Treatment of agro-industrial effluents by Fenton based processes

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1. Introduction – Advanced oxidation processes (AOPs) are centered on the generation of very reactive oxidizing free radicals, especially hydroxyl radicals, due to their high oxidant power [1] produced, for example, by Fenton reagent. The Fenton reagent is a homogeneous catalytic oxidation process involving the reaction of hydrogen peroxide with ferrous ions. This reaction generates hydroxyl radicals (HO•) that have a high oxidation potential:

$$\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{HO}^- + \text{HO•}; k = 76 \text{ M}^{-1}\text{s}^{-1}.$$ 

2. Results and Discussion - Agro-industries like olive oil extraction, wine production and different food processing and transformations activities give rise to highly contaminant wastewater. This is a major environmental problem in Mediterranean countries in general, and particularly in certain areas of Spain and Portugal where there are a great many small plants. Most of these wastewater pollutant properties have been ascribed to phenolic compounds, because of their toxicity and power to inhibit biological treatments.

In this work we present different oxidation processes involving the Fenton reagent and alternative processes such as photo-Fenton, photo-Fenton in a CPC solar reactor and UV-A/LEDs/photo-Fenton, aiming the treatment of different agro-industrial effluents [2].

The application of Fenton’s reagent is a possible method to partially treat olive mill wastewaters allowing achieve a significant decrease of COD. Fenton’s reagent at initial pH 3.5, temperature = 30ºC, molar ratio $\text{H}_2\text{O}_2:\text{Fe}^{2+} = 15$ and weight ratio $R=\text{H}_2\text{O}_2/\text{COD}=1.75$, leads to a COD reduction of 70%. A modified pseudo-first-order equation allowed to describe well the process and led to the determination of kinetic parameters useful for the design of industrial reactors.

Degradation of winery wastewater was studied in a pilot-scale compound parabolic collector (CPC) solar reactor. Photo-Fenton experiments led to 46% TOC degradation in simulated wastewater prepared with diluted wine (WV) and 93% in wastewater prepared with diluted grape juice (WG), and if ethanol is previously eliminated from mixed wine and grape juice wastewater (WW) by air stripping, it removes 96% of TOC. Furthermore, toxicity decreases during the photo-Fenton reaction very significantly from 48% to 28%. At the same time, total polyphenols decrease 92%, improving wastewater biodegradability. Finally, the treatment of crystallized-fruit effluents, characterized by a very low biodegradability (BOD₅/COD <0.19), through the application of a UV-A LED photo-Fenton process. Under the optimal conditions ([H₂O₂] = 5459 mg/L; [Fe³⁺] = 286 mg/L; time >180 min), a COD removal of 45, 64 and 74% was achieved after 360 min, using an irradiance of 23, 70 and 85 W/m² respectively. Then a combination of UV-A LED photo-Fenton with coagulation-flocculation-decantation attained a higher COD removal (80%), as well as almost total removal of turbidity (99%) and total suspended solids (95%). Subsequent biodegradability of treated effluents increased, allowing the application of a biological treatment step after the photochemical/CFD with 85 W/m².

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References