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Factorial experimental design of winery wastewaters treatment by heterogeneous photo-Fenton process

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ABSTRACT

Winery wastewaters are difficult to treat by conventional biological processes because they are seasonal and experience a substantial flow variations. Photocatalytic advanced oxidation is a promising technology for wastewaters containing high amounts of organic matter.

In this work, the photo-Fenton process in heterogeneous phase is presented as an alternative methodology for the treatment of winery wastewaters.

As a consequence of the great number of existing variables, an experimental design methodology has been used in order to study the influence and interaction of various variables and to obtain a reduced empirical model which describes the organic matter degradation process.

Applying photo-Fenton treatment in heterogeneous phase under energetic conditions for synthetic samples simulating winery wastewaters results in purification levels of up to 50% (measured as total organic carbon). Different reduced models are obtained and their utilization depends mainly on the degree of degradation of organic matter required.

1. Introduction

The wine industry annually generates large volumes of wastewaters, originating mainly from various washing operations during the crushing and pressing of grapes as well as the rinsing of fermentation tanks, barrels and other items of equipment (Petroccioli et al., 2000).

Furthermore, wine and grape wastewaters are more difficult to treat than other wastewaters from food processing plants. Wineries generate industrial effluents that due to their composition, high organic strength, seasonal variability, acidity and unpleasant odours constitute both environmental and aesthetic problems in wine producing countries (Alvarez et al., 2004).

Aragón is one of the most important wine-producing regions in Spain. A typical vineyard usually produces about 17,300 tons of grapes per year. Though some medium-scale wineries are equipped with aerobic biological treatment plants, the majority of them work unsatisfactorily due to their seasonal variability, composition and high organic concentration of the effluents. A possible solution to the problem could be the application of advanced oxidation processes for the elimination of a major part of the organic matter followed by an aerobic biological treatment.

Advanced oxidation processes are innovative technologies increasingly being applied in the treatment of wastewaters. They offer an alternative for the treatment of effluents with a high organic matter content. Our research group has been found that photocatalytic advanced oxidation based on hydrogen peroxide is an appropriate purification treatment for winery wastewaters (Navarro et al., 2005).

The Fenton reagent, a mixture of Fe^{2+} salts with hydrogen peroxide (H_2O_2), can easily oxidize organic compounds (Bidga, 1995; Lee and Hosomi, 2001) because it produces in a very

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simple way hydroxyl radicals (1) for wastewater treatment. Furthermore, it has been found that the reaction can be enhanced by UV/VIS light, producing additional hydroxyl radicals and leading to the regeneration of the catalyst (2) (Arana et al., 2001; Kositzi et al., 2004)

$$Fe^{2+} + H_2O_2 \rightarrow OH^- + OH\cdot \quad (1)$$

$$Fe^{3+} + H_2O + h\nu \rightarrow Fe^{2+} + Fe^{+2} + H^+ + OH\cdot \quad (2)$$

The main disadvantage of the Fenton reagent is that homogeneous catalysts, added as iron salt, cannot be retained in the process thus causing additional water pollution (Lücking et al., 1998). As a consequence, heterogeneous Fenton processes are of particular interest since most of the iron remains in the solid phase. The development of supported Fenton catalysts has recently become important in the emerging field of advanced oxidation technologies (Teel et al., 2001; Yuranova et al., 2004).

Several authors have studied the degradation of the characteristic compounds present in winery wastewaters (alcohols, phenols, acids and sugar) in isolation using photo-Fenton processes. Walling and Kato (1971) researched into alcohol degradation and Bidga (1995) studied the degradation of the total phenols present in aqueous samples.

The photo-Fenton process in heterogeneous phase depends on various parameters that can modify the degra dation of organic matter present in aqueous samples, such as H_2O_2 concentration, the characteristics of the catalyst, pH, reaction time, initial composition of the wastewaters to be treated and concentration of organic matter in the wastewaters.

The number of the influential variables in the selected system is high, and for this reason it is useful to apply experimental design techniques. These techniques provide a systematic way of working that allows conclusions to be drawn about the variables (or combinations of them) that are most influential in the response factor while carrying out the minimum possible number of experiments (Montgomery, 2001).

The final objective of the results analysis is to obtain a reduced empirical model that directly relates the response factor with the most influential factors and that describes the process appropriately. This serves to facilitate later treatment of the process and to reduce the number of factors to the lowest possible.

Several authors have studied the application of experimental design not only to the determination of important variables in advanced oxidation processes but also to know their influence in the degradation process (Fernández et al., 2002, 2004). However, it has never been applied to this type of wastewater treatment.

In this research work, photo-Fenton treatment in heterogeneous phase is used to remove organic matter present in synthetic samples, representing winery wastewaters, in order to investigate the influence of different variables and to obtain, using experimental design, a reduced model that describes the organic matter degradation process.

2. Experimental procedure

2.1. Materials

Due to one of the main characteristics of these wastewaters, their seasonal character (winery wastewaters are not generated during nine months of the year), it is necessary to reproduce the winery effluents by means of synthetic samples. Sampling carried out in several wineries located in Aragón (Spain) has enabled the characteristics of their wastewaters to be established and consequently reproduced in the form of synthetic samples (Navarro et al., 2005).

These synthetic samples were prepared by diluting commercial red wine (WW) or commercial grape juice (WG) in ultra pure water, obtaining approximately the same characteristics as the real ones and the same amount of organic matter ($COD = 5000-10\,000\,mg\,O_2/L$; $TOC = 1500-3000\,mg\,C/L$) and $pH = 3.5$.

Commercial H_2O_2 (30% (v/v), Carlo Erba) was added to the sample until H_2O_2 concentrations in solution in the range of $3{*}10^{-3}$–0.3 M were reached. The solid material used as heterogeneous catalyst was a natural clay without pretreatment supplied by SAMCA S.A, chosen due to its low cost and high availability. The clay was analysed using scanning electron microscopy (SEM) and X-ray powder diffraction and the results indicated that the clay contained different amounts of metals (Fe 4.58 wt%, Al 12.42 wt%, Ti 0.41 wt%, etc.). The range of particle size selected for photochemical experiments was 80–500 μm and the concentration in solution was 0.1–2 g/L.

2.2. Chemical analysis

The amount of organic matter was quantified by means of two different parameters: total organic carbon (TOC) and chemical oxygen demand (COD). TOC was determined using a TOC-VCSH SHIMADZU analyser. COD was measured by the open reflux method (Method 5520B of Standard Methods, Cleresci et al., 1998). H_2O_2 concentration in the solution was controlled during and after the treatments using a Merck peroxide test (O_2^{2-}) (0–25 mg H_2O_2/L and 0–100 mg H_2O_2/L). The pH was checked by a pH-meter (CRISON 507). Ethanol and acetic acid were determined by gas chromatography with a FID detector HP5890. The total polyphenolic content was measured by UV–VIS spectrophotometry at 765 nm by the Folin–Ciocalteau method, using Gallic acid (mg GAE/L) as standard (Box, 1983). Tartaric acid was measured at 505 nm by the Metavanadato method (Zoecklein et al., 1995). Malic acid, glucose and fructose were measured at 340 nm by enzimatic methods (Zoecklein et al., 1995). The spectrophotometer used was a Thermo Spectronic Helios α. Fe in solution was analysed by induced coupled plasma.

2.3. Photochemical reactions

Photocatalytic experiments were carried out using 100 ml quartz flasks placed inside an ATLAS SUNTEST CPS+ solar chamber air-cooled at 35 °C. The xenon lamp emitted 5–6% of the photons in the 290 and 400 nm spectral range. The profile