



A green solar photo-Fenton process for the elimination of bacteria and micropollutants in municipal wastewater treatment using mineral iron and natural organic acids



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ABSTRACT

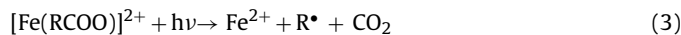
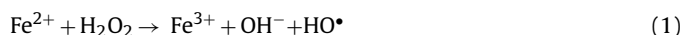
In this investigation, a new, green photo-Fenton process for wastewater treatment is proposed, involving the use of a natural iron source and natural additives, deriving from wastes, acting as iron chelators. The use of mineral iron as precursor in the photo-Fenton process, instead of iron salts, was still able to promote *E. coli* inactivation. Furthermore, the addition of four low weight organic acids (citric, tartaric, ascorbic and caffeic) showed a significant enhancement of the process, reaching total inactivation except for caffeic acid, which showed no significant effects. Two natural products, rich in the promising organic acids were tested as additives, lime and orange juice, plus their infusion. Lime-based additives showed better results compared to orange-based ones, which could be attributed to the excessive addition of organic matter in the orange systems. The formation of photoactive complexes with the mineral iron and the organic acids from the natural products induced the production of reactive species and ferrous ion, sustaining a homogeneous Fenton reaction. Finally, the proposed modified process was tested against different secondary effluents from a municipal wastewater treatment plant. Total bacterial inactivation was reached in the lime-based system, with no visible microorganism regrowth after 48 h. Additionally, the process was able to eliminate 40% of the total identified micropollutants of the secondary effluent reaching almost 50% of removal of the total effluent organic matter.

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1. Introduction

Over the last years, the photo-Fenton process became one of the most interesting alternative process for wastewater treatment, given its simplicity and feasible application [1–5]. Based on the photo-activity of the ferric species, this process can be considered catalytic, and an enhanced form of the classic Fenton reaction inducing the formation of extra hydroxyl radicals (Eqs. (1) and (2)). However, due to the insolubility of the ferric aquo or hydroxy species, the system is pH-dependent and its full scale application is subject to limitations [6,7]. Consequently, up to date, many inves-

tigations deal with the possibility to perform the photo-Fenton process at near-neutral pH [8]. Based on previous reports, the pH dependence can be minimized by the formation of ferric organo-complexes [9–11]. The substitution of aquo or hydroxyl groups for organic molecules as ligands involves the following facts: (i) the increment of dissolved iron at near-neutral pH [12]; (ii) the use of sunlight, as light radiation to induce the photochemistry of the complexes [2,13]; (iii) the formation of ferrous ion (Eq. (3)) [7,14,15], which promotes the classical Fenton reaction; (iv) the production of organic radicals that could contribute in the organic matter oxidation or produce extra transients (Eqs. (3) and (4)).



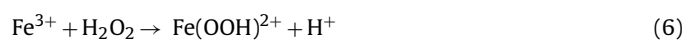
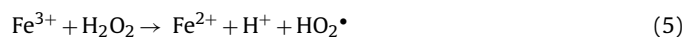
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Different organic compounds have been tested as effective ligands for ferric complexes, leading to an improved photo-Fenton process [10,16,17]. Among the organic compounds, carboxylic acids and phenols have been highlighted given their high chelating effect [7,18]. In fact, a previous investigation showed that the use of solar photo-Fenton for bacterial inactivation in wastewater was greatly enhanced by the addition organic acids such as citric, tartaric, ascorbic and caffeic acid [19]. This investigation evidenced the opportunity to improve the solar photo-Fenton efficiency against bacterial inactivation during wastewater treatment using natural products rich on the above-mentioned acids.

Besides the enhancement of the photo-Fenton process for wastewater treatment using natural products and solar radiation, another important factor worthy of consideration is the iron source. Up to date, different iron materials have been tested as precursors of the photo-Fenton process, including natural iron oxide [20], residue-based iron [21], zero valent metallic iron [22], magnetic composites [23] or modified clays and carbon-based materials [24] to promote organic pollutant degradation. However, among the iron species, a special attention is associated to the ferric ion, given that in natural conditions, Fe^{2+} is oxidized to Fe^{3+} by oxygen or H_2O_2 , increasing the investigative interest for ferric sources. The use of natural iron materials has extra advantages associated to the stability of the material against light radiation, oxidation by dissolved oxygen and pH variation [25]. In addition, the presence of ferric ion in the system involves additional reactions (Eqs. (5)–(7)), in which extra oxidative species, such as superoxide radical (HO_2^{\cdot}), are produced.



However, the existing literature on photo-Fenton treatment of WW is currently limited to studies where wastewater treatment is focused on either chemical [11] or microbiological contamination [3]. Moreover, the investigations with alternative iron materials are usually carried out in distilled water [22,20,21], which provide important information on alternative ferric sources but on the other hand, are far from a possible real application. Therefore, the aim of this investigation is to evaluate the use of a natural iron material as precursor of the photo-Fenton process, in order to promote the bacterial inactivation and micropollutants degradation of real secondary effluents. Additionally, the effects of the addition of natural products is sought, such as lime, orange juice and infusion, and valorizing alimentary and agricultural wastes, or turning the process into a greener alternative is also investigated.

2. Materials and methods

2.1. Reagents

Hydrogen peroxide 30%, citric acid $\geq 99.5\%$, L-ascorbic acid $\geq 99.0\%$, L-(+)-tartaric acid $\geq 99.5\%$, caffeic acid $\geq 98.0\%$, acetate buffer solution pH 4.65, ferrozine 97% and hydroxylamine hydrochloride 99% were purchased by Sigma Aldrich. Titanium oxysulfate was supplied by Fluka; chloride acid, sulfuric acid and sodium hydroxide were supplied by Merck.

Preliminary experiments were carried out using simulated municipal secondary effluent reported by Muthukumaran et al. [26] and real effluents from the municipal wastewater treatment plant Vidy (Lausanne, Switzerland) previously treated by activated sludge or coagulation/flocculation process. The simulated wastewater characteristics are 39 ppm of chemical oxygen demand (COD),

9.8 ppm of dissolved organic carbon (DOC) and pH 7.5. The real wastewaters characteristics are presented in SM 1. Concerning the preliminary investigations, *E. coli* K-12 strain (MG 1655) was provided from “Deutsche Sammlung von Mikroorganismen und Zellkulturen”. The working bacteria solution was prepared as previously reported [27] obtaining a 10^9 CFU/mL initial concentration. The real WW experiments deal with the indigenous population of the matrix as described in Giannakis et al. [6].

2.2. Iron material

As iron source, a natural material from an iron mine of Colombia (Duitama, Boyacá) was used without pretreatment. The specific surface area was estimated in $19.79 \text{ m}^2/\text{g}$ by the Brunauer–Emmett–Teller (BET) theory, and N_2 physisorption measurements on a Micromeritics 3Flex apparatus was used for its measurement. Analyses took place at liquid nitrogen temperature, and between 10^{-5} and 0.99 relative N_2 pressure. Around 150 mg sample was dried for 4 h at 120°C ($2^\circ\text{C}/\text{min}$) under vacuum ($<10^{-3}$ mbar) and a leak test was assayed before analysis. For the high-resolution TEM, FEI Osiris was used and operated in 200 kV, with Spot size of 5, dwell time $50 \mu\text{s}$, real time 600s. Fig. 1 shows the grain size and distribution of the elements. EDX mapping was acquired using Esprit software and shown in supplementary material (SM 2). An XRF analysis using a pellet of the material (area $1.8 \times 2.3 \text{ cm}^2$, spot size $30 \mu\text{m}$, 1000 ms dwell time, Matrix 128×100 ; duration 5.1 h) and a mapping showed 81.26% of iron content (SM 3). The crystallographic phases were determined by X-ray diffraction (XRD) using $\text{Cu K}\alpha$ radiation at a grazing incident angle of 4° (X’Pert MPD PRO from PANalytical). The sample was sieved to separate big aggregates (to avoid x-ray reflection due to size), suspended in MQ-water then dropped/fixated on glass slide. The XRD pattern of the natural iron is presented in SM 4 of the Supplementary material.

2.3. Process description

A lab scale Suntest solar simulator (Hanau) equipped with an air-cooled Xenon lamp 1500-W, with illumination surface of 560 cm^2 and $600 \text{ W}/\text{m}^2$ of solar intensity (global irradiance) was used to perform the solar photo-Fenton experiments. The emitted radiation is characterized as follows: 0.5% of UVB (290–320 nm) and 5–7% of UVA (320–400 nm), while after 400 nm the solar spectrum is simulated. Finally, UVC and IR wavelengths were filtered by an uncoated quartz glass light tube and cut-off filters, respectively.

Bacterial inactivation tests were carried out in Pyrex glass bottle reactors, using constant stirring at 400 rpm. In absence of light, 100 mL of wastewater (for both experiments in synthetic and real WW) was mixed during 10 min with the tested additives, followed by the addition of $500 \mu\text{L}$ of the iron material suspension ($100 \mu\text{g}/10 \text{ mL}$) and a subsequent mixing for 10 min $100 \mu\text{L}$ of *E. coli* of working bacteria solution was added in the reactor (sample $t = 0$ min, bacterial concentration: 10^6 CFU/mL). After 10 min of stirring, hydrogen peroxide was added into the system (25 ppm in the reactor) and the sunlight simulator is turned on. Aliquots of $1000 \mu\text{L}$ from the bulk of the solution were sampled at pre-determined time points, and each experiment was performed at least in duplicate.

2.4. Natural products extractions

Natural products were tested as additives using commercially available fruits: orange (*citrus tangelo*) and lime (*citrus lime*). Juice and aqueous extraction (infusion) from the peels of both fruits were tested, as described in Villegas-Guzman et al. [19]. The juice was separated from the peel by hand squeezing. The peels were grinded after drying at 60°C for 24 h followed by an aqueous

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