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Treatment of municipal WWTP secondary effluents by solar photo-Fenton: an implementation proposal based on continuous flow operation

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Tratamiento de efluentes secundarios de EDAR mediante el proceso foto-Fenton solar: una propuesta de implementación basada en la operación en modo continuo

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ABSTRACT

The use of reclaimed wastewater for agricultural purposes has long been extensively practised around the world, although, the lack of proper treatment can actually cause pollution to spread. In fact, over the last few decades, the advances in analytical chemistry have allowed the identification of anthropogenic substances, at low concentrations (ng L^{-1}, µg L^{-1}), in aquatic bodies.

Such substances, called micropollutants (MPs) or contaminants of emerging concern (CECs), come from discharges of untreated wastewater, but also from effluents of wastewater treatment plants (WWTPs); because the current installations are designed to eliminate biodegradable nutrients, but they are unable to remove recalcitrant molecules, especially at low concentrations, giving rise to the need for the installation of additional treatment steps.

It can be seen then that MP removal presents technological and economic challenges, in a context where the legislation about it is also in development. In the European Union, some efforts have been made to regulate MP discharge into the environment, through the implementation of a program that monitors certain substances. If they pose a verified risk to the environment, they are subsequently catalogued as priority substances, meaning local governments have the power to include them in their legislation.

Having said that, MP removal is only regulated in a few places like Switzerland, Australia and California. This is due to the complexity of deciding which substances should be monitored, their limit of emission, and the installation of technologies to reach such aims.

To date, several technologies have been tested, although the choice of the technology to be implemented for each site corresponds to specific demands. Advanced oxidation processes (AOPs), in particular the photo-Fenton process, have been observed as a promising technology which is able to remove MPs.

The photo-Fenton process consists of the catalytic decomposition of hydrogen peroxide in the presence of iron species, to produce hydroxyl radicals (2.8 eV), which degrade MPs by radical oxidation. The iron species are in a redox cycle thanks to UV radiation that allows photoreduction,

and when the process is operated using solar light, the process has the added value of being able to use a renewable source of photons instead of when using lamps.

Apart from that, throughout the development of the solar photo-Fenton process, several steps have been given forward for coupling it as a tertiary treatment in WWTPs. One of the most important steps was the simplification of the reactor geometry, replacing tubular reactors with raceway pond reactors (RPRs). This change was made due to excess of photons in tubular reactors when the process is operated with low iron concentrations (5 mg L^{-1}), and as such, the use of raceway pond reactors (RPRs) with longer light path length, and better use of most of the photons reaching the reactor surface, was implemented successfully.

Furthermore, short treatment times (tens of minutes) are necessary to achieve acceptable MP degradations. Operating in continuous flow mode therefore appears to be the logical next step for the improvement of this technology.

To satisfy this need, this present PhD thesis deals with the commissioning of a plant to carry out the continuous solar photo-Fenton process to degrade MPs in secondary effluents from municipal wastewater treatment plants, along with the technical, economic and environmental assessment of its operation. All the experimentation was carried out in outdoor condition at pilot scale, in order to give a closer perspective of how the process could be performed on a demonstrative scale.

The thesis is divided into four main sections related with the objectives established, 1) operation in continuous flow at acidic pH, 2) operation in continuous flow at neutral pH, 3) the technical and economic comparison of both operation strategies and 4) the environmental evaluation of the operation at acidic pH.

Operation in continuous flow at acidic pH is discussed in Section 4.1. As far as the authors' knowledge goes, before 2016, there were no instances regarding about the operation of the solar photo-Fenton process operated in continuous flow mode. Consequently, this operation mode has been reported for the first time, thus demonstrating its operational feasibility.

The experimentation was carried out firstly, in spiked synthetic secondary effluents, testing hydraulic residence times (HRTs) of 120 and 80 min with a liquid depth (LD) of 5 cm in a fibreglass

RPR of 120 L capacity (pilot scale), in outdoor conditions. Low iron (0.1 mM) and hydroxide peroxide (0.88 mM) concentrations were used as photo-Fenton reactants. The results showed that at least 90% of the model pollutant (acetamiprid, ACTM) was removed, without a substantial influence of the solar irradiation on the stability of the process, during the 4 h of continuous flow operation.

Later, real secondary effluents, from the municipal Wastewater Treatment Plant “El Bobar”, Almería, Spain, were treated at two liquid depths, 5 and 15 cm (at an HRT 80 min), and three hydraulic residence times, 80, 40 and 20 min (LD 5 cm), maintaining the same reactant concentrations. The duration of the operation in continuous mode was also 4 h.

The experiments to prove the effectiveness of the liquid depth were carried out in PVC reactors with capacities of 16 and 77 L, for 5 and 15 cm, respectively. These resulted in almost the same MP degradation, 89% and 87% removal for 5 and 15 cm, respectively.

Due to this small difference, and the amount of water required to conduct experiments with increased flow rate (from 0.2 to 0.8 L min^{-1} when the HRT decreases from 80 to 20 min, in the 16 L reactor, or from 0.96 to 3.85 L min^{-1}, for the 77 L reactor), the LD was set at 5 cm to prove the effect of the HRT on the MP degradation, which reached values of 79, 84 and 89% for HRTs of 20, 40 and 80 min, respectively. Therefore, under conservative conditions, a treated wastewater volume of 450 L m^{-2} d^{-1} for a 5 cm-deep RPR operated in continuous mode at 40 min HRT for 6 hours a day in winter, reaching 84% MP removal can be expected.

Once the viability of operating at acidic pH in continuous flow was demonstrated, the next challenge was the study of the operation at neutral pH, whose objective was handled in Section 4.2. To operate the reaction at neutral pH, a chelating agent to form a complex with ferric iron was used, with the aim of conserving iron photoactivity, and to keep it in solution, solving the problems related with heterogeneous reactions.

Ethylenediamine-N,N'-disuccinic acid (EDDS) was selected as the chelating agent to form a complex with ferrous iron. The application of the complex Fe(III)-EDDS has been largely studied to operate photo-Fenton systems in batch mode. The results of such research indicated that the complex has a better performance than other organic complexes, and as EDDS is biodegradable its application does not represent an environmental risk to discharging or reusing the treated effluents.

The study related with the operation in continuous mode, using the complex Fe(III)-EDDS, involved the evaluation of the complex molar ratio and the effect of the residence time on MP degradation, as well as the short stability of the complex. The experimentation was conducted outdoors, for 5 h of continuous operation in a PVC RPR (16 L, 5 cm depth), measuring the MPs naturally present in real secondary effluents and their degradations. The secondary effluents were collected from the municipal Wastewater Treatment Plant “El Bobar” and for each experiment, the volume of secondary effluent necessary was close to 300 L.

The reactant concentrations were set at 0.88 mM and 0.1 mM, for H_2O_2 and iron, respectively, while the EDDS was varied between values of 0.1 and 0.2 mM accordingly to the molar ratio tested, 1:1 and 1:2. The comparison between the molar ratios 1:1 and 1:2 reveals an increase of 6%, in MP removal when the concentration of EDDS is doubled, pointing out that for the operation in continuous flow mode, to maintain the stoichiometric molar ratio of the complex (1:1) is a better option to avoid an increase in reactant cost.

Similarly, the increase of HRT from 20 to 40 min gave rise to an increase of 5% in MP degradation. In this regard, operating at an HRT of 20 min and molar ratio 1:1 looks like the more suitable option, considering the trade-off’ between MPs degradation, the reactant cost and treatment capacity.

Such operating conditions: HRT 20 min at 5 cm LD, and reactant concentrations of 0.88 mM H_2O_2, 0.1 mM Fe(III)-EDDS (molar ratio 1:1), were repeated for three consecutive days in order to show the short-term stability of the process. Indeed, the positive results of this task demonstrated a treatment capacity of 900 L m^{-2} d^{-1} with MPs removal percentages of around 60%.

Lately, a technical and economical comparison between the operation at acidic and neutral pH was performed in Section 4.3. To this end, outdoor experiments were conducted in a PVC RPR (77 L), testing HRTs of 15, 20 and 30 min at 15 cm liquid depth, for both operation strategies. The water matrix selected was a real secondary effluent from the wastewater treatment plant “El Toyo”, Almería, Spain, and the MPs present were monitored to determine their degradation.

Due to the high secondary effluent flow rate value (2.57-5.13 L min^{-1}) needed for these experimental conditions, and the evidence of a similar MP degradation for 5 h of experimentation, the duration of the experiments was reduced in order to treat around 1000 L for each experiment. Accordingly, the experiments with 15 min HRT were conducted for 2 h, and on a different day, HRTs of 20 and 30 min were tested, for 2 and 3 h, respectively.

The reactants were set at 0.88 mM H_2O_2 and 0.1 mM of iron. For the operation at acidic pH, the iron source was ferrous sulfate and the complex Fe(III)-EDDS at a molar ratio 1:1 was used to operate the reactor at neutral pH

For continuous operation, the degradation of MPs was 85 and 77%, for acidic and neutral pH at both HRTs of 30 and 20 min, while for 15 min the degradation was set at 75 and 72 for acidic and neutral pH, respectively. Since MP degradation produced similar results under the conditions tested, economic evaluation plays a determining factor in the selection of the operation parameters.

As such, in order to ascertain how the operation parameters can affect MP degradation and the treatment cost, kinetic models were used to predict MP degradation under different operating conditions and then calculate the treatment capacity and cost.

For the operation at neutral pH, a recently published kinetic model was used while for the acidic conditions, an improvement of another model was made. The models were validated with the experimental results, analysing the degradation of three pollutants: O-Desmethyltramadol (O-DSMT), O-desmethylvenlafaxine (O-DSMV), and gabapentin GBP.

After that, the combination of several liquid depths and hydraulic residence times, for both operating pHs, were simulated to generate a table of MP degradation and treatment capacities, considering an operation time of 7.5 h per day and, coming from a total of 2729 h with a UV radiation of at least 10 W m^{-2} for a whole year. The results suggest that operating at neutral pH allows increasing the liquid depth without decreasing the MP degradation, while operating at acidic pH demands longer HRTs to achieve high MP degradation values. However, there is a point where operating conditions converge with almost the same MP degradation, 80 and 77 % for neutral and acidic pH, respectively. This is observed when the process is operated at an HRT of 30 min at 15-cm liquid depth. Considering an operating time of 7.5 h d^{-1}, the treatment capacity achieved can be as high as 2250 L m^{-2} d^{-1}.

Later, the neutralization of the acidic photo-Fenton effluents by passing them through a tower packed with $CaCO_3$ was proposed. The neutralization experiments exhibit a final pH value of 6.8 with a residence time of 4 min and, additionally, the feasibility to neutralize and remove the iron in just one step was demonstrated. Moreover, since the $CaCO_3$ can be obtained from the stone industry as a by-product, the cost of the neutralization can be affected positively.

Taking into account the obtained results, the treatment cost was estimated for the operation at acidic and neutral pH, also considering the photo-Fenton process and the pre and postconditioning of the secondary effluent. For the photo-Fenton process, a treatment capacity of 2250 L m^{-2} d^{-1} (an HRT of 30 min at 15-cm liquid depth) was considered. Preconditioning was defined as the acidification (2.8) of the secondary effluent or carbonate stripping up to 15 mg L^{-1} of inorganic carbon, according to the operating pH. Postconditioning was considered as filtration in column by $CaCO_3$ for the acidic effluents and silex sand filtration for the effluents treated at neutral pH.

In this regard, the treatment cost at acidic and neutral pH can be estimated at 0.27 € m^{-3} and 0.57 € m^{-3}, respectively. Such values are mainly affected by the reactant cost, particularly for the iron source, and because of the high cost of EDDS, operating at acidic pH is still cheaper for the same MP degradation goal, in comparison with operating at neutral pH.

Finally, the environmental evaluation of operating at acidic pH was carried out using the Life Cycle Assessment methodology. In this regard, a baseline scenario and two comparative scenarios were used. The baseline scenario implied the discharge of secondary effluents into the sea and groundwater extraction for agricultural purposes; while the two other scenarios involved the tertiary treatment of secondary effluents to use reclaimed water for agricultural irrigation. The tertiary treatments selected were ozonation and solar photo-Fenton process operated at acidic pH.

The environmental impacts, that were quantified by ReCiPe and USEtox as life cycle impact assessment (LCIA) methods, showed that the water stress for the location of the project (Almeria, Spain) can be decreased by the installation of tertiary treatments, because it avoids the extraction of groundwater. As such, according to the ReCiPe endpoint method, 37% of the environmental damage can be decreased by the implementation of ozonation~~.~~

Moreover, the environmental performance of the ozonation was better in comparison with the solar photo-Fenton process as, in terms of USEtox indicators, the ozonation process contributes 2-4 times less than the photo-Fenton process (CPC), and three times less to climate change (ReCiPe midpoint characterization). The photo-Fenton reactants, especially hydrogen peroxide have greater impact than the ozone production. In this regard, the photo-Fenton reactants have six times more impact than the ozone production, according to the ReCiPe endpoints method. Additionally, major drawbacks like the liberation of CO_2 during the pH adjustment ($\approx$0.36 g CO_2 eq L^{-1}), and the need for additional storage for collecting secondary effluent at night are issues that should be addressed in order to lessen the impact related with them.

However, it is important to note that the use of RPRs instead of CPCs means a reduction of 24% in the impact related with the infrastructure, and continuous mode operation allows a decrease of 25% in the reactor size of the RPR. Thus, even though further challenges should be addressed in order to make it a more attractive technology, in environmental terms, the implementation of RPR and continuous mode operation has allowed the progress of the environmental performance of this technology.