UNIVERSIDAD DE ALMERIA
Facultad de ciencias experimentales

INTEGRACIÓN DE PROCESOS FOTOQUÍMICOS SOLARES CON OTRAS TÉCNICAS AVANZADAS DE ANÁLISIS PARA EL TRATAMIENTO Y REVALORIZACIÓN DE AGUAS RESIDUALES COMPLEJAS

Ana Ruiz Delgado

Tesis Doctoral
Almería - Septiembre 2019

CIESOL
Centro de Investigación en Energía Solar
Centro Mixto UAL - PSA CIEMAT

UNIVERSIDAD DE ALMERIA

Facultad de Ciencias Experimentales

"Doctorado en Química Avanzada"

INTEGRACIÓN DE PROCESOS FOTOQUÍMICOS SOLARES CON OTRAS TÉCNICAS AVANZADAS DE ANÁLISIS PARA EL TRATAMIENTO Y REVALORIZACIÓN DE AGUAS RESIDUALES COMPLEJAS

"INTEGRATION OF SOLAR PHOTOCHEMICAL PROCESSES WITH OTHER ADVANCED TECHNIQUES OF ANALYSIS FOR THE TREATMENT AND REVALORIZATION OF COMPLEX WASTEWATER"

Memoria presentada para aspirar al grado de Doctor:

ANA RUIZ DELGADO

Fdo. Ana Ruiz Delgado

Almería a 3 de septiembre de 2019

DIRECTORES DE TESIS:

Dra. Dña. Isabel Oller Alberola
Investigador Contratado OPI
CIEMAT
Ministerio de Ciencia, Innovación y Universidades

Dra. Dña Ana Agüera López
Catedrática del Departamento de Química y Física
Universidad de Almería

SUMMARY

The steady increase in industrialization, urbanization and exponential population growth are leading to an alarming increase in water scarcity throughout the planet. This is coupled with the problem of environmental and health risks associated with poor water quality available in some areas of the world. This makes the treatment and reuse of urban wastewater a major issue as a potential alternative source of water for certain applications and economic sectors. In addition, the treatment of industrial and urban wastewater is a requirement to guarantee the quality of natural water. Conventional wastewater treatment plants, based on biological treatments, have low effectiveness against the elimination of contaminants of emerging concern, industrial wastewater discharges or effluents of bio-recalcitrant origin (or highly toxic), such as landfill leachate. Therefore, it is necessary to develop new strategies for the management and treatment of these wastewaters that include: (i) a characterization of them, using advanced analytical techniques (liquid and gas chromatography coupled with spectrometry for the identification of unknown organic pollutants), microbiological analyses, toxicological analyses (short and long term) and biodegradability analyses, as well as (ii) integration/combination of multiple highly efficient physical and chemical oxidation processes, which allow to reduce costs and improve the quality of the discharge. In this sense, the high potential of Advanced Oxidation Processes (AOPs) for decontamination of water containing this type of

substance is widely recognized. In this way, AOPs aim to increase the biodegradability of this wastewater enough to implement a subsequent biological system, designed specifically for the treatment of water with particular characteristics and that will always go associated with an overall target of reducing operating costs.

The main aim of this PhD Thesis is the treatment of industrial and/or non-biodegradable wastewater for regeneration, reuse and revaluation through nutrients recovery, by studying new strategies and making use of solar energy. To that effect, a treatment line is proposed based on the combination, at pilot plant scale, of a pre-treatment physico-chemical (coagulation/flocculation), AOP (ozonation and solar photo-Fenton) and biological systems (fluidized bed bio-reactor) with a final polishing stage based on membrane systems (membrane distillation), for the purification and possible reuse of landfill leachate (as an example of complex and/or industrial wastewater). The evaluation of the technologies studied has been carried out through the application of analytical techniques, both conventional (turbidity, pH, conductivity, COD, DOC, total nitrogen, anions, cations, carboxylic acids, amines, etc.) and advanced (liquid and gas chromatography coupled to mass spectrometry), microbiological techniques (microorganism plate count, DNA extraction, qPCR or metagenomic techniques) and toxicity and biodegradability studies through respirometry.

Firstly, the optimization of a pre-treatment based on physico-chemical coagulation/flocculation (C/F) techniques at laboratory scale was carried out, using different commercial flocculants and coagulants and two commonly known coagulants used for industrial wastewater pre-treatment: $FeCl_3$ anhydrous and $Ca(OH)_2$. It was found out that the most effective system for reducing a higher percentage of turbidity, colour, COD and DOC was the addition of 0,5 g/L of $FeCl_3$ after reducing the pH of the wastewater to 5 (3 min at 100 rpm, 30 min at 30 rpm and 30 min of sedimentation). Subsequently, this stage was replicated on a pilot plant scale in order to obtain a higher volume of pre-treated wastewater to continue experimentally with the other suggested stages in the treatment line at pilot plant scale. The non-biodegradable character and the medium toxicity (short-term) of landfill leachates was maintained after this first stage of C/F, making it necessary to assess the effect of the application of an AOP on the improvement of these parameters, prior to the possible combination with a biological treatment.

Two AOPs evaluated were: ozonation and solar photo-Fenton. Ozonation efficiency at alkaline pH was studied, to evaluate the effect of the presence of hydroxyl radicals resulting in an indirect oxidation process, which is added to the direct oxidation through ozone, with two different ozone productions: 20% and 50% (1.4 g O_3/h and 3.6 g O_3/h, respectively). In all cases, the solar photo-Fenton process offered better results in improving biodegradability and reducing toxicity, compared to the ozonation experiments. 43% DOC elimination was obtained and a biodegradability (measured by respirometry) of 0.62 was achieved with the solar photo-Fenton process after 7 h irradiation time, accumulated UV energy of 52 kJ/L and a total consumption of 0.5 g/L of H_2O_2; compared to a DOC removal of 7-6% and a biodegradability of 0.0046-0.19 obtained after ozonation at 20% and 50% of production of O_3, respectively. As a result, the solar photo-Fenton process was selected as the most interesting for its combination with subsequent biological treatment.

For the biological treatment, a fluidized bed aerobic biological reactor was used. This bio-reactor was colonized by active sludge from a municipal wastewater treatment plant (MWWTP) of Almería (Spain), fixed on polypropylene supports. This type of bioreactor offers clear advantages over conventional, including the durability and resistance to sudden changes in inlet wastewater characteristics. The biological system was operated in discontinuous and continuous mode after a first phase of adapting biomass to partially treated landfill leachates by several dilutions with influent wastewater from the MWWTP. The bio-reactor discontinuous operation offered maximum treatment capacity of 1.35 mg DOC/L·h (6 days of residence time) with a feed mixture of 10 L of pre-treated landfill leachate using solar photo-Fenton (after C/F, 700 mg/L DOC) and 28 L of inlet wastewater to the secondary treatment of MWWTP (initial DOC of the mixture of 270 mg/L), achieving an 80% elimination of the initial DOC. With regard to nitrification, a maximum capacity of 2.65mg N-NH_4^+/L·h was achieved. During the continuous operation mode, it was achieved a maximum treatment capacity of 0.71 mg DOC/L·h and a maximum nitrification capacity of 1.40 mg N-NH_4^+/L·h, with 9.6 mL/min as flow feeding with a mixture of 4 L pre-treated landfill leachate (700 mg/L DOC, approx.) and 34 L of inlet wastewater to the secondary treatment of the MWWTP (initial DOC of the mixture of 170 mg/L). As in discontinuous operation mode, the organic charge was removed until a residual concentration of about 70 mg/L (60% DOC degradation), finding out, as a highlight, a significant ammonium accumulation in the effluent, originating from the nitrogenous organic compounds oxidation (200 mg N-NH_4^+/L). Such a residual concentration would require the combination with another complementary biological system that would focused on the specific elimination of nitrogen. However, the work developed in this PhD Thesis focused on trying to take advantage of this effluent of the biological system rich in ammonium for crops irrigation, having gone by through a nitrogen recovery stage in ammoniacal form.

This study was carried out by applying a tertiary system based on membrane distillation during a three-month stay in the "Laboratory of Separation and Reaction Engineering – Laboratory of Catalysis and Materials (LSRE-LCM)" from the Faculty of Engineering of the University of Porto (Portugal), under Dr. Adrián Manuel Tavares Da Silva supervision. First, optimization of a direct contact membrane distillation system (DCMD) was carried out with a commercial PTFE membrane (high-density polyethylene) at laboratory scale, for the recovery of ammonium from simulated WWTP secondary effluent (according to Zhang et al., 2007) through a comprehensive two-tiered general factorial experimental design developed in Minitab® 18 program. The effects of ammonium concentration (between 100 and 400 mg N-NH_4^+/L), of the pH (between 7 and 12) and the temperature (between 40 and 80ºC) of the feed flow and of the concentration of the receiving solution of H_2SO_4 (between 0.01 and 0.5 mol/L according to bibliography and stoichiometric calculations) were studied, employing in each case a fixed flow of 300 mL/min of both currents and a temperature of 20 ºC on the permeate side. Membrane distillation is based on a thermal separation where, after the evaporation, steam molecules go by through a hydrophobic microporous membrane. In both sides of the membrane a pressure gradient that is the driving force for steam to flow through the membrane and condense on the other side is created. There are several configurations for membrane distillation. One of them is direct contact membrane distillation, where direct contact occurs between the surface of the membrane permeate side and the aqueous solution. The permeated component condenses directly into the coolant that flows through the module on the permeate side. This technology has great potential for wastewater reuse and the recovery of added value substances contained in it, for example, ammonium recovery, one of the objectives of this PhD Thesis. For that purpose, it is required a receiving solution of concentrated sulfuric acid on the permeate side, to favour the ammonia uptake through the formation of ammonium sulfate as a final recovery product. Optimal operating conditions found to maximize ammonium recovery in DCMD system

were pH 12, 80 ºC of temperature on the feeding side, and a concentration of 0.01 M and 0.5 M H_2SO_4 to the concentrations of 100 mg N-NH_4^+/L and 400 mg N-NH_4^+/L in the feeding, respectively. In addition, it was checked that the nitrates concentration, which are present at high concentration at the effluent of a biological system when nitrification works properly, did not have any significant influence in the ammonium recovery efficiency through the membrane distillation system. Finally, these optimal operating conditions were applied to the accumulated ammonium recovered from the treated effluent, obtained after the landfill leachates proposed treatment line, achieving a recovery percentage of 53.3%.

This study was complemented by advanced microbiological techniques application for the evaluation of the new bacterial population originating in the biological system, after the adaptation of the sludge from the MWWTP to the partially treated landfill leachates, highlighting the increase in the population of amino oxidizing bacteria (qPCR analysis) and a growth of 21 to 51% of proteobacteria (metagenomic techniques), which include pathogens such as *E. coli*, *Salmonella* or *Helicobacter.* Finally, advanced chromatographic techniques coupled to mass spectrometry were applied for the identification and monitoring of organic compounds present in the treated wastewaters. This was intended to improve current knowledge on the landfill leachates composition with a high-scope analysis, as well as to assess the effectiveness or performance of the proposed treatment line concerning the elimination of the initially unknown contaminants, which were found in the treated landfill leachate samples. To do this, *target analysis* strategies were used, using LC-QqLIT-MS/MS, and scanning of suspect *screening*, using LC-QTOF-MS and GC-Q-MS, which were applied to both raw landfill leachates and to landfill leachates effluents obtained after each stage along the proposed treatment line. All of the contaminants detected were quantified in concentrations of µg/L, highlighting ketoprofen, nicotine, gabapentin, trigonelin, mecrocop or diclofenac, among others (concentrations between 319 and 17 µg/L). A clear reduction in the content of quantized micropollutants (MCs) from 94% with respect to the initial charge was observed. In addition, it was revealed that three MCs had not previously been reported for this type of wastewater: the di-n-nonyl phthalate, o-phenylphenol and tonalide.

Another partial objective of this PhD Thesis was the reuse of industrial wastewater for several applications, among which it is particularly interesting the valorization of certain residues contained in some complex wastewater, such as additives to improve the

efficiency of AOPs. These substances include phenolic compounds, which can act as complexing agents of iron, keeping this reagent in solution at circumneutral pH, and thus favoring the application of processes such as photo-Fenton at natural pH for the elimination of MCs present in less complex wastewaters (usually above 6). MCs are substances that, although found in very low concentrations (µg/L-ng/L), have been recognized as potentially dangerous to human health and the environment. The AOPs, and more specifically the solar photo-Fenton process, has been extensively studied as a viable technique for the complete elimination of MCs in different types of water. In addition, the use of solar energy offers a sustainable view from the energetic point of view, framing this technology within green chemistry. In this PhD Thesis, we have dealt with different process operating strategies of photo-Fenton solar at neutral pH, as tertiary treatment for eliminating MCs. For this study, four MCs (at a concentration of 200 g/L each) were selected: chlorfenvinphos, diclofenac, pentachlorophenol and terbutrine. All of them are contained in the European Directives 2013/39/EC and 2008/105/EC as priority hazardous substances and are present in different types of wastewater. As an alternative to the use of complexing commercial agents such as EDDS, other natural alternatives have been evaluated to form stable complexes with iron during the solar photo-Fenton process, such as the use of olive mill wastewater (alpechín, industrial residual wastewater with high polyphenol content) or humic-like substances (STH, extracted from the alperujo, residue coming from molturate olives), with the consequent revalorization, in this case, of a specific type of waste and complex wastewater.

The selected MCs removal through solar photo-Fenton in demineralized water (at circumneutral pH), adding EDDS in a 1:2 molar ratio of Fe^{3+}:EDDS and starting from a Fe^{3+} concentration of 5.5 mg/L at pilot plant scale in a CPC photo reactor were carried out. More than 80% degradation with respect to the sum of MC (800 µg/L in total), after 10 min of irradiation time, 1.68 kJ/L of accumulated UV energy and a H_2O_2 consumption of 41.2 mg/L, was obtained. In addition, the use of alpechín (OMW) was studied to carry out the Fe^{3+} complexion and promote the process of photo-Fenton solar at neutral pH for the degradation of MCs. To this end, the stability of iron (5.5 mg/L Fe^{3+}) was first studied taking into account the polyphenolic content of the alpechín after different dilutions. The main goal was to find the best Fe^{3+}: polyphenols rate to keep the iron in dissolution, testing several dilutions of the alpechín above and below 1:200, corresponding to a 1:2 molar rate of Fe^{3+}:polyphenols, and coincident with the best Fe^{3+}: EDDS relation found by other authors and used in this PhD Thesis. The results indicated that the iron formed a stable complex with components of alpechín, but with colloidal characteristics, being able to be active across the full pH range and favouring the photo-Fenton solar process. A 1:1200 dilution (24 mg/L DOC) was selected due to, mainly, the fact that minor dilutions contributed a large extra amount of DOC, presenting little significant improvements in the iron complexion required to carry out the oxidation process effectively.

Once the best dilution of alpechín was chosen, the removal of MCs contained in different water matrices (demineralized water, natural water, simulated natural water, simulated natural water without carbonates and simulated secondary effluent of MWWTP) and at different concentrations of them (200 and 40 µg/L of each them) through solar photo-Fenton process at neutral pH in a CPC photo-reactor was evaluated. The high efficiency of polyphenols present in alpechín as a complexing agent of iron at neutral pH was demonstrated, although the developed experimentation showed that the oxidation process was active only for the first 20 minutes of treatment, which translates into a low stability of the Fe^{3+}:polyphenols complex in the long term. The reduction in pH to 4 (slightly higher than optimal for the photo-Fenton process) resulted in a significant increase in the rate of degradation of MCs, due to improved complex stability formed with polyphenols, as it would be expected.

As an alternative to the alpechín, the use of solid waste from the olive industry was assessed. This is the case of the STHs extracted from alperujo, which were provided by the Polytechnic University of Valencia (Alcoy Campus) and used as complexing iron agents in solar photo-Fenton process. In order to determine the efficacy of these substances, first, operational parameters were optimized at lab-scale. The concentration of hydrogen peroxide (10 and 20 mg/L), pH (5 and 7) and STH concentration (10, 20 and 50 mg/L) with 5.5 mg/L of Fe^{3+} in natural water and 200 µg/L of each MC, were tested. The operating conditions selected as more favorable were 10 mg/L of STH, 10 mg/L of H_2O_2 and neutral pH, with which a 66% of degradation of the sum of MCs was achieved. Next, the best operating conditions described above were evaluated at pilot plant scale in a CPC photo-reactor in different water matrices (natural water and simulated secondary effluent of MWWTP) and 200 µg/L of each MC resulting in a 80% degradation of the MCs sum after 240 minutes of treatment and 50 kJ UV/L.

In general, the work developed in this PhD Thesis highlights the existing problem with complex industrial wastewater and its subsequent treatment, reuse and/or revalorization, a treatment line for landfill leachates is proposed, by way of example. The combination of physico-chemical processes, AOPs, biological treatments and a refining stage by membrane distillation allows improving the quality of these effluents while improving the recovery of residual ammonium after biological treatment for irrigation purposes and reduces the total load of MCs. In the same way, this work opens the doors to new alternatives for the application of solar photo-Fenton process at neutral pH as tertiary treatment for the elimination of MCs in MWWTP effluents, valuing complex industrial waste like alpechín and alpeorujo, used as complexing iron agents (III).