UNIVERSITY OF ALMERIA

Department of Chemical Engineering

CONTINUOUS DISINFECTION OF WWTP SECONDARY EFFLUENTS BY SOLAR PHOTO-FENTON AT NEUTRAL PH IN RACEWAY POND REACTORS. REMOVAL OF CECS AND ARBS

by

IRENE DE LA OBRA JIMÉNEZ

Supervised by:

Dr. José Antonio Sánchez Pérez

ABSTRACT

The growing water scarcity combined with the need of environmental protection have created a real concern for the reuse of treated urban wastewater for irrigation in agriculture, particularly in many world areas where water scarcity implies health risks. In this regard, pathogenic bacteria inactivation is the first target of tertiary treatments aimed at the reuse of wastewater treatment plant (WWTP) secondary effluents. Nonetheless, the presence of persistent organic compounds, namely pharmaceuticals, at very low concentrations (tens or hundreds of ng L^{-1}) known as contaminants of emerging concern (CECs), in secondary effluents is another threat. Among them, special attention is paid to antibiotics as their accumulation in the natural media is causing the proliferation of antibiotic resistant bacteria (ARB). Advanced Oxidation Processes (AOPs) are proposed as tertiary treatments and those driven by solar radiation are of special interest, such as the solar photo-Fenton process. To accomplish this process in a WWTP, three conditions should be considered: i) working at neutral pH to reduce costs associated with pH conditioning; ii) using low cost photo-reactors with high volume to surface ratio, such as raceway pond reactors (RPRs); and iii) the operation in continuous flow mode allows, to maximize the treatment capacity, making suitable the scaling up the process.

This PhD thesis is aimed at studying the bacterial inactivation of WWTP secondary effluents by the solar photo-Fenton process in continuous flow at neutral pH. The experimentation was carried out with RPRs paying attention to two main concerns regarding wastewater reuse for crop irrigation: the removal of CEC and ARB, because beyond pathogenic bacteria inactivation, the tertiary treatments should address these threats for safe water reuse.

To this end, the specific objectives and main results are described as follows.

Section 4.1. is focused on the comparison of pharmaceuticals removal in a MWWTP secondary effluent by solar photo-Fenton with Fe^{3+}:EDDS complex at circumneutral pH in RPR taking into account the effect of liquid depth in RPRs.

For that purpose, a simulated secondary effluent was spiked with a mixture of two pharmaceuticals (carbamazepine and ibuprofen) and three antibiotics (flumequine, ofloxacin and sulfamethoxazole) at 100 $\mu g \cdot L^{-1}$ each. These

contaminants were chosen due to the significant problems that their presence provokes in real wastewater effluents. In a preliminary stage, two operation strategies, sequential ferrous sulphate additions of 0.1 mM and Fe^{3+}: EDDS complex (1:2) at 0.05 and 0.1 mM were compared. The results showed the Fe^{3+}:EDDS complex at 1:2 molar ratio as the best operational option. Once the operation strategy was chosen, the effect of RPR-liquid depth (10, 15 and 20 cm) was evaluated in a real secondary effluent matrix. Although the process was limited by the availability of photons, the results showed 90% of contaminant removal for every tested liquid depth. Under these circumstances, 15 cm was selected as the optimal liquid depth for pharmaceutical removal. Considering these results, a comparative study between tubular reactors with compound parabolic collectors (CPCs) and RPRs, in terms of efficiency (expressed as mass of degraded micropollutant per kJ of solar UV energy incident on the reactor surface) has been performed. From this evaluation, the efficiency of pharmaceutical removal showed efficiency values four times higher in 15-cm deep RPRs with regard to CPC reactors, being 1.07 and 0.26 $mg \cdot kJ^{-1}$ respectively.

Once the high efficiency of RPRs in comparison with CPCs for micropollutant removal was shown and consequently the possibility to reduce the high cost associated with the conventional reactors, one step further to the large-scale implementation is required.

To this end, Section 4.2. was aimed to investigate the scalable operational conditions to accomplish the photo-Fenton process in the WWTPs and thus the operational mode should be changed. In this sense, this study showed, for the first time, the inactivation of Total Coliforms, *Escherichia coli* and *Enterococcus* sp. in MWWTP secondary effluents by the solar photo-Fenton process in continuous flow operation at neutral pH in raceway pond reactors. Firstly, due to the significant role of hydraulic residence time (HRT) over the continuous mode operation, different values (15, 30 and 60 min) were evaluated at indoor conditions, showing only successful results in term of bacterial inactivation for 60 and 30 min of HRT in all microbial groups selected. Taking into account the results obtained at laboratory scale, 60 and 30 min of HRT were tested outdoors in 5 cm-deep RPRs in both summer and winter irradiance conditions.

Although the Fe^{3+}:EDDS was the best option for CEC removal by photo-Fenton at neutral pH, the efficiency of using ferrous sulphate for secondary effluent disinfection has been demonstrated with both, CPC and RPR. Therefore, in the following research ferrous iron was used because of the lower cost with regard to the Fe^{3+}:EDDS complex.

The continuous operation was carried out during three consecutive days with inlet concentrations of 20 mg $Fe^{2+}\cdot L^{-1}$ and 30 mg $H_2O_2\cdot L^{-1}$ to avoid large excess of hydrogen peroxide in steady state. Bacterial inactivation results showed 30 min of HRT to be the most efficient operational condition capable of producing 305 $m^3\cdot m^{-2}\cdot year^{-1}$ of disinfected water while complying with the Spanish Law (RD 1620/2007) for water reuse. In addition, a reduction of iron (from 10 to 2.5 mg $Fe^{2+}\cdot L^{-1}$) in continuous mode with 30 $mg\cdot L^{-1}$ of H_2O_2 was evaluated. The results showed an efficient bacterial inactivation in the cases of 10 and 5 mg $Fe^{2+}\cdot L^{-1}$. This implied a significant reduction of iron concentration in the steady state regarding the optimal dose established in the batch mode operation for the first time. Once the continuous flow process was successfully tested, arose a need to study the viability of the process with regard to the removal of ARB present in wastewater secondary effluents.

For that purpose, Section 4.3. is focused to carry out an exhaustive and comparative kinetic study on the inactivation of both total and cefotaxime resistant bacteria by solar photo-Fenton at neutral pH for the same bacterial species studied in Section 4.2. To this end, the effects on bacterial inactivation of different operational conditions, such as operating mode (batch and continuous), seasonal solar irradiance (winter, spring and summer), iron concentrations (20, 10, 5 and 2.5 $mg\cdot L^{-1}$) and hydraulic residence times (22.4, 16.3, 9.0 and 4.7 min) were analyzed. No significant differences were found between the inactivation rate constants of total and cefotaxime resistant bacteria in any operational conditions mentioned above. Besides, the inactivation rate constants increased with solar irradiance and showed a linear increase with iron concentration. High differences in the inactivation rate constant between batch and continuous mode operation were the main finding of this work, being significantly higher in the last case due to the synergic effect of the variables involved in the disinfection process. This fact points out the continuous mode operation suitable for large scale application.

Once the behavior of resistant bacteria was evaluated, additional experiments were carried out under controlled indoor conditions with the aim of deepening in this process. For that purpose, different assays were carried out reducing the HRT from 22.4 to 4.7 min (a significantly lower value than those tested in Section 4.2). The results showed 22.4 min with 5 mg $Fe^{2+}\cdot L^{-1}$ and 30 mg $H_2O_2\cdot L^{-1}$ as the minimum HRT capable to inactivate the bacteria below the detection limit (1 $CFU\cdot mL^{-1}$). Finally, the efficiency, in terms of figure of merits of the photo-Fenton process as the collector area per order ($m^2\cdot m^{-3}\cdot order^{-1}$) was also evaluated for both operational modes, batch and continuous, for the three seasonal periods, different iron concentrations and different HRTs. In this sense, the inactivation rate constants values obtained for discontinuous mode operation were three orders of magnitude higher than those obtained for continuous mode. Among the three seasons, summer gives rise to the lowest collector area values. Regarding the effect of the iron concentration in batch mode operation, the higher the iron concentration the lower the area required and the higher the efficiency. Under these circumstances, the efficiency, in terms of figure of merits, was 2.7 m^2 of solar collector area to reduce one log of *E. coli* concentration per m^3 of treated water and per hour in the case of 22.4 min of HRT under 30 $W\cdot m^{-2}$ of average of solar irradiance.

Once the continuous flow mode was proven as a much more efficient operation mode than batch mode for total and resistant bacteria inactivation, Section 4.4 was focused on studying the possibility of changing the catalyst from iron salts to natural iron oxides in order to improve the economy of the system (in terms of cost) without yielding the disinfection efficiency in its application to WWTP secondary effluents.

As a result, in this part of the work, the use of iron oxides has been proposed as photo-Fenton catalysts for the disinfection of naturally occurring bacteria, and their related operational parameters have been assessed. As such, the addition of 3 natural iron oxides (Hematite, Wustite, Magnetite) and iron from a mine have been assessed, as well as magnetic nano-oxides. The catalyst concentration used was 20 $mg\cdot L^{-1}$ although other concentrations were tested to obtain the best operational conditions. 20 $mg \cdot L^{-1}$ achieved the most efficient bacterial disinfection taking place, at least 5-log of bacterial reduction around 120 min of experimental time. Hence, the subsequent step was to elucidate the mechanisms of Fe-Ox driven photo-Fenton disinfection for the optimal configuration in batch mode: i) the semiconductor action mode driven by illuminated iron oxides, ii) the photo-leaching of iron in the solution (homogeneous photo-Fenton) and iii) the action of Fe-oxides as solid catalysts (heterogeneous photo-Fenton process). Furthermore, the implications of the presence of matrix constituents, namely organic matter and bicarbonates were also investigated, as well as the possibility to apply this system after a series of secondary treatment processes (activated sludge, moving bed bioreactors or coagulation-flocculation). Finally, besides the goal of disinfection, an investigation was carried out about the simultaneous decontamination of wastewater, monitoring the elimination of 25 emerging contaminants present in the secondary effluents. The mode of operation was assessed, with the operation either in batch or continuous mode; for the required conditions for disinfection of WWTP secondary effluents, monitoring also the elimination of micropollutants.

The results of this work prove that under normal operating conditions, iron oxides can effectively replace the use of iron salts, giving way to an easier and cheaper implementation of the solution. Iron oxides have been proven to be successful in maintaining an effective photo-Fenton process, hence in the envisioned application there will be no need for acidification of the water and subsequent neutralization, avoiding costs of acids/bases, generation of salts and corrosion of the equipment. Furthermore, easy separation of the catalyst can be applied, as iron oxide particles sediment fairly quickly, so microfiltration, magnetic separation (for ferromagnetic oxides) or simple decantation could be sufficient. Efficiency-wise, the 5-log reduction of fecal bacteria enables safe discharge and efficient reuse, with more than 30% complementary removal of emerging contaminants. The feasibility and efficacy of the process demonstrated pave the way to further scale-up of the system and its establishment as a viable alternative to wastewater treatment.

Overall, this Ph.D. thesis opens the doors to the large-scale implementation of the solar photo-Fenton process in RPRs at neutral pH in wastewater treatment plants as a feasible tertiary treatment. Besides, continuous mode operation has proven to be successful not only in pathogen inactivation but also in ARBs and CECs allowing a significant treatment capacity increase. Furthermore, a reduction of operational costs has been proposed replacing the use of conventional iron salts for iron oxides as photo-Fenton catalyst due their effectiveness in both bacterial inactivation and micropollutant removal.