Sunlight, iron and radicals to tackle the resistant leftovers of biotreated winery wastewater†

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Winery wastewater is characterized by high organic content consisting of alcohols, acids and recalcitrant high-molecular-weight compounds (*e.g.* polyphenols, tannins and lignins). So far, biological treatment constitutes the best available technology for such effluents that are characterized by high seasonal variability; however the strict legislation applied on the reclamation and reuse of wastewaters for irrigation purposes introduces the need for further treatment of the bioresistant fraction of winery effluents. In this context, the use of alternative treatment technologies, aiming to mineralize or transform refractory molecules into others which could be further biodegraded, is a matter of great concern. In this study, a winery effluent that had already been treated in a sequencing batch reactor was subjected to further purification by homogeneous and heterogeneous solar Fenton oxidation processes. The effect of various operating variables such as catalyst and oxidant concentration, initial pH, temperature and lamp power on the abatement of chemical oxygen demand (COD), dissolved organic carbon (DOC), color, total phenolics and ecotoxicity has been assessed in the homogeneous solar Fenton process. In addition, a comparative assessment between homogeneous and heterogeneous solar Fenton processes was performed. In the present study the homogeneous solar Fenton process has been demonstrated to be the most effective process, yielding COD, DOC and total phenolics removal of about 69%, 48% and 71% in 120 min of the photocatalytic treatment, respectively.

Introduction

Various cleaning activities during the crushing and pressing of grapes generate the major part of wastewater within a winery. Volumes and organic loads significantly change over the year, in relation to the working period and the winemaking technologies used.[1] The environmental impact of waste and wastewater from the wine industry is noticeable, due to the high organic load, the large volumes and the pronounced seasonal variability.[2]

The high biodegradability of winery wastewaters justifies often the choice of a biological treatment.[1] However, such treatments may not be capable of completely mineralizing the effluent, while there is always concern regarding the disposal of the sludge or other by-products derived from such processes.[2,3] The organic content of winery wastewater consists of alcohols, acids and recalcitrant high molecular weight compounds (*e.g.* polyphenols, tannins and lignins) which are not easily removable by biological means only.[1] As a result, the use of alternative

treatment technologies, aiming to mineralize or transform refractory molecules into others which could be further biodegraded, is a matter of great concern. Among them, AOPs have gained considerable attention for the treatment of industrial effluents, including amongst others agro-industrial wastewater.[1,4] Moreover, they have been successfully used as a pre-treatment step in order to reduce the concentrations of toxic organic compounds that can inhibit biological waste treatment processes.[4]

Recent studies have reported the degradation of winery wastewater by the photo-Fenton process.[3,5] Under optimal conditions, the photo-Fenton process reached purification levels up to 95% (measured as TOC) for synthetic samples containing diluted commercial grape juice (TOC concentration ranging between 1500 and 3000 mg L^{-1}).[5] The organic matter degradation of a partially treated winery wastewater with a COD of 1060 mg L^{-1} increased with increasing treatment time reaching COD removal as high as 80% after 240 min of the reaction; hence, the combined biological + photo-Fenton oxidation resulted in 95% COD removal.[3] Mosteo *et al.*[4] studied the degradation of winery wastewater (initial COD 3300 mg L^{-1}) by the heterogeneous solar Fenton process coupled with activated sludge. After 24 h of treatment, the organic matter was reduced to about 50%, while activated sludge allowed the elimination of 90% of the initial TOC. Another study investigated the effectiveness of different ozone-based AOPs (O$_3$, O$_3$/UV and O$_3$/UV/H$_2$O$_2$) for the treatment of winery wastewater (initial TOC 1255 mg L^{-1}) in a pilot-plant reactor. The highest TOC removal recorded was

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64% after 300 min.[1] Moreover, heterogeneous photocatalysis (TiO_2, TiO_2/H_2O_2, $TiO_2/Na_2S_2O_8$) in a pilot-scale compound parabolic collector showed low efficiency with 25% TOC degradation after 400 min of the reaction (initial TOC concentration 1155 mg L^{-1}). Conversely, the homogeneous solar Fenton process in the same CPC reactor resulted in 93% TOC removal after 400 min.[6]

Fenton oxidation is based on the ferrous ion and hydrogen peroxide, and exploits the reactivity of the hydroxyl radicals produced in an acidic solution by the catalytic decomposition of H_2O_2.[7]

The homogeneous Fenton process is advantageous because Fe^{2+} is abundant and non-toxic at low concentrations, while the process usually operates at ambient temperatures and pressures without the need for sophisticated equipment.[8] Furthermore, there are no mass transfer limitations since all of the reagents are in the liquid phase. In the presence of Fenton's reagent, photochemical reactions can be driven with low energy photons, belonging to the visible part of the spectrum. Thus, the photo-Fenton process is a potentially low cost AOP that can operate under solar irradiation.[8–10]

However, homogeneous photo-Fenton processes suffer a major drawback associated with the narrow pH range of operation, typically 2–4, to avoid the formation and subsequent precipitation of iron oxyhydroxides.[11] Not only does this mean additional cost through the consumption of reagents for acidification and subsequent neutralization, but also an increase of the treated water's salt loads.[12] In this respect, the immobilization of the catalyst on a heterogeneous matrix would enable its use under non-controlled pH conditions, as well as its easy recovery from the treated effluent.[11–13] In this context, a comparative heterogeneous study was performed employing the heterogeneous catalyst $Fe_2O_3/SBA-15$ to assess the efficiency of the heterogeneous solar Fenton process.

The aim of the present work was to investigate the homogeneous and heterogeneous solar Fenton processes as a polishing step for winery wastewaters that had already been subjected to biological treatment. These processes are considered as highly competitive for the removal of bioresistant organic pollutants. It should be emphasized that such technologies utilizing solar irradiation, a natural and abundant energy source, contribute to the sustainable management of winery effluents.

Bench scale experiments were carried out to evaluate the influence of catalyst and hydrogen peroxide concentration, pH, temperature and lamp power on COD, DOC, color, total phenolics removal and ecotoxicity.

Experimental

Chemicals

Solar Fenton experiments were performed using $FeSO_4 \cdot 7H_2O$ (Riedel-de Haen) and an iron-containing SBA-15 mesostructured material ($Fe_2O_3/SBA-15$) as homogeneous and heterogeneous catalysts, respectively. Reagent-grade H_2O_2 (35% w/w, Merck) was used as the oxidant and H_2SO_4 (95–97%, Merck) for pH adjustment. Residual H_2O_2 was removed from the treated samples with powder MnO_2 (≥90%, Sigma-Aldrich) for COD and DOC measurements and catalase (*Micrococcus*

lysodeikticus, Fluka Biochemika) for toxicity measurements in the homogeneous solar Fenton treatment, and Na_2SO_3 solution (Sigma-Aldrich) for COD, DOC and BOD_5 measurements in the heterogeneous solar Fenton treatment. For the measurement of total dissolved iron, 1,10-phenanthroline ($C_{12}H_8N_2 \cdot H_2O$) and ascorbic acid ($C_6H_8O_6$) were supplied by Sigma-Aldrich, while ammonium acetate (CH_3COONH_4) was supplied by Fluka.

Winery wastewater

Winery wastewater that had already been subjected to biological treatment in a sequencing batch reactor (SBR) was employed for Fenton oxidation experiments; its properties (determined according to standard methods[14]) are shown in Table 1.

Experimental set-up and procedures

Photocatalytic experiments were performed in two bench scale solar simulators. A Newport 91193 (Lamp Xe-OP 1 kW) was used for homogeneous solar Fenton experiments while an Oriel 96000 (Lamp Xe-OP 150 W) was used to perform the comparative study between homogeneous and heterogeneous solar Fenton processes. All runs were conducted in batch reactors made of borosilicate glass and equipped with a double wall for temperature control. In a typical run, an appropriate volume of wastewater was loaded in the reaction vessel, along with an appropriate amount of catalyst. The pH of the reaction mixture was adjusted, when necessary, prior to catalyst addition. A predetermined volume of 35% H_2O_2 was added all at once in the reaction mixture and the lamp was immediately turned on. This was considered as time zero of the reaction. The reaction mixture was magnetically stirred, while samples were withdrawn at frequent time intervals and filtered (0.22 μm Milli-pore and 0.45 μm, RC, PALL) prior to analysis.

Methods

DOC was measured on a Shimadzu TOC-V$_{CPH/CPN}$ analyzer, while COD was measured using Merck® Spectroquant kits

Table 1 Characterization of winery wastewater after SBR treatment

Parameter	Value[a]
pH (20 °C)	8.3
Total solids (mg L^{-1})	3672–3740
Total volatile solids (mg L^{-1})	2430–2612
Suspended solids (mg L^{-1})	225–245
Suspended volatile solids (mg L^{-1})	140–175
Total phenolics (mg L^{-1})	3.8–4.7
Total nitrogen (mg L^{-1})	6.7
COD (mg L^{-1})	264–270
DOC (mg L^{-1})	100–110
BOD_5 (mg L^{-1})	111–113
Total phosphorus (mg L^{-1})	32–46.8
Fats and oils (mg L^{-1})	4–6
Cu (mg L^{-1})	0.18–0.20
Cd (mg L^{-1})	0.17–0.19
Fe (mg L^{-1})	0.05–0.07
Sodium (mg L^{-1})	1.42–1.50
Potassium (mg L^{-1})	4.5–4.9

[a] Average of at least three measurements.

(WTW Photolab S6). The concentration of phenolics was assessed by the Folin–Ciocalteu method[15] using a UV/Vis Jasco V-530 spectrophotometer. Color determination was based on the ADMI Tristimulus Filter Method (Method 2120E in standard methods).[14,16] Colorimetric determination of total iron concentration with 1,10-phenanthroline was done according to ISO 6332. H_2O_2 was analyzed spectrophotometrically using ammonium metavanadate, which allows H_2O_2 concentration to be determined immediately based on a red-orange peroxovanadium cation formed during the reaction of H_2O_2 with metavanadate, with a maximum absorbance at 450 nm.[17] Toxicity measurements were performed in samples withdrawn at various treatment times using the Daphtoxkit FTM *magna* toxicity test. The procedures for conducting this assay were based on the ISO 6341 standard protocol. All runs were performed in duplicate or triplicate and mean values are quoted as results.

Results and discussion

Effect of solar irradiation

In order to evaluate the benefit of solar irradiation on COD reduction, the following experiments were carried out: (i) photolysis (*i.e.* solar irradiation only), (ii) solar irradiation + Fe^{2+}, (iii) solar irradiation + H_2O_2 (photo-bleaching), (iv) Fe^{2+} + H_2O_2 (dark Fenton), and (v) solar irradiation + Fe^{2+} + H_2O_2 (solar Fenton). In all experiments, the concentration of Fe^{2+} was 5 mg L^{-1} and the concentration of H_2O_2 was 500 mg L^{-1}; results are shown in Fig. 1.

The combination of solar irradiation and catalyst in the absence of hydrogen peroxide leads to negligible COD reduction (*i.e.* 9% after 120 min), and so does direct photolysis (*i.e.* 7% after 120 min). On the other hand, photo-bleaching results in about 38% reduction; this may be due to the generation of hydroxyl radicals from H_2O_2 dissociation since its absorbance spectrum marginally coincides with that of the lamp (at about 290 nm). Dark Fenton oxidation yields 45% COD reduction, while the respective solar process gives the highest COD reduction (*i.e.* 69% after 120 min of treatment).
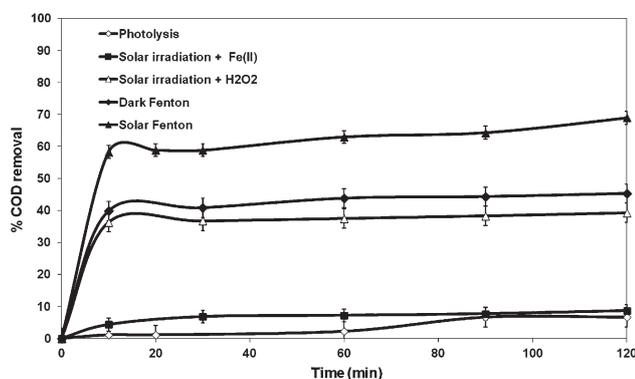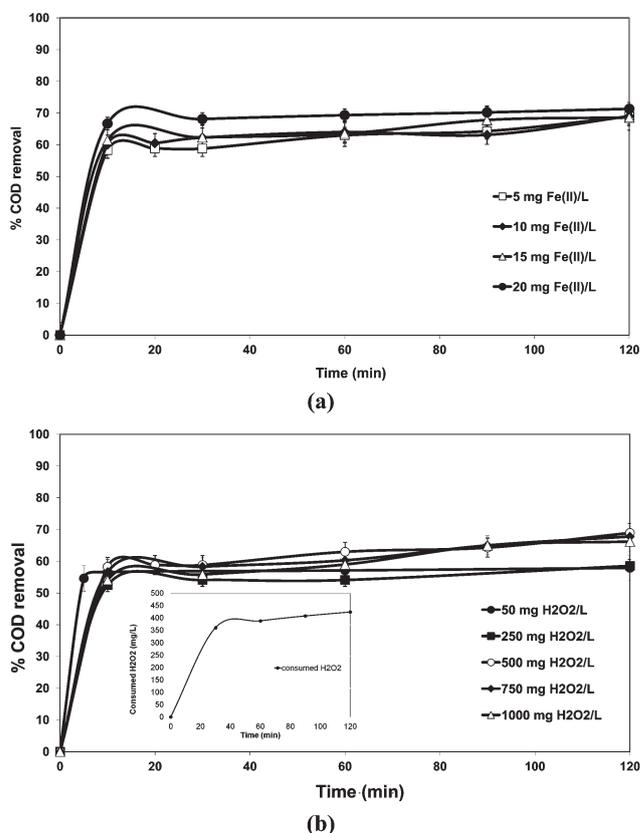

Fig. 1 COD removal of winery wastewater under different processes. $[Fe^{2+}]_0$ = 5 mg L^{-1}, $[H_2O_2]_0$ = 500 mg L^{-1}, lamp power = 1000 W, pH = 2.9, T = 25 °C.

Effect of the ferrous ion and hydrogen peroxide concentration

To obtain the optimal Fe^{2+} and H_2O_2 concentrations, experiments were conducted at several combinations of catalyst (5–20 mg Fe^{2+} L^{-1} at constant oxidant concentration 500 mg H_2O_2 L^{-1}) and oxidant (50–1000 mg H_2O_2 L^{-1} at constant catalyst concentration 5 mg Fe^{2+} L^{-1}) concentrations. An increase of the ferrous salt had an insignificant effect on the reduction of COD, which reached 70 ± 1% after 120 min of the reaction, irrespective of the Fe^{2+} concentration tested, as shown in Fig. 2(a). Catalyst dosage is crucial for large-scale wastewater treatment plants since it can affect not only the capital costs as it determines the size of the photoreactor but also the operating costs. In addition, at high catalyst concentrations the need for an additional separation step becomes more pronounced. Consequently, it is preferable to select a lower concentration by which it would be possible to achieve as short reaction times as possible without the need for further treatment for iron removal.[18] For these reasons, the optimum ferrous iron concentration was considered to be 5 mg L^{-1}.

Regarding the effect of oxidant, an increase of H_2O_2 concentration from 50 to 500 mg L^{-1} enhanced COD reduction from 58% to 69% after 120 min, as shown in Fig. 2(b). This can be explained by the effect of the additionally produced hydroxyl

(a)

(b)

Fig. 2 Effect of (a) initial ferrous concentration and (b) initial hydrogen peroxide concentration on the COD removal of winery wastewater effluent. $[Fe^{2+}]_0$ = 5–20 mg L^{-1}, $[H_2O_2]_0$ = 50–1000 mg L^{-1}, lamp power = 1000 W, pH = 2.9, T = 25 °C. The inset graph in (b) shows the consumed concentration of H_2O_2 during the homogeneous solar Fenton process.

radicals. Further increase of the concentration of H_2O_2 from 500 to 1000 mg L^{-1} caused no significant change in COD reduction. Therefore, 500 mg L^{-1} of H_2O_2 was considered as the optimal dosage at the conditions in question. The change in the hydrogen peroxide concentration during the 120 min process is shown in the inset graph of Fig. 2(b), from where it is obvious that at the end of the process there is sufficient residual hydrogen peroxide.

It should be noted here that the aforementioned experiments were performed at a solution pH of 2.9 which is considered optimum for homogeneous Fenton reactions. To test this, a series of experiments were performed by varying pH in the range 2–4 at 5 mg L^{-1} Fe^{2+} and 500 mg L^{-1} H_2O_2. Adjusting the pH at 2.9 was indeed beneficial, leading to 69% COD reduction after 120 min, with the respective values at pH 2 and 4 being 45% and 38%. At pH = 2.9 precipitation does not take place and the dominant iron species in the solution is $[FeOH(H_2O)_5]^{2+}$ (eqn (1)), which is the most photoactive ferric iron–water complex.[12]

$$[FeOH(H_2O)_5]^{2+} + h\nu \rightarrow Fe^{2+} + HO^{\cdot} \qquad (1)$$
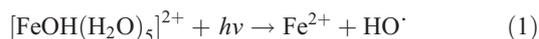
Effect of temperature

The effect of temperature on COD reduction was investigated in the range 15–40 °C and the results are shown in Fig. 3. An increase from 15 °C to 25 °C brings about a noticeable increase in COD reduction, *i.e.* from 46% to 69% after 120 min; nonetheless, a further temperature rise up to 40 °C has little effect (*i.e.* 73% COD removal). The beneficial effect of temperature is associated with the faster regeneration of ferric to ferrous ions occurring at higher temperatures.[12] However, a high increase in temperature may also invoke unnecessary thermal decomposition of hydrogen peroxide, thus diminishing the available reagent.[12,13] Therefore, the net temperature effect on the performance will eventually be dictated by the relative importance of the two opposing phenomena. This observation is in agreement with the results of other studies, where elevated temperatures significantly increased the activity of the photo-Fenton system and had a beneficial effect on the reaction kinetics.[19,20]
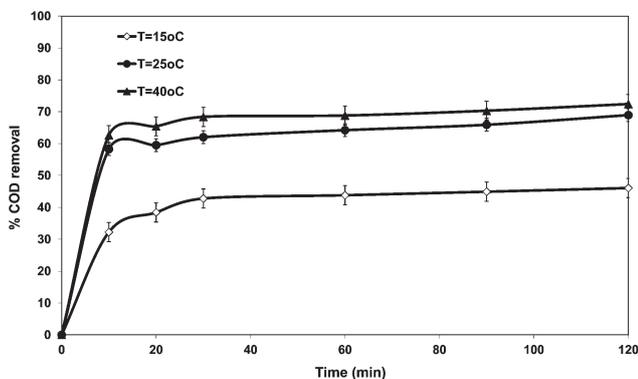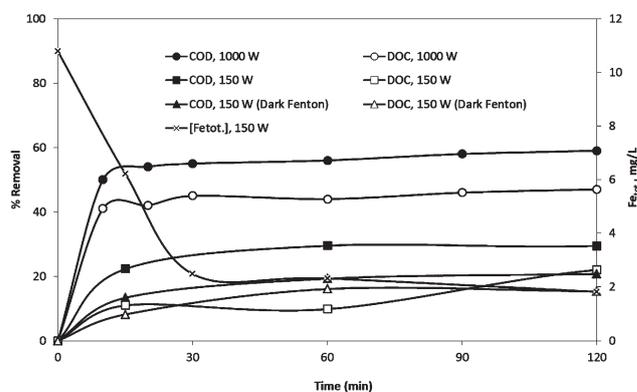
Effect of irradiation power

Fig. 4 shows the effect of lamp power on the elimination of the organic content of the pre-treated winery effluent during homogeneous photocatalytic treatment at initial pH 2.9, catalyst loading 10 mg L^{-1} Fe^{2+} and 100 mg L^{-1} H_2O_2. In this case we use 10 mg L^{-1} Fe^{2+}, which is the optimum iron concentration found, using the low power solar simulator (150 W). The experimental runs were performed in two solar simulators equipped with irradiation sources of different nominal power, *i.e.* 1000 W and 150 W.

From Fig. 4 it is obvious that at high irradiation intensity (*i.e.* 1000 W) the mineralization proceeds more rapidly, reaching a plateau (*i.e.* 55% and 45% COD and DOC removal, respectively) within 30 min of the reaction. For the corresponding homogeneous photocatalytic run at low irradiation intensity (*i.e.* 150 W) the COD and DOC removals do not exceed 29% and 22% respectively, even after prolonged treatment (*i.e.* 120 min). The slowing down of the reaction rate observed in both experimental runs after the first 15 min can be attributed to the fact that most of the initially dissolved iron concentration (*i.e.* 10 mg L^{-1}) is captured during the course of the reaction by scavenging species present in the effluent (*e.g.* phosphates, according to winery wastewater effluent characterization); this also agrees with the gradual decrease of the dissolved iron concentration observed as the reaction proceeds.

During the run performed with the 1000 W lamp, both COD and DOC removal increased rapidly within the first 20 min of the reaction, reaching respectively 54% and 42%. Extending the reaction beyond that point (*i.e.* up to 120 min), an additional 5% removal was achieved for both the COD and DOC content. The discrepancy observed between the DOC and COD removal values throughout the reaction measures *ca.* 10%; this is due to the occurrence of partial oxidation reactions leading to incomplete mineralization of the wastewater in addition to total oxidation reactions that result in the formation of CO_2.

For the corresponding run performed with the 150 W lamp, the elimination of the organic content proceeds through a similar pattern; during the first 15 min of the reaction, the COD and DOC content decreases by 22% and 11%, respectively. The

Fig. 3 Effect of temperature on COD removal of winery wastewater. $[Fe^{2+}]_0 = 5$ mg L^{-1}, $[H_2O_2]_0 = 500$ mg L^{-1}, lamp power = 1000 W, pH = 2.9, $T = 25$ °C.

Fig. 4 Effect of irradiation power on COD and DOC removal during homogeneous solar photocatalytic treatment of winery effluent. $[Fe^{2+}]_0 = 10$ mg L^{-1}, $[H_2O_2]_0 = 100$ mg L^{-1}, lamp power = 150 and 1000 W, pH = 2.9, $T = 25$ °C.

reduction trend of the organic content slows down as the reaction continues up to 120 min, resulting in 29% and 22% of COD and DOC removal, respectively. It should be noted that the corresponding experimental run in the dark (data not shown) was less efficient in regard to the COD and DOC removal (*i.e.* 20% and 15%, respectively after 120 min) implying the favorable influence of the solar light radiation in catalytic reactions.

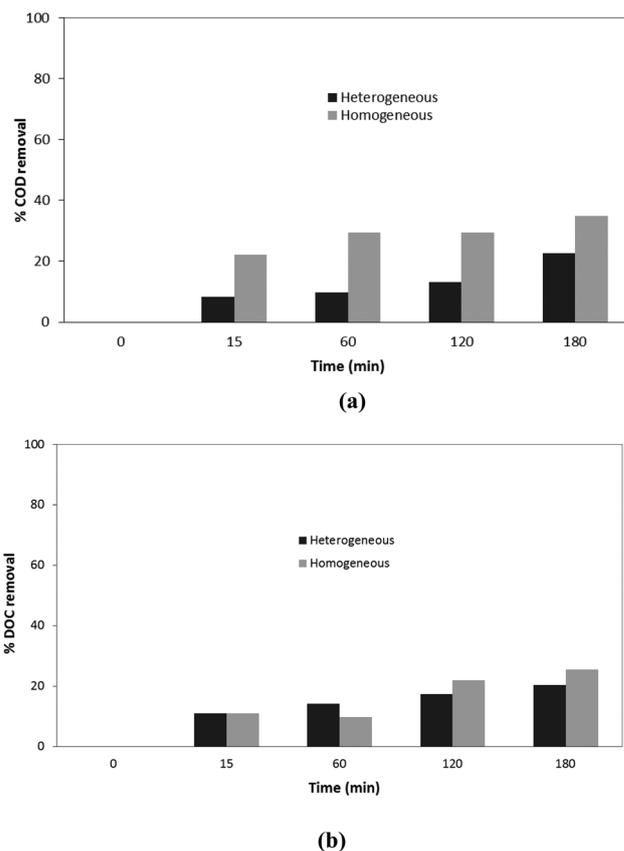## Comparison between homogeneous and heterogeneous solar Fenton reactions

In order to compare the homogeneous photo-Fenton reaction with that of the heterogeneous system, two different experimental runs took place at the low intensity solar simulator (*i.e.* 150 W). Both runs were performed at the optimal conditions for each process; initial pH was adjusted to 2.9, hydrogen peroxide at 100 mg L^{-1} and iron concentration at 10 mg L^{-1} (homogeneous run) or 100 mg L^{-1} (heterogeneous run).

To determine the optimal experimental conditions for the homogeneous photocatalytic process a number of experiments were performed employing $FeSO_4 \cdot 7H_2O$ as the catalyst; iron concentration varied between 5 and 20 mg L^{-1}, pH_0 was adjusted at 2.9 and 8 and H_2O_2 was injected at 100 and 300 mg L^{-1} (data not given). The optimal experimental conditions for the heterogeneous process were similarly determined; iron concentration (17% iron content in Fe_2O_3/SBA-15) varied between 50 and 200 mg L^{-1}, pH_0 was adjusted at 2.9 and 8 and H_2O_2 ranged between 50 and 300 mg L^{-1} (data not given). Adsorption effects on the heterogeneous catalyst Fe_2O_3/SBA-15 were found to be negligible.

From Fig. 5 it can be seen that the homogeneous system is more effective than the heterogeneous one, resulting in 35% and 26% COD and DOC abatement, respectively, after 180 min of the reaction. The corresponding COD and DOC removal achieved with the optimized heterogeneous process reaches about 22% and 20%, respectively. Although in both treatments the formation of CO_2 initiates in the first few minutes of the reaction, the homogeneous system seems to slightly favor partial oxidation reactions in comparison with the heterogeneous one, resulting in higher overall efficacy in regard to the degradation of the organic content of the winery effluent. The poor results of the heterogeneous solar Fenton process can be attributed to (i) light scattering effects caused by the high concentration of iron particles in the solution, which inhibit the effective utilization of the photonic energy, and (ii) mass transfer limitations due to the heterogeneous matrix of the catalyst. Further attempts to lower the catalyst concentration down to 10 mg L^{-1} led to a detrimental decrease in the heterogeneous process efficiency.

Removal of total phenolics, decolorization and mineralization

As seen in Fig. 6, the solar Fenton process is capable of removing 71% of the phenolic content of the wastewater after 120 min of treatment, alongside an equal removal of COD; this is accompanied by partial decolorization (*i.e.* 53%), which mostly (*i.e.* 44%) takes place during the first 5–10 min of the reaction. The extent of mineralization (as assessed by DOC) is about 25% lower than the COD decrease, thus implying that partial

(a)

(b)

Fig. 5 Comparison between homogeneous and heterogeneous systems on the elimination of (a) COD and (b) DOC during solar photocatalytic treatment of winery effluent. $[Fe^{2+}]_0 = 10$ mg L^{-1} (homogeneous), $[Fe_{SBA-15}]_0 = 100$ mg L^{-1} (heterogeneous), $[H_2O_2]_0 = 100$ mg L^{-1}, lamp power = 150 W, pH = 2.9, $T = 25$ °C.
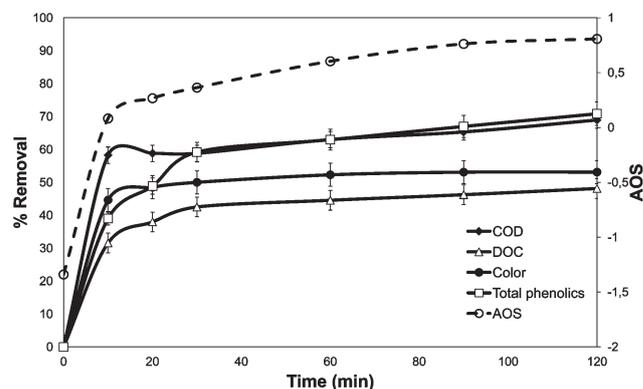
Fig. 6 COD, DOC, color and total phenolics removal of winery wastewater. $[Fe^{2+}]_0 = 5$ mg L^{-1}, $[H_2O_2]_0 = 500$ mg L^{-1}, lamp power = 1000 W, pH = 2.9, $T = 25$ °C.

oxidation reactions of the organic content prevail over total oxidation to carbon dioxide and water.

The efficiency of the oxidative process is more clearly shown by the AOS parameter (average oxidation state), which can be calculated by eqn (2), in which DOC and COD are expressed in
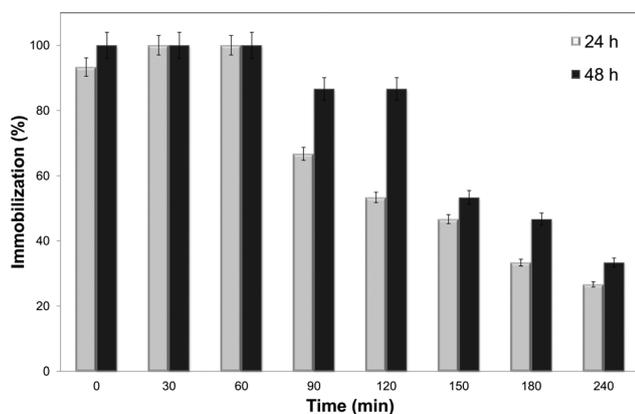
moles of C L^{-1} and in moles of O_2 L^{-1}, respectively, at each specific sampling time.[21]

$$AOS = 4\frac{(DOC - COD)}{DOC} \qquad (2)$$

AOS constitutes a potentially valuable parameter that can be used to estimate the degree of oxidation in a complex solution consisting of the parent compounds and their oxidation by-products, and can take values from +4 for CO_2, the most oxidized state of C, and −4 for CH_4, the most reduced state of C.[21] As shown in Fig. 6, AOS increases with treatment time until reaching a plateau. This result suggests that more oxidized organic intermediates are formed at the beginning of the photocatalytic process, and after a certain time, the chemical nature of most of them no longer varies substantially, even if solar Fenton treatment continues.[21]

Evaluation of toxicity

Since complete mineralization of the wastewater was not achieved at the conditions employed in this study, we decided to investigate the possible toxicity of the solar Fenton oxidation products. Winery wastewaters are complex mixtures containing numerous organic as well as inorganic compounds, whose individual and combined contribution to toxicity is not known. The complexity makes it almost impossible to carry out a hazard assessment based on chemical analyses. In this perspective, simple toxicity tests were performed using *D. magna* species. Young daphnies, aged less than 24 h at the start of the test, were exposed to the test substance for a period of 24 and 48 h. As seen in Fig. 7, the untreated wastewater is extremely toxic resulting in 93.3 ± 2% and 100% immobilization after 24 and 48 h of exposure, respectively. Solar Fenton oxidation for 30–60 min is not capable of reducing toxicity and this may be due to the fact that (i) the residual organic content is still highly toxic, and/or (ii) certain oxidation by-products are toxic to microorganisms. Nonetheless, toxicity decreases upon prolonged treatment, *e.g.* at 33.3 ± 2.5% and 26.7 ± 1.5% after 180 and 240 min respectively, for 24 h of exposure.

Conclusions

The organic content removal of a partially biologically treated winery effluent was studied by means of homogeneous and heterogeneous solar Fenton reactions. The main conclusions drawn from this work are summarized as follows:

(1) Organic matter degradation at ambient conditions, and $[Fe^{2+}] = 5$ mg L^{-1} and $[H_2O_2] = 500$ mg L^{-1}, increases with increasing treatment time and can reach COD and DOC removal values as high as 69% and 48%, respectively, after 120 min of the homogeneous solar Fenton reaction.

(2) The heterogeneous solar Fenton process, under optimum conditions, $[Fe_{SBA-15}]_0 = 100$ mg L^{-1} (heterogeneous), $[H_2O_2]_0 = 100$ mg L^{-1} and $T = 25$ °C, leads to approximately 20% COD and DOC removal values after 180 min of treatment, while the homogeneous solar Fenton process ($[Fe^{2+}]_0 = 10$ mg L^{-1}, $[H_2O_2]_0 = 100$ mg L^{-1}) depicts higher overall efficiency with regard to the organic content elimination (35% COD and 26% DOC removal).

(3) The heterogeneous solar Fenton treatment proceeds through complete oxidation reactions, while the respective homogeneous treatment proceeds through partial oxidation reactions.

(4) Under the optimum experimental conditions of the homogeneous solar Fenton treatment, 71% of the total phenolics and 53% of color were removed after 120 min.

Ecotoxicity was reduced significantly after the homogeneous solar Fenton treatment, from 100% to 27% after 240 min of treatment.

Acknowledgements

Fig. 7 Evolution of toxicity to *D. magna* during the solar Fenton treatment of winery wastewater. $[Fe^{2+}]_0 = 5$ mg L^{-1}, $[H_2O_2]_0 = 500$ mg L^{-1}, lamp power = 1000 W, pH = 2.9, $T = 25$ °C.

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