Green Electrocatalytic Wastewater Refinery to Synthesize Value-added Products by Electro-Fenton Degradation of Acetaminophen

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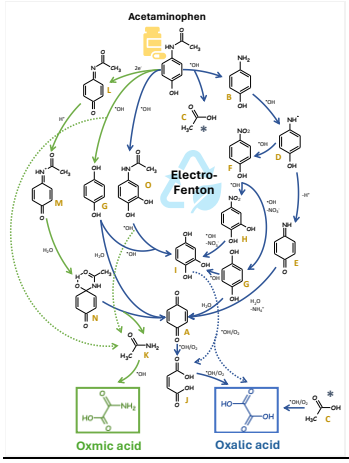

The Electro-Fenton process (EF) has been conventionally applied to degrade refractory and/or toxic pollutants. However, in this work, EF was used as a reverse engineering tool to selectively synthesize highly value-added products (oxalic or oxamic acid) through the degradation of the model pharmaceutical pollutant acetaminophen. It was found that the production of either oxalic or oxamic acid was dictated by the applied current density. Under optimal conditions (0.71 mA cm^{-2} and 100 mg L^{-1} of initial TOC concentration), up to 227.1 ± 26.3 mg L^{-1} of oxalic acid were produced, with high yield and selectivity of 54.9 ± 5.1% and 94.7 ± 9.9%, respectively. In the case of oxamic acid, the highest concentration of 33.8 ± 2.1 mg L^{-1} was produced at 2.13 mA cm^{-2} and an initial TOC of 50 mg L^{-1}, which represented a yield of 18.7 ± 0.3% and 60.9 ± 9.3% selectivity. This is a pioneer work on EF applications to the field of wastewater valorization through the recovery of value-added products within a circular economy.

Introduction

The Electro-Fenton process (EF), an Electrochemical Advanced Oxidation Process (EAOP), is now well recognized as a powerful emerging technology for wastewater treatment [1,2]. Due to its great oxidation power, EF has been traditionally used as a destructive technique to degrade mainly organic pollutants ideally until full mineralization (conversion to CO_2), aiming at decreasing the amount of organic matter contained in wastewater. On the other hand, the new paradigm around wastewater treatment recognizes wastewater as a resource from which energy and value-added products can be recovered (Kehrein et al., 2020; Meese et al., 2021; Renfrew et al., 2022). In this sense, new technologies for wastewater treatment must consider not only water purification, but also wastewater valorization through resources recovery within a circular economy. Accordingly, even though EF (as well as other AOPs) has reached a high maturity level as a treatment technology, it must move forward with the new trends on wastewater treatment to also include resources recovery.

In this context, this work explores the use of the EF process as a green electrocatalytic synthesis approach to produce valuable oxalic and oxamic acids with high selectivity and yields making use of organic wastewater pollutants as a renewable carbon source, with simultaneous wastewater purification. For this, the widely widespread pharmaceutical acetaminophen was used as model pollutant. To the best of our knowledge, this is the first time EF is directly evaluated as a wastewater valorization process through recovery of value-added products, which opens new possibilities for EF as a key technology for wastewater treatment and valorization to comply with the Sustainable Development Goals related to the intricate water-energy-food-environment nexus.

Material and Methods

EF experiments were conducted in a glass tubular undivided electrolytic reactor containing a concentric carbon felt cathode and a mesh Ti/IrO_2-RuO_2 anode. The experiments were conducted at room temperature under galvanostatic mode and continuous stirring and aeration. 350 mL of acetaminophen solutions at pH 3 were used for the experiments with Fe^{2+} as the catalyst source. All the experiments were conducted in duplicate, and results are reported as the mean with their standard deviations.

Results and Discussion

Fig. 1 shows the effect of current density on the production of oxalic and oxamic acids through the EF degradation of acetaminophen. It can be seen that for current density values of 0.36 and 0.71 mA cm^{-2}, the amount of oxalic and oxamic acids

increased with electrolysis time, which is explained by the continuous degradation of acetaminophen and its degradation by-products. Their accumulation after 4 h is due to their slow reaction with •OH.

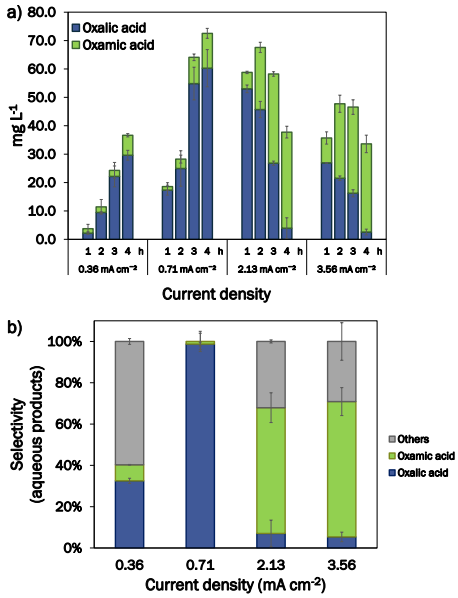

Figure 1. Effect of current density on a) production of oxalic and oxamic acids, and b) selectivity of aqueous products in 4h during the EF treatment of acetaminophen solutions with 50 mg L^{-1} of initial TOC, 0.2 mmol L^{-1} of Fe^{2+} 0.05 mol L^{-1} of Na_2SO_4, and pH 3.

Interestingly, **Fig. 1** also shows that current density had an important impact on the main products that were generated (oxalic or oxamic acid), evidencing that the reaction mechanisms governing acetaminophen degradation by EF are current density dependent. Low current density drove the reaction towards oxalic acid as the main degradation product, while high current density favors the production of oxamic acid. It is worthy to note that under the conditions reported in **Fig. 1**, the highest concentration of oxalic acid that was produced (60.3 ± 6.6 mg L^{-1} at 0.71 mA cm^{-2}) corresponded to a high selectivity of aqueous products of 98.7 ± 0.9% (**Fig. 1b**) (33.0 ± 4.5% of reaction yield), which means that 98.7 ± 4.5% of the residual TOC after 4 h of EF at 0.71 mA cm^{-2} was in the form of oxalic acid. The other 1.3 ± 0.2% of TOC came from oxamic acid, summing up 100% of the organic matter in the solution after EF. This represents a selectivity of 100% for both compounds. The rest of the organic carbon initially present as acetaminophen was lost as CO_2. In the case of oxamic acid, the highest concentration produced at 2.14 mA cm^{-2} (33.8 ± 2.1 mg L^{-1}) represents a selectivity of 60.9 ± 9.3% (**Fig. 1b**), with a reaction yield of 18.7 ± 0.3%.

In the case of oxalic acid production at low current density, the degradation mechanism was dominated by homogeneous •OH produced by the Fenton reaction, while acetaminophen oxidation at the anode by direct electron transfer played an important role in the generation of oxamic acid at high current density. Details on the mechanisms with be presented at the conference.

Finally, when increasing the initial acetaminophen concentration to 100 mg L^{-1} of TOC, oxalic acid production increased to 227.1 ± 26.3 mg L^{-1} at a low current density of 0.71 mA cm^{-2}, with high yield and selectivity of 54.9 ± 5.1% and 94.7 ± 9.9%, respectively (data not shown). Overall, the results demonstrate the great potential of EF to recover either oxalic or oxamic acid with high selectivity as value-added chemicals using wastewater as a renewable carbon source, while clean water is generated.

Conclusions

The reversed engineered EF process presented here emerges as a potential wastewater valorization option to recover value-added chemicals in the context of a circular economy. Additionally, it may represent an alternative to the chemical sector that is largely dominated by fossil fuels for both feedstock and energy. This work also advances the use of AOPs not only as destructive treatment technologies, but also as powerful valorization processes.

Acknowledgments

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