in the UASB reactor. **D**. Evolution of nitrate and ammonium during anaerobic treatment in the UASB reactor. $[Fe^{+3}]_o$ = 10 mg L^{-1}, $[H_2O_2]_o$ = 150 mg L^{-1}, Fe:COPE = 1:0.16, $[Pharmaceuticals]_o$ = 0.0066 mM.

The MWW pre-treated by the SPF process, was used to fed the UASB reactor. Such water had an initial TOC around 100 mg L^{-1}. The UASB reactor was operated in continuous mode during 72 h with an HRT of 1 day. Figure 20C shows the evolution of mineralization. Under such operational conditions, ~71% of average mineralization was recorded each day (this evidenced a stable anaerobic digestion without apparent toxicity). Interestingly, this system exhibited mineralization degrees close to typically reported as high values (80%) for UASB (Bandara et al., 2012; Chong et al., 2012; Nair & Ahammed, 2013; Orozco-Gaviria et al., 2014; Yetilmezsoy & Sakar, 2008). At this point, it can be mentioned that the microorganisms also consumed nitrates and generated ammonium (Figure 20D), which indicates the correct operation of the UASB reactor (Bandara et al., 2012; Bhatti et al., 2014; Cajacuri et al., 2013; Fernández & Seghezzo, 2015).

In the case of elimination of the remaining concentration of pharmaceuticals by the UASB reactor, Figure 20C presents the evolution of elimination when reactor was operated during 72 h with an HRT of 1 d. An average elimination percentage up to 93%, 52%, 49% and 37% of ACT, SMX, CBZ and DCF, respectively was achieved. It could be inferred that if a higher elimination of pharmaceuticals is reached (above 95% of pharmaceuticals) during SPF, it could be expected that in anaerobic process only biodegradation of residual organic matter will be carried out (Gerba & Pepper, 2014).

So, it was found that the global elimination of the pharmaceuticals by the CPC+UASB combination reached 97.93%, 81.68%, 87.34% and 79.75% for ACT, SMX, CBZ and DCF, respectively. According to these results, the CPC + UASB combination achieved high degradation of the target pharmaceuticals, but their elimination could be increased if the reactors are optimized in future researches. Indeed, if SPF is able to degrade more amount of the pharmaceuticals, the treated water that feeds the anaerobic microorganisms will have a low concentration of such pollutants, which would reduce its presence in the biological sludge (European Cooperation in Science and Thecnology, 2017; Oller, Malato, & Sánchez-pérez, 2011; Rizzo et al., 2019) .

Finally, it is important to analyze the differences, at laboratory and pilot scale, of pharmaceuticals elimination during the SPF process. It has been mentioned that the decrease in the pharmaceuticals degradation on the CPC reactor is related to the need of both a proper hydrogen peroxide concentration and Fe: COPE ratio. However, there is a key factor for the efficiency of the solar photoreactor: the physical geometry, which ensures that the solar radiation is effectively collected. In this work, high efficiency in the sunlight distribution did not occur in the used CPC reactor, because aspects related with the geometry, such as construction and installation of the semi-parabola materials with reduced reflectance and the flow graduation of water inside the tubes was not achieved. In addition, parameters such as photoreactor light-path length, optical-path length (OPL) and molar absorptivity of homogeneous photocatalysts (Fenton reagent) were not taken into account during the reactor design (Jović, Kosar, Tomašić, & Gomzi, 2012; Ochoa-Gutiérrez, Tabares-Aguilar, Mueses, Machuca-Martínez, & Li Puma, 2018).

In fact, the CPC reactor was build 10 years ago as a reactor for heterogeneous photocatalytic processes. Likewise, the irradiance and distribution of sunlight was not constant during the four hours of exposition. The reactor design allowed only 10 L (total volume 15 L) of irradiated volume. According to this, the accumulated energy in the CPC reactor was defined considering correction factors such as real illuminated area (1 m^2), illuminated volume (10 L) and the average of the incident intensity of UVA radiation.

Furthermore, factors such as reagents concentration, contact time, flow patterns, mixing rate, mass transfer, and the axial and radial scale-up were included in the reactor design in order to maximize the exposed surface area per unit of reactor volume; and then to achieve an optimal distribution of sunlight inside the reactor (Ochoa-Gutiérrez et al., 2018; Spasiano, Marotta, Malato, Fernandez-Ibañez, & Di Somma, 2015).

Another key factor is the temperature. In this sense, the CPC reactor, used in this work, did not have temperature control and the influence of this parameter on the

performance of the reactor was not evaluated. That is an important topic because of its significant effect in the Fenton reaction (Spasiano et al., 2015)

On the contrary, at lab-scale, the used solarbox, which was operated in batch mode, allowed the control of both temperature and irradiance. Likewise, the system was operated with high and uniform distribution of the simulated sunlight, and adequate and constant agitation, which improved the contact between the pollutants in the MWW and the radicals generated into the system.

6.4 Conclusions of Chapter

The starting-up of the biological reactor (UASB) at pilot scale under non-controlled conditions of temperature and humidity (Colombian Amazonia environment) showed that after 39 days, the TOC removal percentage (between 65 and 70%) was stabilized. The UASB reactor effectively induced the denitrification and ammonium production indicating its well-operated acclimatization to MWW from Florencia. Also, this system exhibited the same elimination trend for the pharmaceuticals found at the laboratory scale.

Regarding the combination of SPF by means of a CPC reactor with anaerobic treatment by using a UASB reactor demonstrated a high efficiency for eliminating the target pharmaceuticals. In this combination, the SPF process applied to the MWW allowed to reach removal percentages above 70% for the pharmaceuticals and 60% for mineralization of the sample. Meanwhile, the biological treatment continued the removal of the pollutants and biodegradable organic matter. Although such removals were not completed, it is interesting to remark that wastewater treated by SPF did not generate toxicity on the anaerobic treatment. However, it is recommended for future works to optimize operative conditions of each reactor to increase the pharmaceuticals elimination and favor the mineralization of organic matter modifying parameters such as HRT, MWW/sludge ratio and nutrients, mass

transfer, among others. That parameters joined to design of new reactors are essential to performance of pilot scale.

References

Bandara, W. M. K. R. T. W., Kindaichi, T., Satoh, H., Sasakawa, M., Nakahara, Y., Takahashi, M., & Okabe, S. (2012). Anaerobic treatment of municipal wastewater at ambient temperature: Analysis of archaeal community structure and recovery of dissolved methane. *Water Research*, *46*(17), 5756–5764. https://doi.org/10.1016/j.watres.2012.07.061

Bhatti, Z. A., Maqbool, F., Malik, A. H., & Mehmood, Q. (2014). UASB reactor startup for the treatment of municipal wastewater followed by advanced oxidation process. *Brazilian Journal of Chemical Engineering*, *31*(3), 715–726. https://doi.org/10.1590/0104-6632.20140313s00002786

Cajacuri, M. P., Behling, E., Rincón, N., Colina, G., & Marín, J. C. (2013). Microbiological diversity of the anaerobic sludge during treatment. *Ingeniería Investigación y Tecnología*, *14*(3), 325–334. https://doi.org/10.1016/S1405-7743(13)72247-9

Chong, S., Sen, T. K., Kayaalp, A., & Ang, H. M. (2012). The performance enhancements of upflow anaerobic sludge blanket (UASB) reactors for domestic sludge treatment--a state-of-the-art review. *Water Research*, *46*(11), 3434–3470. https://doi.org/10.1016/j.watres.2012.03.066

European Cooperation in Science and Thecnology. (2017). *Understanding the contribution of biological processes to antibiotic resistance spread into the environment (Report of WG4)*.

Fernández, F., & Seghezzo, L. (2015). *Diseño de reactores upflow anaerobic sludge blanket (UASB)*. (Proyecto Mejora De Las Economías Regionales Y Desarrollo Local, Ed.). Retrieved from www.ue-inti.gob.ar

Gerba, C. P., & Pepper, I. L. (2014). *Municipal Wastewater Treatment*. *Environmental Microbiology: Third Edition* (3rd ed.). Elsevier Inc. https://doi.org/10.1016/B978-0-12-394626-3.00025-9

Jović, F., Kosar, V., Tomašić, V., & Gomzi, Z. (2012). Non-ideal flow in an annular photocatalytic reactor. *Chemical Engineering Research and Design*, *90*(9), 1297–1306. https://doi.org/10.1016/j.cherd.2011.12.014

Lei, Z., Yang, S., Li, Y. you, Wen, W., Wang, X. C., & Chen, R. (2018). Application of anaerobic membrane bioreactors to municipal wastewater treatment at ambient temperature: A review of achievements, challenges, and perspectives. *Bioresource Technology*, *267*(June), 756–768. https://doi.org/10.1016/j.biortech.2018.07.050

Manrique-Losada, L., Vera-barragán, M., & Peláez-Rodríguez, M. (2012).

Evaluación de inóculos para la digestión anaerobia de aguas residuales domésticas en condiciones del Piedemonte Amazónico. *Momentos de Ciencia*, *9*(2), 97–105.

Nair, A. T., & Ahammed, M. M. (2013). The reuse of water treatment sludge as a coagulant for post-treatment of UASB reactor treating urban wastewater. *Journal of Cleaner Production*. https://doi.org/10.1016/j.jclepro.2013.12.037

Ochoa-Gutiérrez, K. S., Tabares-Aguilar, E., Mueses, M. Á., Machuca-Martínez, F., & Li Puma, G. (2018). A novel prototype offset multi tubular photoreactor (OMTP) for solar photocatalytic degradation of water contaminants. *Chemical Engineering Journal*. https://doi.org/10.1016/j.cej.2018.02.068

Oller, I., Malato, S., & Sánchez-pérez, J. A. (2011). Combination of Advanced Oxidation Processes and biological treatments for wastewater decontamination: A review. *Science of the Total Environment, The*, *409*(20), 4141–4166. https://doi.org/10.1016/j.scitotenv.2010.08.061

Orozco-Gaviria, C. A., Triviño-Cabrera, C. C., & Manrique-Losada, L. (2014). Arranque de un reactor UASB para el tratamiento de aguas residuales domésticas en condiciones andino amazónicas. *Revista Facultad de Ciencias Básicas*, *10*(2), 170–185.

Pupo-Nogueira, R. F., Oliveira, M. C., & Paterlini, W. C. (2005). Simple and fast spectrophotometric determination of H2O2 in photo-Fenton reactions using metavanadate. *Talanta*, *66*(1), 86–91. https://doi.org/10.1016/j.talanta.2004.10.001

Ramón, J. A., Amaya, J. D., & Manrique-Losada, L. (2013). Degradación fotocatalitica de rojo congo en un colector parabolico solar y dióxido de titanio en suspensión. *Revista de Investigación de La Universidad Del Quindío*, *24*(1), 71–83. Retrieved from http://www.riuq.edu.co/index.php/riuq/article/viewFile/209/202

Rizzo, L., Malato, S., Antakyali, D., Beretsou, V. G., Đolić, M. B., Gernjak, W., … Fatta-Kassinos, D. (2019). Consolidated vs new advanced treatment methods for the removal of contaminants of emerging concern from urban wastewater. *Science of the Total Environment*, *655*, 986–1008. https://doi.org/10.1016/j.scitotenv.2018.11.265

Spasiano, D., Marotta, R., Malato, S., Fernandez-Ibañez, P., & Di Somma, I. (2015). Solar photocatalysis: Materials, reactors, some commercial, and pre-industrialized applications. A comprehensive approach. *Applied Catalysis B: Environmental*, *170–171*, 90–123. https://doi.org/10.1016/j.apcatb.2014.12.050

Stitt, E. H., & Simmons, M. J. H. (2011). Scale-Up of Chemical Reactions. In Dr. Ian Houson (Ed.), *Process Understanding: For Scale-Up and Manufacture of Active Ingredients*. Wiley Online Library. https://doi.org/https://doi.org/10.1002/9783527637140.ch6

Torres-Lozada, P. (2012). Perspectivas del tratamiento anaerobio de aguas

residuales domésticas en países en desarrollo. *Revista EIA*, *18*, 115–129.

Torres-Lozada, P., & Perez, A. (2010). Actividad metanogénica específica: una herramienta de control y optimización de sistemas de tratamiento anaerobio de aguas residuales. *Ingeniería de Recursos Naturales y Del Ambiente*, (9), 5–14.

Wood-Black, F. (2014). Considerations for Scale-Up – Moving from the Bench to the Pilot Plant to Full Production. *Academia and Industrial Pilot Plant Operations and Safety*, *January*(1), 37–45. https://doi.org/10.1021/bk-2014-1163.ch003

Yetilmezsoy, K., & Sakar, S. (2008). Improvement of COD and color removal from UASB treated poultry manure wastewater using Fenton's oxidation. *Journal of Hazardous Materials*, *151*(2–3), 547–558. https://doi.org/10.1016/j.jhazmat.2007.06.013

CHAPTER 7. CONCLUDING REMARKS AND FUTURE WORK

This doctoral thesis addressed the treatment of municipal wastewaters from a concept of sustainability, where the processes involved were efficient under local conditions to face relevant CECs and organic matter load in the samples. The characterization of the MWW from Florencia-Caquetá allowed to identify presence of relevant substances (ACE, SMX, DCF and CBZ), which can be used as a pollution indicator of the wastewaters.

The exploration of conventional processes such as biological processes (aerobic and anaerobic) for treating MWW from Florencia, allowed to demonstrate the technical viability of these systems under Amazonian conditions to remove biodegradable organic matter. In turn, the application of the solar photo-Fenton in presence of copoazu extract evidenced the high potentiality of Amazonian fruit (or agro-industrial wastes) for improving this process in order to degrade relevant CECs in MWW.

The performance at lab scale SPF/anaerobic process combination, indicated the relevance of this configuration to build and operate it at pilot scale. Such combined system takes advantages of the beneficial environmental conditions for the anaerobic reactor in the Amazonia and the enhancing effect of fruit extracts plus direct solar light availability. Furthermore, this represents a first approach toward better systems for MWW treatment in Florencia or other towns belonging to Colombian Amazonia by using low-cost natural resources and generating effluents with low pollution load. Finally, this could avoid the problems associated with the presence of CECs in natural water bodies where municipal effluents are typically disposed.

Future work and open issues

After development of this thesis, some topics can be identified for future works. A list of the most important ones is given below:

i. Specific toxicity tests must be applied to discard adverse effects on biological treatment.

ii. Determination of byproducts of pharmaceuticals during biological treatment to identify/confirm biodegradation mechanism. Likewise, byproducts during AOP can be a goal of future work too.

iii. For the anaerobic process at pilot scale, it should be done an extensive study in order to determine the best conditions to obtain an optimum efficiency of degradation of CECs and mineralization. The study could include aspects such as hydraulic retention time, sludge retention time, V_{MWW}/Vs ratio, C/N ratio, feeding MWW concentration and design parameters.

iv. For the SPF at near neutral pH with COPE at pilot scale, it has to be done more experiments to determine the best conditions to achieve complete degradation of CECs and higher mineralization level, through changes of the existing reactor by increasing the illuminated volume of the reactor, recirculation flow, reaction time, reduction of dead spaces, improvement of the mixture in the reaction system, among others.

v. About SPF at near neutral pH improved with the addition of natural products: The search for iron complexing agents present in natural products should be continued considering that other Amazonian fruits or agro-industrial wastes easily acquired in the region contains organic acids in high concentrations suggesting that they have an interesting potential for application in SPF system.

vi. COPE as iron complexing agent could be evaluated as enhancer of bacterial inactivation in MWW through of SPF at near neutral pH.

APPENDIX 1. RESEARCH CONTRIBUTIONS

Journal Publications

- A.M. Botero-Coy, D. Martínez-Pachón, C. Boix, R.J. Rincón, N. Castillo, L.P. Arias-Marín, L. Manrique-Losada, R. Torres-Palma, A. Moncayo-Lasso, F. Hernández. (2018). An investigation into the occurrence and removal of pharmaceuticals in Colombian wastewater. Science of the Total Environment 642, 842–853.
- L. Manrique-Losada, C. Quimbaya-Ñañez, R. Torres-Palma. (2019). Eliminación de fluoxetina presente en aguas contaminadas usando procesos fotoquímicos de oxidación avanzada y luz solar. Revista EIA, Volume 16 Number 32. July-December 2019, 27-42.

Conference Proceeding

- Manrique-Losada Lis, Quimbaya-Ñañez Carolina, Torres-Palma Ricardo. (2017). "*Elimination of fluoxetine using photochemical advanced oxidation process and sunlight"*. Oral presentation in 3rd Iberoamerican Conference on Advanced Oxidation Technologies (III CIPOA). Guatapé Antioquia, Colombia.
- Manrique-Losada Lis, Monje Santiago, Castiblanco Paola Andrea, Torres-Palma Ricardo. (2017). "*Arazá fruit as enhancer of antibiotic degradation by photo-Fenton at natural pH*". Poster in 3rd Iberoamerican Conference on Advanced Oxidation Technologies (III CIPOA). Guatapé Antioquia, Colombia.
- Manrique-Losada Lis, Torres-Palma Ricardo. (2017) "*Eliminación de contaminantes emergentes presentes en aguas residuales municipales de Florencia-Caquetá por medio de foto Fenton solar*". Oral presentation in I Simposio Internacional de Investigación. Universidad de la Amazonia and SENA. Florencia Colombia.
- Manrique-Losada Lis, Torres-Palma Ricardo and Oller Isabel. (2018). "*MWWTP Municipal Wastewater inlet treatment by Solar photo Fenton at*

natural pH and aerobic biological oxidation: Evaluation at pilot scale". Oral presentation in 3er Congreso Colombiano de Procesos de Oxidación Avanzada. Universidad de la Amazonia, Florencia-Caquetá, Colombia.

- Manrique-Losada Lis, Monje Santiago, Torres-Palma Ricardo. (2018). "*Araza seeds as promotors of solar photo-Fenton degradation of antibiotics in waters at natural pH: case of norfloxacin*". Poster in 10th European Meeting on Solar Chemistry and Photocatalysis: Environmental Applications. Palacio de Exposiciones y Congresos Cabo de Gata - Ciudad de Almería, Spain.
- Manrique-Losada Lis, Monje Santiago, Torres-Palma Ricardo. (2019). "*Removal of pharmaceuticals present in municipal wastewater by biological treatment: effect of reaction media and chemical structure*". Oral presentation in VII Seminario Internacional de Química Aplicada para la Amazonia. Universidad de la Amazonia, Florencia-Caquetá, Colombia.
- Santanilla Heidy, Manrique-Losada Lis, Torres-Palma Ricardo. (2019). "*Comparation of amozonian extracts as Fe(III) complexing agents for degradation of pharmaceuticals by Solar photo Fenton at natural pH*". Oral presentation in III Congreso Internacional de Investigación. Fundación Universitaria Navarra, Neiva Huila, Colombia.
- Muñoz Brayan, Manrique-Losada Lis, Torres-Palma Ricardo. (2019). "*Municipal wastewater treatment thorough combination of solar photo Fenton and anaerobic biological oxidation at pilot scale*". Poster in III Congreso Internacional de Investigación. Fundación Universitaria Navarra, Neiva Huila, Colombia.
- Quimbaya-Ñañez Carolina, Manrique-Losada Lis, Torres-Palma Ricardo. (2019). "*Photo electro Fenton for degradation of pharmaceuticals present in municipal wastewater*". Oral presentation in VII Seminario Internacional de Química Aplicada para la Amazonia. Universidad de la Amazonia, Florencia-Caquetá, Colombia.
- Santanilla-Calderón Heidy L, Manrique-Losada Lis, Torres-Palma Ricardo. (2019). "*Evaluation of copoazu extract as enhancer of solar photo Fenton process at natural pH applied to degradation of pharmaceuticals present in*

municipal wastewaters". Oral presentation in VII Seminario Internacional de Química Aplicada para la Amazonia. Universidad de la Amazonia, Florencia-Caquetá, Colombia.

Research Stays

- Plataforma Solar de Almería (Spain). CIEMAT (Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas. From march 1 to august 30, 2018. www.psa.es - www.ciemat.es.

Tutoring

- Carolina Quimbaya Ñañez. "Degradación de fluoxetina por procesos de Oxidación Avanzada y Luz Solar". Tutoring to undergraduate Project. Chemistry, Universidad de la Amazonia. 2016.
- Paola Andrea Castiblanco Gutierrez. "Residuo agroindustrial como potencializador del proceso foto-Fenton a pH natural para la degradación de un contaminante orgánico". Tutoring to undergraduate Project. Chemistry, Universidad de la Amazonia. 2016.
- Henry Manuel Morales. "Montaje de un reactor anaerobio UASB de flujo ascendente para el tratamiento biológico de aguas residuales en el municipio de Florencia-Caquetá". Tutoring to undergraduate Project. Biology, Universidad de la Amazonia. 2017.
- Juan Camilo Arriola Mahecha. "Tratamiento aguas residuales municipales de Florencia mediante la combinación de oxidación anaerobia y foto-Fenton solar a escala de laboratorio". Tutoring to undergraduate project. Chemistry, Universidad de la Amazonia. 2018.
- Heidy Santanilla. "Evaluación de un residuo agroindustrial como complejante de hierro durante la degradación vía foto Fenton solar a pH natural de fármacos presentes en aguas residuales municipales". Tutoring to undergraduate project. Chemistry, Universidad de la Amazonia. 2019.

- Brayan Steven Muñoz Sierra. Evaluación de la eficiencia de la combinación de oxidación biológica y foto Fenton solar a pH natural a escala de laboratorio, para el tratamiento de aguas residuales municipales de Florencia-Caquetá. Tutoring to undergraduate project. Chemistry, Universidad de la Amazonia. 2019.

Derived Research Projects

- "Residuos agroindustriales modificados con potencial uso como catalizadores heterogéneos para la degradación de contaminantes vía foto-Fenton". *10ma primera convocatoria institucional para concurso de proyectos, en el marco de los Semilleros de investigación*. Funded by Universidad de la Amazonia. 2016.
- "Ecotoxicidad y biodegradabilidad de los productos de degradación de dos fármacos al ser sometidos a oxidación vía foto Fenton solar". *11ava primera convocatoria institucional para concurso de proyectos, en el marco de los Semilleros de investigación*. Funded by Universidad de la Amazonia. 2017.
- "Eliminación de un contaminante emergente presente en aguas residuales municipales de Florencia-Caquetá, a partir de procesos fisicoquímicos avanzados". *Convocatoria para proyectos de investigación en el marco de los grupos de investigación, resolución 0509*. Funded by Universidad de la Amazonia. 2016 – 2017.
- "Foto-Electro-Fenton solar aplicada al tratamiento de aguas residuales municipales de Florencia-Caquetá a escala de laboratorio". *12ava primera convocatoria institucional para concurso de proyectos, en el marco de los Semilleros de investigación*. Funded by Universidad de la Amazonia. 2018.
- Strengthening of the research infrastructure of the Research Center "*César Augusto Estrada Gonzalez*" (CIMAZ - Macagual - Florencia) at the Universidad de la Amazonia: Due to the creation and direction of the *Environmental Chemistry Laboratory* of the Universidad de la Amazonia, management was made to achieve the "*provision of the laboratory*" and the

"*acquisition of equipment (robust or not)*" in order to allow the development of this doctoral thesis and leave the basis for the evolution of research in this area of knowledge from CIMAZ. Funded by Universidad de la Amazonia. 2015-2018.

- "Desarrollo experimental de un sistema de tratamiento de aguas residuales municipales a escala piloto en el departamento del Caquetá". Project prepared and presented through the Government of Caquetá to *Fondo de Ciencia, Tecnología e Innovación en el marco del "Sistema General de Regalías Caquetá – ", vigencia 2018*. Current status of the project: phase 3 project, included in "*Plan y acuerdo estratégico departamental de Ciencia y Tecnología e innovación – PAED"* and continues in process.

Conference Organization

- President of the Organizing Committee. V Seminario de Química Aplicada para la Amazonia (V SEQUIAMAZ). From nov 11 to nov 13. 2015. Universidad de la Amazonia, Florencia-Caquetá Colombia.
- President of the Organizing Committee. V Seminario Internacional en Medio Ambiente, Biodiversidad y Desarrollo (V SIMABID). From nov 11 to nov 13. 2015. Universidad de la Amazonia, Florencia-Caquetá Colombia.
- President of the Organizing Committee. 3 Congreso Colombiano de Procesos de Oxidación Avanzada (3CCPAOx). From October 31 to November 2. 2018. Universidad de la Amazonia, Florencia-Caquetá Colombia.
- Member of the Organizing Committee. 3rd Iberoamerican Conference on Advanced Oxidation Technologies (3rd CIPOA). From November 14 to November 17. 2017. Guatapé Antioquia, Colombia.
- Member of the Organizing Committee. 4to Congreso Colombiano de Procesos de Oxidación Avanzada (4CCPAOx). Event to be held from April 18 to April 22. 2020. Universidad de Cartagena. Cartagena de Indias, Colombia.