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Gaining further insight into photo-Fenton treatment of phenolic compounds commonly found in food processing industry

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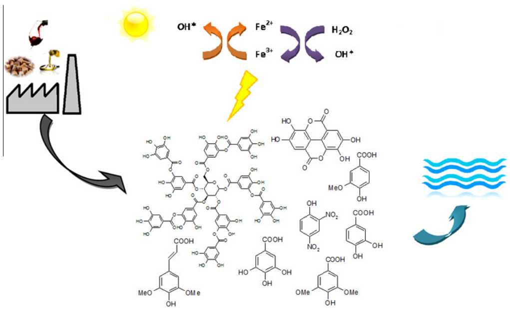
HIGHLIGHTS

- Solar photo-Fenton is able to degrade phenolic pollutants at pH = 3.9.
- Different bioassays show detoxification along the photo-oxidative process.
- EEM fluorimetry shows the removal of fluorescent moieties from the solution.

GRAPHICAL ABSTRACT



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ABSTRACT

A mixture of eight phenolic compounds, namely 2,4-dinitrophenol, tannic, ellagic, gallic, protocatechuic, vanillic, syringic and sinapic acids, have been treated by means of a photo-Fenton process under simulated and real sunlight. An experimental design methodology, based in Doehlert matrixes, was employed to check the effect of the concentration of Fe(II) and H_2O_2, as well as pH. Response surfaces show that photo-Fenton can be extended to pH values clearly above 2.8, probably due to complexation of iron with the phenolic substances. Experiments performed under solar irradiation at pH = 3.9 showed that complete removal of the monitored pollutants was achieved in less than 3 min; mineralisation was also efficient, although some organics remained in the solution. Toxicity was monitored according to *Pseudokirchneriella subcapitata* and *Daphnia magna* bioassays; Recombinant Yeast Assay (RYA) was employed to assess estrogenic and dioxin-like activities. 2,4-Dinitrophenol was demonstrated to be the major concern and, in general, photo-Fenton resulted in a detoxification of the solution. Finally, excitation emission matrix (EEM) fluorimetry was employed to obtain complementary information on the behaviour of organic matter. Most peaks associated with the parent pollutants disappeared after short irradiation periods and, at 12 min of irradiation chromophores were destroyed, what can be associated with the removal of complex molecules.

1. Introduction

Aqueous wastes from food processing industry, such wine, olive oil or coffee production, canning industry or cork stew, represent an important environmental concern. They show a complex composition including mineral salts, sugars, biological macromolecules, fatty acids, tannins, phenols or polyphenols at variable concentrations. In particular, phenols and related compounds such tannins are difficult to treat by classical means as they are reluctant to biodegradation or even toxic, thus inhibiting the removal of the biodegradable fraction [1,2].

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Advanced oxidation processes (AOPs) have been demonstrated as promising alternatives to deal with phenolic compounds; these technologies involve the in situ generation of highly reactive species via chemical, thermal or photochemical pathways [3]. Several studies have been published showing the ability of AOPs to remove those compounds from synthetic model solutions [4,5], but also from real effluents [6–10]. Interestingly, AOPs exhibit some selectivity for phenolic compounds vs. other more degradable organics, as observed in paper mill effluents [11,12]; this is an important advantage, as combination of AOP as a pre-treatment to remove the non-biocompatible fraction with biological processes is a meaningful strategy for food industry effluents [13,14].

The use of sunlight in photochemical AOPs represent an enhanced sustainability for those treatments. Photo-Fenton, one of the processes that can be driven under solar irradiation, is based on the ability of iron salts to catalyse decomposition of hydrogen peroxide to generate reactive species, such as hydroxyl radical [15]; this process is pH-dependent being the optimum value ca. 2.8. Results have been published dealing with the use of photo-Fenton in the treatment of phenolic compounds or real food processing industry effluents [14,16]. Briefly, the mechanism of oxidation of this family of compounds by hydroxyl radicals involves further hydroxylation of the aromatic ring, formation of quinones and, finally, cleavage of the aromatic ring to form carboxylic compounds, as described for nitrophenols [9]. However, some important issues still deserve further research. For instance, being elimination of the toxicity mainly associated to phenols one of the goals of the photo-oxidative treatment, it is interesting to assess detoxification according to different methods, as these results vary depending on the species that is employed [17]. Furthermore, monitoring the endocrine disrupting behaviour of those substances throughout the process seems a meaningful step forward, as this effect is not detected by classical toxicity bioassays [18].

Another issue that deserves further research is the role of pH in complex effluents. It is well known that substances able to modify the coordination sphere of iron may change the optimum pH for photo-Fenton [19,20]. In fact, it has been recently reported that the photo-Fenton treatment of olive oil mill wastewater can be applied at pH = 5 with only a slight change in efficiency when compared with 2.8 [6]. This result is interesting, as the costs associated to pH modification might be reduced. Also regarding with the behaviour of complex systems, applying new techniques to gain further insight into changes in their composition seems meaningful. In this context, excitation emission matrix (EEM) fluorimetry might be a useful tool. It has been commonly used in the characterisation dissolved organic matter [21,22], although the use of EEM has been recently extended to other fields [23]. Hence, it is interesting to check if EEM can provide useful information on the behaviour of phenolic compounds submitted to AOPs, as a previous step before developing tools for a mathematical modelling of the process.

In order to investigate the issues above described, a mixture of eight phenolic substances commonly found in food processing effluents has been submitted to a photo-Fenton process under simulated and real sunlight. This approach has already been used for other type of chemicals (e.g. pesticides or pharmaceuticals) and it has been demonstrated to provide useful information as the system is not so complex as real effluents (its composition is well determined and constant) but, it is not as simple as a single model compound and hence, more representative of the phenolic fraction [24,25]. The mixture consisted of tannic acid as example of tannins, ellagic acid as an example of a polyphenol, 2,4-dinitrophenol, and five phenolic acids with different substitution, namely gallic, protocatechuic, vanillic, syringic and sinapic acids (see Fig. 1 for structures). An experimental design methodology based on Doehlert matrixes has been employed to determine the effect of pH, H_2O_2 amount and iron concentration; the Doehlert design has been commonly employed as a chemometric tool, enabling to minimise the number of experiments required to obtain the equations that predicts the behaviour of the system in the studied region [26]. In addition to pollutants concentration, EEM have been used to provide complementary information on the process. Finally, two types of bioassays have been applied to assess the environmental risks associated with the pollutants and the treated mixture: (1) toxicity assays with the algae *Pseudokirchneriella subcapitata* and the crustacean *Daphnia magna*, according to their respective guidelines and (2) Recombinant Yeast Assay (RYA) to assess estrogenic and dioxin-like activities. RYA uses two genetically modified yeasts: ER-RYA system that contains the human estrogenic hormone receptor, and AhR-RYA system that expresses human aryl hydrocarbon receptor. Both strains contain a reporter plasmid expressing the *Escherichia coli* enzyme β-galactosidase. This enzyme will only be expressed in the presence of the receptor–ligand complex. The expression of gen is easy to follow using convenient enzyme substrates [27].

2. Experimental

2.1. Reagents

Tannic acid, ellagic acid, 2,4-dinitrophenol, gallic acid, protocatechuic acid, vanillic acid, syringic acid and sinapic acid were purchased from Sigma–Aldrich and used as received. Hydrogen peroxide (30% v/v) and ferrous sulphate were supplied by Panreac. Water employed in the experiments was Milli-Q grade.

The alga *P. subcapitata* and dormant eggs of crustacean *D. magna* were supplied by ECOtest S.L. (Valencia, Spain). The recombinant strains of *Saccharomyces cerevisiae* (BY4741 strain (ER strain) and YCM4 strain (AhR strain)) capable to detect estrogenic and aryl hydrocarbon receptor (AhR) agonist activities, respectively, were kindly provided by Dr. Benjamin Piña from Institute of Environmental Assessment and Water Research (IDAEA-CSIC), Barcelona, Spain. All medium constituents were supplied by Difco (Basel, Switzerland). Prototrophic markers, standards (17-β-estradiol (E2) and β-naphthoflavone (β-NF)) and enzymatic substrate (4-methylumbelliferone β-D-galactopyranoside and β-mercaptoethanol) were supplemented by Sigma–Aldrich. Assay buffer (Triton X-100) and Y-PER (Yeast Protein Extraction Reagent) were supplied by Fisher Chemical and Thermo Scientific, respectively.

2.2. Reactions

Laboratory scale experiments were carried out in cylindrical Pyrex vessels (55 mm internal diameter). A solar simulator (Sun 2000, ABET Technologies) equipped with a 550 W Xenon Short Arc Lamp was used as irradiation source; a glass filter was used to cut off the small fraction of radiation with $\lambda < 300$ nm. For each experiment, the reactor was loaded with 250 mL of solution containing the mixture of all eight pollutants (1 mg/L of each). Iron (II) was added as sulphate salt, with an initial concentration in the range 1–5 mg/L. The pH was adjusted by dropwise addition of diluted sulphuric acid or, eventually, sodium hydroxide. Then, hydrogen peroxide was added with an initial amount that ranged from 13.8 mg/L until 96.7 mg/L (corresponding, respectively, to 1/4 and 7/4 of the stoichiometric amount of H_2O_2 required to oxidise completely all the pollutants). Samples were periodically taken to be analysed.

Eventually, reactions were scaled up in a solar photoreactor Solardetox Acadus-2001 (Ecosystem), based on compound para-