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Solar photo-Fenton treatment of winery effluents in a pilot photocatalytic reactor

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ABSTRACT

A pilot-scale solar Fenton process has been applied for the treatment of winery wastewater collected during the vinification period. The importance of the experimental variables was investigated at lab-scale experiments through the application of experimental design methodology. The pilot-scale study was conducted on a pilot CPC photocatalytic reactor under natural solar irradiation. The results show that at low catalyst dose (i.e. $[Fe^{2+}] = 5\ mg\ L^{-1}$) mineralization (i.e. ca. 50%) is dependent on the oxidant consumption (i.e. $500\ mg\ L^{-1}$), irrespective of the excess oxidant present; however, shorter reaction times are required under excess H_2O_2, indicating higher reaction rates due to higher availability of oxidant molecules in the bulk liquid. Increasing the catalyst dose enhances the reaction rate due to higher H_2O_2 decomposition and $HO^•$ production. This is corroborated with the lower H_2O_2 consumption (i.e. $1270\ mg\ L^{-1}$) occurring at low catalyst, signifying, however, a more effective use of the oxidant (i.e. less oxidant is required to achieve similar mineralization).

1. Introduction

Wine industry is an ever growing sector of the food industry worldwide. In 2011 the world wine production exceeded 26,600,000 t noting a 2.9% increase compared to the respective production of 2008 [1]. Wine industry has traditionally been subject to a lesser amount of regulatory attention when compared to other industries e.g. chemicals and mining, with obvious environmental impacts; however, there are several environmental issues with which wine producers have to contend [2,3], as the quality of their product is directly linked to the qualitative characteristics of the raw materials (i.e. grapes), which in turn reflect to the soil and water quality of viticulture practices.

Wine making is accompanied by various processes that commence immediately after grape harvesting; destemming, crushing and primary (alcoholic) fermentation are followed by cold stabilization and secondary (malolactic) fermentation at which point the wine is ready to be bottled for further maturation or marketing purposes [4]. All the aforementioned processes require the use of high volumes of water for washing activities i.e. floor washing from accidental spills of grape juice and/or wine, equipment cleaning, as well as fermentation tank and bottle rinsing; a rough estimate is that for each liter of wine produced, about 1.5 L of wastewater is generated alongside.

The main organic content of winery wastewater (WWW) comprises of soluble sugars (fructose and glucose), various organic acids (tartaric, lactic and acetic), alcohols (glycerol and ethanol) and high-molecular-weight compounds, such as esters, polyphenols, tannins and lignin [5,6].

The presence of inorganic ions (i.e. potassium and sodium, with low levels of calcium and magnesium) is mainly owed to the use of cleaning agents, stabilizers and/or pesticide residues [7–9]. The precise composition, however, is extremely difficult to assess, as WWW is subject to seasonal variations in both volume and quality (e.g. vintage and non-vintage periods) while also adopts its specific characteristics due to differences in vinification processes and techniques, grape varietal and amounts of water that each winery uses; in this context, COD, BOD_5 and pH values have been reported to range from 320 to 296,000 $mg\ L^{-1}$, 125 to 130,000 $mg\ L^{-1}$ and 3 to 12, respectively [5,8,10–14].

As the main volume (>90%) of WWW is produced during the harvesting period, (i.e. contains a major fraction of highly biodegradable compounds such as sugars), most studies address the issue of WWW treatment by employing biological processes either as single treatment or integrated with a physicochemical

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process [15–17]; however, due to the extreme seasonal variations in WWW production (i.e. both in generated volume and physicochemical characteristics) there are practical limitations to the operation of a biological system (i.e. demands for continuous operation with constant inlet flow characteristics); in this context, conventional strategies often result in inadequate treatment.

Furthermore, WWW present an additional challenge owed to the presence of polyphenols; a study performed by Vlyssides et al. [18] revealed that the polyphenolic content in WWW during production of white and red wine may be as high as 280 mg L^{-1} and 1450 mg L^{-1}, respectively. The problem with polyphenols arises due to their potential phytotoxicity and proven resistance to aerobic degradation [19,20].

Greek legislation dictates the use of a treatment method for the wastewater generated during the production of wine. As most wineries in Greece are small scale facilities (i.e. less than 2000 t of wine produced), they are obliged to adopt a septic tank leach field as a treatment technique, which is, nonetheless, a very basic treatment option with serious drawbacks; inadequate treatment leads to surrounding soil pH modifications, but also to accumulation of ions (e.g. Na^+, Ca^{2+},NO_3^-) and/or metals (e.g. Zn^+, Cu^{2+}, Fe^{2+}), thus posing a risk for plant growth inhibition and the occurrence of modifications in soil microbial communities [21,22].

The aforementioned limitations further stress the need to adopt reactive systems much more effective and whose operation would be unaffected by the dynamic nature of WWW [5,23,24].

Advanced Oxidation Processes (AOPs) constitute a special class of oxidation techniques which usually operate at or near ambient temperature and pressure, exploiting the high reactivity and non-selectivity of hydroxyl radicals [25,26]. Photo-Fenton process has received much attention for the treatment of industrial effluents and elimination of organic pollutants, as it is considered the most apt of all AOPs to be driven by sunlight; the formation of soluble iron-hydroxy and iron-organic acid complexes extents the adsorption wavelength toward the visible region (400 nm < λ < 700 nm) so that sunlight can be more efficiently exploited for the detoxification of heavily polluted effluents with significantly lower cost [27]. The main drawback of photo-Fenton process is the necessity to work at acidic pH values (i.e. around 2.8) in order to keep the iron in soluble form, thus maintaining high degradation efficacy; nonetheless, this should not pose a major problem for WWW as their inherent pH value is, according to literature, less than 5.5 and in many cases lies between 3 and 4 [28]. The low pH values of WWW are ascribed to the presence and/or formation of low molecular weight organic acids (e.g. acetic acid, citric acid and tartaric acid) [29].

So far, there are numerous studies dealing with treatment of winery effluents with photocatalysis, however, only one study has assessed the treatability of actual wastewater [30], whereas the majority has used simulated winery effluents by diluting wine or grape juice with deionized water [31–34].

The present work aims at assessing a homogeneous solar-driven Fenton process ($h\nu/Fe^{2+}/H_2O_2$) for the elimination of the organic content of actual winery wastewater. The effect of photo-Fenton reagents' initial concentration has been assessed with preliminary experimental runs in a lab-scale solar simulator by employing experimental design methodology; the influence of iron (Fe^{2+}) and hydrogen peroxide (H_2O_2) initial concentrations has been evaluated and further optimization in the pilot-scale photocatalytic reactor has been performed. The main goals of the pilot scale study were to monitor the mineralization of the effluent under limiting and excess oxidant conditions, to assess the degradation kinetics at different iron concentrations and to evaluate the toxicity of the treated effluent toward *Aliivibrio fischeri*.

2. Experimental

2.1. Materials and methods

2.1.1. Chemicals

Solar Fenton experiments were performed using iron sulphate ($FeSO_4{\cdot}7H_2O$, Riedel-de Haen), reagent-grade hydrogen peroxide (30%, w/w, Merck) and H_2SO_4 for pH adjustment (95–97%, Merck). The residual hydrogen peroxide was removed from the treated samples with catalase (*Micrococcus lysodeikticus*, Fluka Biochemika).

2.1.2. Winery wastewater

The effluent was collected from a local winery at Chania, W. Crete, Greece (200 t yr^{-1} wine production) shortly after the vinification period (January–February) when wine stabilization and filtration processes were completed. The effluent had undergone preliminary physical treatment (i.e. primary sedimentation) and contained high amounts of wine vinasse. Frequent measurements showed that it was chemically and biologically stable throughout the time of experimentation.

All samples were analyzed before use for a number of quality characteristics, which are summarized in Table 1. These values were obtained from multiple sample analyses (at least triplicate for each sample) and are the average values of the parameters measured. All parameters were measured according to standard methods [35]. It is worth noting that the WWW collected contains high amounts of acetic acid which is an intermediate compound generated along with the degradation of the long-chain acids present in wine such as tartaric, malic and lactic acids.

2.1.3. Experimental design

The evaluation of the effect of the Fenton reagent concentrations (i.e. iron and hydrogen peroxide initial concentrations) in the photocatalytic degradation of the raw winery effluent (i.e. $COD_o = 1200 \pm 150$ mg O_2 L^{-1}) (Table 1) was based on an experimental design approach; a full experimental design, consisting of 9 experiments – including the central points for statistical consistency – was composed, to assess the effect of the two independent variables assuming two values or levels (i.e. low and high, indicated by −1 and +1 coded values, respectively). The low level corresponds to 5 mg L^{-1} iron and 100 mg L^{-1} hydrogen peroxide, while the high level corresponds to 25 mg L^{-1} and 900 mg L^{-1}, respectively.

Running multiple replicates at the center point provides an estimate of pure error. Although running multiple replicates at any treatment level can provide an estimate of pure error, the other advantage of running center point replicates in the design is in checking for the presence of curvature which investigates whether the model between the response and the factors is linear.

Table 1
Quality characteristics of winery wastewater sampled during vinification season.

Parameter	Raw winery effluent
pH (20 °C)	5.5–6.5
COD (mg L^{-1})	1200 ± 150
Soluble BOD_5 (mg L^{-1})	750
Total Nitrogen (μg L^{-1})	2120
Total Phosphorous (μg L^{-1})	290[a]
DOC (mg C L^{-1})	435
Cl^- (μg L^{-1})	29
Na^+ (μg L^{-1})	1940
SO_4^{2-} (μg L^{-1})	820
Ca^{2+} (μg L^{-1})	535
Mg^{2+} (μg L^{-1})	630
CH_3COOH (mg L^{-1})	54.4

[a] As PO_4^{3-}.