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Heterogeneous Fenton using ceria based catalysts: effects of the calcination temperature in the process efficiency

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ABSTRACT

The need of more efficient solid catalysts for the heterogeneous slurry Fenton process led many investigators to research new compounds activities. Ceria based iron catalysts have proved their good performance enhancing the removal of organic compounds, reducing toxicity and improving biodegradability in the depuration of phenolic wastewaters. This work evaluates the calcination temperature (300 °C, 600 °C and 1000 °C) during the preparation of the catalysts—co-precipitation of the precursors salts, while the same previously optimized conditions were adopted (pH 3.0, 1.0 $g L^{-1}$ of Fe–Ce–O 70/30 as the catalyst, $[H_2O_2] = 244$ mM and 120 min of room temperature reaction) to treat a simulated wastewater comprising 0.1 $g L^{-1}$ of each of the six common phenolic acids found in Olive Mills wastewaters. The three obtained solids were characterized regarding superficial area, average pore diameter, FT-IR and XRD. Catalysts calcinated at 300 °C, 600 °C and 1000 °C presented superficial areas of 188, 86 and 2 m^2/g, respectively, and their average pore diameter are 66, 87 and 151 Å, correspondingly. As showed in the XRD, the increase of the calcination temperature promotes the crystallinity of the obtained solid—higher amount of prominent peaks, meaning that the catalysts have different states of valence for iron (Fe^{2+} or Fe^{3+}) and ceria (Ce^{2+} to Ce^{4+}), what would explain their singular behaviours during the reaction. As expected, the solids with higher superficial areas had better performances in every aspect: more COD, TOC and phenolic acids removal, pointing the lowest calcination temperature as leading to a more efficient solid to enhance hydrogen peroxidation, involving, however, more metal leaching. The higher the calcination temperature is, the more oxidized the solid will become because the calcination occurs without atmospheric control and so the oxygen contained in the air will interfere on the valence of iron ions at the solid's surface. This means that a solid calcinated at a higher temperature will have increased Fe^{3+} content and, as one can find in the literature, Fe^{2+} is more effective than Fe^{3+} at hydrogen peroxidation, explaining the better efficiency of the catalyst calcinated at the lowest temperature. Toxicological and biodegradability studies were still performed and showed enhancement in all cases.

1. Introduction

People's needs, which once were simple, have greatly increased through ages. The meaning of the word "evolution" sometimes only encompasses the fulfilling of those needs, without noticing that this thirst becomes, in a certain way, an enemy of life itself. New products are being elaborated every day and, as the number of different substances that happen to be often in our daily activities increases, another necessity—not rarely forgotten, raises: to treat these compounds before disposal.

Wastewater treatment, sooner than having practical application, is a scientific study that needs plenty of effort concerning the environment's welfare—giving priority to remediate the streams of discharge that will reach water courses in order not to damage them.

Fenton's oxidative reaction was discovered in the early 1890s. Basic mechanisms for the reaction were proposed only almost 40 years later [1,2]. Even today there is still a polemic argumentation over which pathways Fenton's reagent may have to oxidize compounds. Although the mechanisms are not well enlightened, this reaction became a very powerful method of wastewater treatment as an advanced oxidation process that has the advantage of occurring at mild conditions. Before reaching industrial scale, procedure studying and efficiency evaluation are fundamental so the system can be optimized to economically fit the meanings to an end. Homogeneous Fenton's process was firstly investigated and literature can be found in the remediation of different kinds of effluents: olive mill wastewaters [3–6], winery [7,8], pesticides [9]. Besides

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specific studies, there are also reviews and overviews that one may consult to obtain overall knowledge comprising several aspects of the reaction separately, such as the works of Neyens and Bayens [10] and Bautista et al. [11].

Although different conclusions are taken according the effluent being handled and the objective of the work (that may focus economic viability, remediation of the wastewater, biodegradability enhancement, color removal, between others), one will find that the most crucial problem laying at the homogeneous Fenton's process is the formation of ferrous sludge—another waste that will require a separation step and further treatment. Avoiding this unwanted drawback, heterogeneous Fenton's process is raising as the natural development of the former procedure. Instead of adding iron ion (Fe^{2+} or Fe^{3+}) precursors, such as the commonly used $FeSO_4{\cdot}7H_2O$, $FeCl_3$ or $Fe(NO_3)_3{\cdot}9H_2O$, the heterogeneous method lays that the iron catalyst will be present but not dissolved, being thus impregnated at the surface of a solid. Activated carbon [12], polymer encapsulation [13], silica [14], clays [15,16], metallic oxides [17,18] have been part of the vast investigation regarding iron supports. Our group of investigation has recently screened heterogeneous catalysts based on cerium, manganese and iron oxides, finding promising results with the former. Different molar proportions of iron-to-cerium were then tested and had their efficiencies evaluated, being possible to observe that the most active cerium based iron oxide has the proportion Fe/Ce of 70/30 [19]. Cerium has proved its good efficiency in different advanced oxidation processes such as catalytic wet oxidation [20,21], and ozonation [22].

Still aiming the optimization of the process, the present work encompasses another parameter in the preparation of the catalyst above-mentioned (Fe–Ce–O 70/30) that was not yet studied: the calcination temperature. Experiments results allowed the catalyst's efficiency assessment while treating a simulated olive mill wastewater comprising six of the most common phenolic acids found in this effluent.

2. Experimental

2.1. Catalyst preparation and characterization

Between the catalysts previously studied by our research group, Fe–Ce–O was highlighted due to its higher efficiency [19]. This work used three different Fe–Ce–O 70/30 catalysts prepared at the laboratory by co-precipitation of an aqueous solution of the former metallic salts: iron nitrate (*Riedel-de-Häen*) and cerium nitrate (*Riedel-de-Häen*) containing the desired molar proportion, 70/30 (other ratios were tested before but this specific one showed higher efficiency). Precipitation is stimulated by an increase on the pH by the addition of 200 mL of a 3 M solution of sodium hydroxide. The precipitate is filtrated, washed with 2.5 L of distilled water, dried at 105 °C for 2 h, powdered by manual milling and then calcinated during 3 h, as the procedure proposed by Silva et al. [20]. As the present study has the intention of determining the best calcination temperature regarding removals of TOC, COD and TPh, as well as toxicity annulment and biodegradability enhancement of the resulting catalyst, three temperatures were chosen: 300, 600 and 1000 °C—which will name the prepared solids as C_{300}, C_{600} and C_{1000}, respectively, to facilitate comprehension and further discussion.

In order to characterize these catalysts, they were submitted to the following analysis: (i) Brunauer–Emmet–Teller surface area (S_{BET}) determined by an accelerated surface area and porosimetry analyzer *ASAP 2000 V2.04* (*Micrometrics*) with nitrogen at −196 °C, (ii) X-ray diffraction (XRD) through a conventional and low angle *X-ray diffractometer Philips model X-Pert*, (iii) mercury porosimetry for porosimetry and pore size distribution assessment at a *Poresizer 9320* (*Micrometrics*), (iv) gas (helium) picnometry in an *AccuPyc 1330 V2.01* (*Micromeritics*), (v) laser dispersion to particle size assessment (*Malvern Mastersizer 2000 V5.60 - Malvern Instruments*) and (vi) scanning electron microscopy (SEM) with a *JEOL JSM-5310*.

Table 1

Characteristics of the synthetic effluent comprising six phenolic acids at 0.1 g L^{-1} each.

COD (mg O_2 L^{-1})	1000 ± 80	EC_{20} (%)	4.5 ± 2
BOD_5 (mg O_2 L^{-1})	279 ± 56	EC_{50} (%)	32.2 ± 2
BOD_5/COD	0.28	Toxicity (%)	67.0 ± 8
TOC (ppm)	418 ± 8	Biodegradability (%)	2.0 ± 8
pH	3.3 ± 0.05		

2.2. Synthetic effluent stock solution confection

The preparation of the phenolic solution consists in the addition of 0.1 g of each of the acids (3-4-5-trimethoxybenzoic acid, 4-hydroxybenzoic acid, protocatechuic acid, syringic acid, vanillic acid and veratric acid) to 1 L of distilled water. To overcome the low solubility of these compounds in water and ensure their dissolution, the solution is submitted to ultrasounds (*Crest ultrasounds equipment*) during 15 min. Afterwards, the pH of the solution is adjusted to 3.0—with $H_2SO_4{\cdot}2N$ or NaOH 0.3 M, in order to obey previously obtained conclusions that affirm this pH value leads to the best efficiency [19]. With this methodology, a solution with the characteristics mentioned in Table 1 was subsequently used.

As shown in Table 1, the simulated wastewater has high toxicity (this parameter is explained in the next section) and low biodegradability (proven by respirometric tests and LUMIStox analysis), being inappropriate for biological depuration [20]—which emphasizes the necessity of chemical treatment.

2.3. The Fenton's process itself

Reactions were carried out in 500 mL capacity glass reactors magnetically stirred in which 300 mL of the synthetic effluent stock solution were poured just before the addition of the required amount of catalyst. Then pH monitoring is started with a *Crison MicropH 2000* probe inserted inside the reactor and continuously adjusted to 3.0—with H_2SO_4 0.2 N or NaOH 0.3 M. The reaction only begins with the slow addition of the desired volume of H_2O_2. At certain time intervals, samples were withdrawn by direct pippeting from the reactor to a vacuum filtration unit (funnel, kitassato and air pump) using a 0.45 μm pore diameter quantitative filter paper to remove the solid catalyst from the liquid phase. Immediately after filtration, NaOH 3 M is added to the filtrated sample in order to raise the pH above 9.5, stopping, this way, the reaction by quenching the remaining H_2O_2 since it interferes with some of the analytical techniques. Samples were then named and stored in the refrigerator at approximately 4 °C until being forwarded to analysis.

2.4. Analytical techniques—synthetic effluent and treated samples

Total organic carbon (TOC) analyses were conducted in a *Shimadzu 5000 Analyser* coupled with an auto-sampler *ASI - 5000A*. Total phenolic content (TPh) was assessed colourimetrically by the Folin-Ciocalteau procedure [23,24] with a *T60 U PG instruments* spectrophotometer for absorbance measurement. Standard Method 5220D was utilized to determine the chemical oxygen demand (*COD*) [25], in which *WTW CR 3000* thermoreactor and a *WTW MPM 3000 photometer* were used. Biochemical oxygen demand in 5 days (BOD_5) was measured by the method proposed on the Standard Methods, being the inoculums obtained from