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Use of an amorphous iron oxide hydrated as catalyst for hydrogen peroxide oxidation of ferulic acid in water

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Abstract

The abatement of ferulic acid (FA), a polyphenolic constituent of olive mill wastewater, is studied in the pH range 5.0–7.0 by using hydrogen peroxide and an amorphous iron oxide as catalyst. The effect of pH, catalyst load, hydrogen peroxide and substrate starting concentrations is assessed during the investigation. A suitable reaction scheme is developed and used to build a mathematical model which satisfactorily describes the system's behavior. Kinetic constants for the proposed scheme as well as the total active site concentration of the catalyst in the studied pH range are estimated.

The occurrence of internal mass-transfer limitation for the adopted granulometric fraction of the catalyst is demonstrated.

Keywords: Ferulic acid; Iron oxide; Olive mill wastewater; Mineral-oxide-catalyzed Fenton

1. Introduction

Among Fenton-derived processes, the mineral-oxide-catalysed Fenton is one of the most interesting mainly due to the fact that it does not require a strict control of pH and that the recovery and reuse of the catalyst (an iron oxide) are quite simple. Previous investigations [1–4] have already demonstrated that the use of an iron oxide suspended in the water to be treated in the presence of H_2O_2 allows one to achieve the abatement of different kind of pollutants. In particular some of the Authors [3] found that the system with goethite (one of the most used iron oxide for this process) and H_2O_2 is characterised by a certain selectivity with respect to the organic species to be removed. In fact as a result of testing a wide group of aromatic molecules it has been shown [5] that the oxidation of an organic species occurs only when the substrate is capable of adsorbing on the surface of the oxide. Therefore, only in the case in which at least two adjacent (ortho) functional groups are present on the aromatic ring an oxidation of the species is observed. In the present work the investigations are extended to the use of an amorphous iron (III) oxide hydrated, which has been less frequently investigated. As a test molecule it is adopted ferulic acid (4-hydroxy-3-methoxycinnamic acid), an antioxidant species which is present in plant tissues [6] and has been reported as one of the main constituent of the polyphenolic fraction of olive oil mill wastewaters (OMW) [7]. These wastewaters are produced annually in great quantities in Mediterranean countries during the manufacturing of olive oil. There is a general consensus that the polyphenolic fraction is the main cause for the poor biodegradability of OMW and its removal has been studied by many researchers. In fact polyphenol removal from OMW or more generally from aqueous solution has been attempted by means of microorganisms [8], by Fenton's reagent [9], ozone [10] and by combined chemical and biological processes [11,12]. None of these attempts gave completely satisfactory results and a reliable solution for the treatment of OMW is still lacking.

Mineral-oxide-catalysed Fenton could represent a valid alternative to the other systems so far investigated due to its selectivity during the oxidation processes [5]. In fact in the case of the use of advanced oxidation processes (AOP) for the (pre)-treatment of a OMW it is important to consider that OH radicals attack not only the polyphenolic species but also the biodegradable molecules present in the wastewater which can be more conveniently removed by means of a biological process. In this

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sense the present work may be considered as a preliminary study before starting an investigation on the real OMW.

2. Experimental

An amorphous iron(III) oxide hydrated [20344-49-4] was used as a catalyst, which was sieved and treated in a drying oven at 120 °C for 2 h. The granulometric fraction (24–38 μm) with a surface area of 187 m^2/g has been used in the experiments.

For each run the catalyst has been added to 0.75 l of water in which ferulic acid (FA) was dissolved. The pH of the solution has been regulated, with perchloric acid and sodium hydroxide addition, in the range 5.0–7.0 and measured by means of an Orion 420A+ pH-meter. Oxidation experiments have been carried out in a batch stirred tank made of Pyrex glass (1.090 l) and equipped with a jacket for temperature control ($T = 298$ K, stirrer speed = 380 rpm). As soon as hydrogen peroxide was added, the reaction started. During each run the pH was monitored by a handheld pH-meter, Piccolo Plus HI 1295 (Hanna Instruments) and regulated at initial value. Samples of liquid were collected from the reactor at different reaction times and filtered by membrane filter Millex HA (pore size 0.45 μm, Millipore) to remove the catalyst. Liquid samples were also analyzed by HPLC apparatus (Hewlett-Packard 1090) equipped with a UV–vis detector ($\lambda = 320$ nm) and a Synergi Hydro-RP 80A column, using a mobile phase (85:15 buffered aqueous solution:acetonitrile) flowing at 1.0 ml min^{-1}. The buffered aqueous solution was prepared with 4 ml phosphoric acid (85% by weight), 25 ml methanol in 1 l of HPLC water. The reactor and all glassware were cleaned with hydrochloric acid and washed several times with bidistilled water before use. All the reagents have been purchased from Aldrich.

3. Results and discussion

3.1. Oxidation of ferulic acid

Preliminary runs have been carried out at pH = 6.0 to evaluate the capability of the substrate to adsorb on the solid surface at different catalyst loads. The results shown in Fig. 1 indicate that FA does not adsorb on the surface of the used iron oxide. It has been also assessed that hydrogen peroxide is not capable of directly reacting with FA in the absence of the catalyst (data not shown).

Fig. 2 illustrates the effect of catalyst load on the oxidation of FA by means of H_2O_2 (symbols). As expected for a catalytic process, the reactivity of the system increases with increasing the catalyst load. Half-life times pass from 90 to 50 min for an iron oxide load by increasing from 100 to 150 mg/l.

In Fig. 3 the data of normalized concentrations versus reaction time, collected during the runs at different substrate starting concentrations, are also shown (symbols). As expected the increase of initial substrate concentration leads a higher system reactivity (for example, for a reaction time of 100 min the concentration decreases of 2.3×10^{-5} M and 1.4×10^{-5} M, respectively, for the highest and lowest concentrated solutions). Further experiments have been carried out to assess the effect of changing the

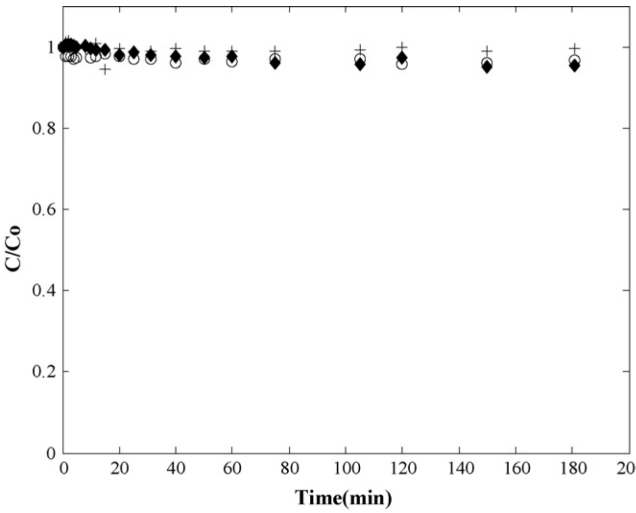

Fig. 1. Adsorption of ferulic acid at various catalyst loads. $[FA]0 = 2 \times 10^{-5}$ M; pH = 6.0; (○), 50 mg/l; (+), 100 mg/l; (♦), 150 mg/l.

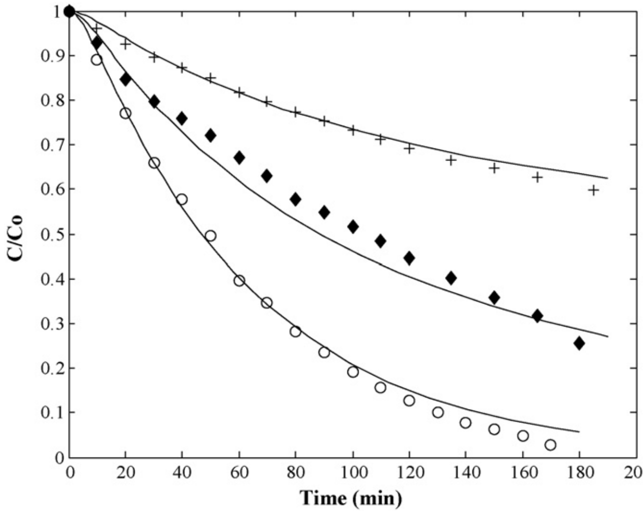

Fig. 2. Influence of catalyst load on FA oxidation. $[FA]0 = 2 \times 10^{-5}$ M; $[H2O2]0 = 1 \times 10^{-5}$ M; pH = 6.0; (+), 50 mg/l; (♦), 100 mg/l; (●), 150 mg/l.

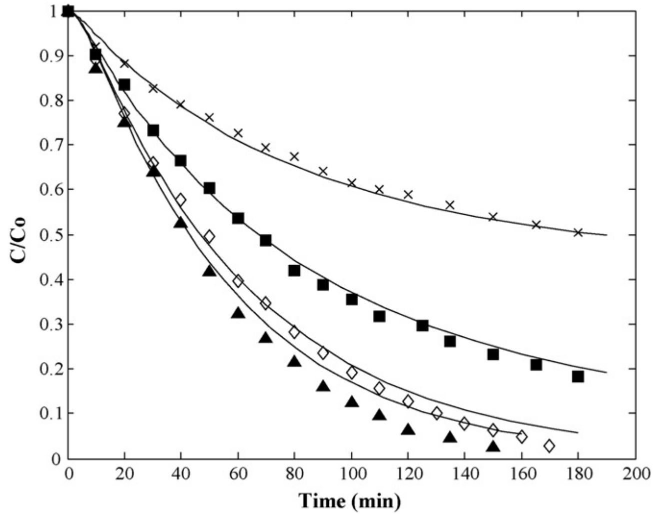

Fig. 3. Influence of starting concentration of ferulic acid ([FA]0). $[H2O2]0 = 1 \times 10^{-3}$ M, pH = 6.0; [Cat]=: 150 mg/l; (▲), 1.6 × 10-5 M; (◇), 2×10^{-5} M; (■:), 4×10^{-5} M; (×), 6×10^{-5} M.