University of Almeria

ASSESSMENT OF SOLAR-DRIVEN PROCESSES AND OZONATION FOR DISINFECTION, DECONTAMINATION AND REUSE OF FRESH-CUT WASTEWATER

Leila Samira Nahim Granados

PhD Thesis

Almería, January 2020

SUMMARY

The world is undergoing global socio-economic changes that involve important environmental problems like water scarcity where agriculture plays a critical role due to its high consumption of freshwater resources. The intensification of water stress generates new water-food challenges to current and future sustainability agriculture. Therefore, the implementation of emerging technologies in order to respond to these pressures in water-scarce countries is crucial. In this regard, agro-food industrial wastewater (WW) reuse for agriculture represents an unconventional water supply, improving the water use efficiency. Among the different agro-food industries, the fresh-cut produce industry stands out for its rapid development in the last years due to the trend of demand for healthy, nutritious and fresh food marketed as 'ready-to-eat'. This industry is one of the major water consumers in the agro-food sector due to the high water volumes (up to 40 m^3/ton of raw product) required mainly during the vegetables wash stage.

The consumption of fresh-cut products is an important route of foodborne pathogens transmission when a proper disinfection treatment is not applied in the production process. In fact, several worldwide outbreaks attributed to the consumption of raw-eat vegetables have been reported over the past few years. In spite of the microbiological risk, the wastewater generated by this industry is also an important source of organic microcontaminants (OMCs) (mainly pesticides) which are not yet regulated. To avoid the associated risk with pathogens, the most common strategy in this industry is the use of chlorine compounds as a sanitizing agent during the washing step. Nevertheless, the commonly hyper-chlorination practice linked with the high quantity of dissolved organic matter in this water matrix leads to the generation of unhealthy disinfection by-products (DBPs) and has resulted in the forbiddance of the chlorination practice in some European countries. Moreover, the chlorination process does not efficiently degrade chemical contaminants and it therefore does not control their accumulation during the processing stage.

Consequently, the search and evaluation of new or alternative water treatments able to reduce simultaneously the microbiological and organic chemical contamination without DBPs formation in this industry has grown recently.

The general aim of this study is to investigate the use of solar-driven technologies (solar photo-Fenton and H_2O_2/solar) and a conventional process (ozone) for the improvement of fresh-cut wastewater (or washing water) to reach the chemical and microbiological quality established on wastewater reuse guidelines for irrigation in agriculture. In this study, the selected targets were two human bacterial pathogens (*E. coli* O157:H7 and *S. enteritidis*) as model of microbial contamination and a mix of OMCs (atrazine, azoxystrobin, buprofezin, imidacloprid, procymidone, simazine, thiamethoxam and terbutryn) as model of chemical contamination (pesticides).

Firstly, a synthetic fresh-cut wastewater (SFCWW) recipe was formulated to be used along this study as a tool to avoid water characteristics fluctuations of real matrices and therefore to perform more realistic comparisons between different treatments and experimental conditions. Although the solar processes have proven to be effective for disinfection of different types of water matrices, the high turbidity (100 NTU) of SFCWW makes necessary to study the disinfection capability of solar processes in this particular water matrix. In line with this, the disinfection capability of four solar processes (solar photo-inactivation, H_2O_2/solar, Fe/solar and solar photo-Fenton) was studied at laboratory scale and under controlled conditions in a solar simulator. The results obtained clearly indicate their capability to disinfect SFCWW in short treatment times (> 5 Log Reduction value (LRV) in < 45 min) in all cases. The best disinfection efficiency was obtained for the H_2O_2/solar process using 20 mg/L of oxidant and requiring less than 20 min of treatment regardless of the year season, making this process a promising option to disinfect fresh-cut wastewater. Nevertheless, the low disinfection capability shown by the iron/solar processes (mainly explained by iron speciation at SFCWW pH, i.e., 6.25) indicates the need to use alternatives iron sources which let improving the disinfection efficiency.

In this context, the assessment of different iron sources (mainly iron chelates and iron complexes) that allow the iron kept in solution longer, increasing the process efficiency is a key research topic in the last years. In this study, the use of a commercial iron fertilizer (Fe^{3+}-EDDHA) employed to remediate iron chlorosis in agriculture has been investigated for the first time as a bactericidal agent in solar water disinfection processes in comparison with the conventional use of iron salts. The study was carried out at laboratory scale (200 mL), under natural solar radiation, with reagent concentrations ranged from 0.5 to 5 mg/L of iron and in two water matrices with different complexity: isotonic water (IW) and SFCWW. The results showed a clear improvement of the solar disinfection efficiency when using the new iron source (45 min) in comparison with the conventional one (iron salts) that required 90 min of treatment time. Moreover, an inactivation mechanism was proposed to explain both, the loss of bacterial viability and the different resistant of each bacterial strain to be inactivated (*S. enteritidis* showed higher resistance than *E. coli* O157:H7). Briefly, the mechanism proposed was mainly attributed to changes in the cell membrane permeability when Fe^{3+}-EDDHA is present and on structural damages caused by hydroxyl radicals ($HO^{\bullet}$) for Fe^{3+}-EDDHA/H_2O_2/solar process.

These promising disinfection results were latter on investigated simultaneously with OMCs decontamination at pilot plant scale in SFCWW to determine the capability of these solar processes to be applied at pre-industrial scale. For this purpose, solar experiments (H_2O_2/solar, Fe^{3+}-EDDHA/solar and Fe^{3+}-EDDHA/H_2O_2/solar) were conducted under natural sunlight using tubular reactors of 60 L treatment capability provided with Compound Parabolic Collector. The experimental results obtained showed high efficiency to reduce the microbiological contamination (>5-LRV in 60 min) and moderate efficiency to reduce the OMCs load (from 20 to 40 %) for all the solar processes studied.

Ozone and peroxone processes (ozone with added H_2O_2) at pilot plant scale (10 L) were also investigated as conventional advanced oxidation processes (AOPs). The capability of both processes for the simultaneous disinfection and decontamination of SFCWW under several operational conditions: natural SFCWW pH (6.25) and basic pH (11), two different initial ozone productions (0.09 and 0.15 gO_3/Lh) and the addition of 20 mg/L of H_2O_2 have been investigated. The results obtained shown that the highest efficiency for OMC removal (85 %) and pathogen inactivation (> 5-LRV) were obtained with the simplest condition, i.e., ozonation treatment at natural pH requiring the following ozone doses: < 10 and < 30 mgO_3/L for SFCWW disinfection and decontamination, respectively.

In summary, the purification results obtained have significant implications due to the solar processes as well as the ozonation process investigated have demonstrated to allow safe wastewater reclamation for irrigation purpose.

Once the treatment capacity of the selected processes were investigated at pilot scale, irrigation tests in an experimental greenhouse using two raw eaten vegetables (radish and lettuce) were performed to investigate the application of treated SFCWW for agriculture purpose, demonstrating also the reduction of the water-footprint of this industry. The irrigation tests were done using the best operational conditions obtained for each solar treatment (H_2O_2/solar and Fe^{3+}-EDDHA/H_2O_2/solar) and ozonation (at natural pH). In addition, untreated SFCWW spiked with target contaminants (used as positive control) and mineral water with a total absence of target contaminants (used as negative control) were also investigated in this study. In general, the analysis of harvested crop samples irrigated with treated SFCWW revealed a complete absence of pathogens, i.e., below the limit of detection (LOD), of 1 CFU/99 g in lettuce and <1 CFU/8 g in radish for all the treatments evaluated and both crops. For OMCs, in all processes in comparison with the results ontained with untreated SFCWW a clear reduction on their uptake by crops was observed. In particular, the crops irrigated with ozonated SFCWW shown the highest reduction of OMCs uptake by crops: 95 and 92 % in lettuce and radish, respectively. In the case of solar processes, the reduction of OMCs uptake varied from 64 to 77 % in lettuce and from 43 to 59 % in radish, for all the solar processes evaluated. Nevertheless, lettuce crops irrigated with treated SFCWW by the solar process that incorporate the iron micronutrient (Fe^{3+}-EDDHA/H_2O_2/solar) showed twice chlorophyll content than those irrigated by ozonated and H_2O_2/solar treated water. Therefore, in view of the results, the physiologic benefit of crops by the employ of Fe^{3+}-EDDHA as iron source to reuse treated water by solar processes was also confirmed. In general, the results obtained support the suitability of the solar processes studied to reduce both: the crops contamination (microbiological and chemical) and the iron chlorosis risk.

Finally, a techno-economic, environmental and health risk evaluation of the global processes was done to determine the implementation viability of the studied processes (ozonation, H_2O_2/solar and Fe^{3+}-EDDHA/H_2O_2/solar) including chlorination as a reference of the more widely applied disinfection process in this type of industry. The environmental evaluation was performed by ecotoxicity studies using different tests applied to the treated SFCWW: *Vibrio fischeri* test to evaluate the impact discharges and *Lactuca sativa* test to determine the suitability for crops irrigation. The results obtained with *V. fischeri* showed non-acute toxicity for solar treated SFCWW, slight acute toxicity for ozonated SFCWW and acute toxicity for chlorinated SFCWW. The results obtained with *Lactuca sativa* tests showed in general non-significant effects for ozonated and solar treated SFCWW and an inhibition grown effect with chlorinated SFCWW. Therefore, these results confirm the suitability of ozone and solar processes for subsequent SFCWW reuse and exacerbate the non-suitability of the chlorination process for the same purpose.

The economic analysis for the simultaneous disinfection and decontamination of SFCWW at the best operational conditions founded shown treatment costs of ca. 1.15 €/m^3 for ozonation and ca. 1.60 €/m^3 for Fe^{3+}-EDDHA/H_2O_2/solar process. These treatment costs are almost twice of the obtained for chlorination (ca. 0.70 €/m^3), which is, at industrial scale, the main barrier for changing to other alternative process.

Lastly, a chemical and microbiological health risk assessment of the crops irrigated with treated SFCWW (by ozone and solar processes) and untreated SFCWW was performed using: i) the estimation of the hazard index (HI) as a tool to estimate the dietary risk assessment for the combined exposure of the chemical contaminants and ii) the quantitative microbial risk assessment (QMRA) based on dose-response models and Monte Carlo simulations using the software FDA-iRISK®. The results obtained from the dietary risk assessment of the OMC residues in lettuce and radish showed that any of the vegetables irrigated with treated or untreated SFCWW entail a significant health risk, being lower the risk associated with treated SFCWW. In the case of the QMRA, the crops irrigated by untreated SFCWW represent an important infection risk for the consumer whereas the crops irrigated by the treated SFCWW demonstrated a reduction of more than 4 orders of magnitude the infection risk associated to the consumption of raw vegetables.