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Degradation of chloroform by Fenton-like treatment induced by electromagnetic fields: A case of study

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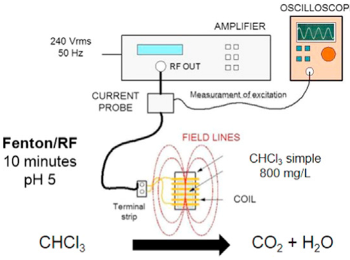
HIGHLIGHTS

- The degradation of chloroform by Fenton/RF was evaluated by the first time.
- Different iron sources were used in the Fenton-like reaction at near neutral pH.
- Presence of radiofrequency increased the yield of Fenton treatments.
- Higher electromagnetic fields could improve the DOC removal yields.

GRAPHICAL ABSTRACT



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ABSTRACT

The objective of this study of chloroform degradation by the first time through Fenton-like processes induced by electromagnetic fields. Fenton-like processes were carried out at natural pH with 25 mg/L of H_2O_2 and different iron sources: i) $FeCl_3 \cdot 6H_2O$ (5, 50 and 100 mg/L Fe^{3+}); ii) magnetite (1 g/L); iii) clay (80 g/L). These treatments were driven in absence and presence of radiofrequency (RF) with an intensity of electromagnetic field of 3.68 kA/m. Aqueous solution of chloroform ($CHCl_3$) was also used to study which oxidant species are responsible for the degradation of organic matter. Because of chloroform is scavenger of primary superoxide radicals ($\bullet O_2^-$.) and required of hydroxyl radical for their total degradation. Initial assays of ferromagnetic material/H_2O_2/RF processes achieved promising results in terms of DOC removal. The highest DOC removal yield (69%) in the treatment of an aqueous solution of $CHCl_3$ was obtained by Fenton/RF treatment using 100 mg/L of Fe(III) and 25 mg/L of H_2O_2. In addition, the combination of Magnetite and Fe(III) reached notable values of $CHCl_3$ degradation. The synergetic effect caused by the ferromagnetic properties of Magnetite and the coagulation-flocculation effect caused by iron salts at natural pH is able to reduce the organic matter in water samples. Furthermore, this treatment can be intensified by induction of RF reaching 63% of DOC removal in the $CHCl_3$ solution.

1. Introduction

Advanced Oxidation Processes (AOPs) are gaining attention in the treatment of water, air and soils, due to the capacity for generation of free radicals, such as hydroxyl radicals ($HO^{\bullet}$). These highly oxidant species can oxidize almost all organic substances and inactivate a wide range of microorganisms. AOPs have been reported to have been used successfully in the treatment of

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effluents from the paper industry (Lucas et al., 2012), dyes and pigments (Wang et al., 2015), landfill leachates (Cassano et al., 2011; Amor et al., 2015), fresh surface water and drinking water (Mosteo et al., 2009; Lanao et al., 2010), cork industry (De Torres-Socías et al., 2013), urban wastewater effluents (Rodríguez-Chueca et al., 2014a, 2014b) and agri-food industries (Durán et al., 2012; Chatzisymeon et al., 2013; Velegraki and Mantzavinos, 2015).

Fenton (1984) reported that ferrous ions strongly promote the oxidation of tartaric acid by hydrogen peroxide. The commonly accepted ideal pH to perform Fenton treatment is 2.8. At this pH almost all iron added to water is dissolved, thus the formation of $HO^{\bullet}$ increases (Pignatello et al., 2006). The main reaction of the process is the oxidation of Fe^{2+} to Fe^{3+} producing $HO^{\bullet}$ radicals (Eq. (1)). Meanwhile, the iron catalyst is regenerated in accordance with Eq. (2).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH\cdot \quad k \approx 70\ M^{-1}\ s^{-1} \tag{1}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\bullet} + H^+ \tag{2}$$

There is a rapidly growing literature on neutral pH Fenton treatment, which indicates that scientific community are focusing their interest to decrease the costs and drawbacks (acidifying and neutralization of effluent) of the Fenton reaction (Conte et al., 2016; Ortega-Gómez et al., 2015; De Luca et al., 2014). In addition, the current literature on wastewater treatment abounds with examples of several modifications of the Fenton process regarding the kind of iron catalyst (homogeneous or heterogeneous) (Yang et al., 2013a; 2013b; Barndõk et al., 2016, Kakavandi et al., 2016; Ruales-Lonfat et al., 2016), kind of radiation (Ortega-Gómez et al., 2016; Zhou et al., 2016) or electro-Fenton and Fenton induced by ultrasounds (Giannakis et al., 2015; García-Segura and Brillas, 2016).

There are few references about water treatment with radiofrequency (RF). During recent years, some authors have reported the application of RF with different environmental purposes, such as the treatment of sewage sludge (Srinivasan et al., 2015), increasing the activity of the microbial fauna (Ji et al., 2010), in the removal of humic acids by electrocoagulation (Ghernaout et al., 2009), in the removal of organic pollutants with H_2O_2 (Sobiecka et al., 2008) or combined with Fenton processes in the removal of hazardous pollutants (Krzemieniewski et al., 2003, 2004; Dębowski et al., 2007; Sobiecki et al., 2008, Kim et al., 2011). Further, our research group reported the application of Fenton-like processes driving by RF in the inactivation of *Escherichia coli* and *Enterococcus* sp. (Rodríguez-Chueca et al., 2014b). This almost unexplored field represents a promising future and a challenge for the scientific community, because of the remaining unanswered questions on mechanisms driving these processes.

The aim of this work was to evaluate the efficiency of Fenton-like processes induced by electromagnetic fields at natural pH of samples, to degrade $CHCl_3$. Additionally, the influence of different iron sources (5 mg/L Fe^{3+}; 1 g/L magnetite; 80 g/L clay) in the presence and absence of hydrogen peroxide (25 mg/L) and electromagnetic fields (3.68 kA m) on the efficiency of Fenton-like processes at neutral pH was also investigated.

2. Materials and methods

2.1. Reagents

Chloroform ($CHCl_3$, Mw = 119.38 g/mol) was provided by Acros Organics (Spain) and used as received. Samples were prepared by dissolving requisite quantity of $CHCl_3$ in Milli-Q® water from a Millipore purification system. The concentration (800 mg C/L) was chosen to be close to the solubility limit in water to ensure chloroform quantification by dissolved organic carbon measures.

Three different materials were used as an iron source: i) Ferric chloride hexahydrate ($FeCl_3 \bullet 6H_2O$, Probus®, Spain) was used to obtain Fe^{3+} concentrations of 5, 50 and 100 mg/L; ii) clay from a building brick was used in concentration of 80 g/L; iii) magnetite was used in concentration of 1 g/L.

The chemistry of Fe^{3+} in solution according to the pH is highly complex. In strongly acidic solution containing no H_2O_2 and only noncomplexing counterions such as ClO_3^- or NO_3^-, Fe^{3+} exists as the hexaaquo ion, $Fe(H_2O)_6^{3+}$. While working under these pH conditions, this ion undergoes extensive hydrolysis (Eq. (3)), depending on counterion, ionic strength, and total iron concentration, which ends the in precipitation of amorphous ferric oxyhydroxides (Sylva, 1972).

$$Fe^{3} \leftrightarrow FeOH^{2+} \leftrightarrow Fe_2(OH)_2{}^{4+} \leftrightarrow \text{other species} \leftrightarrow Fe_2O_3 \cdot nH_2O \tag{3}$$

Clay used in this research work came from a building brick. This building brick was milled with a steel balls mill, and finally it was sieved, collecting the fraction of clay with a grain diameter of less than 0.150 mm. The clay was characterized by means of X-ray diffraction (D-Max Rigaku with a rotating anode), X-ray fluorescence (XFR; Thermo Electron ARL Advant XP equipped with a Rhodium X-ray tube), Scanning Electron Microscopy (SEM model JEOL JSM 6400, equipped with microanalysis system INCA 300 X-Sight from Oxford Instruments) and BET adsorption isotherm (TriStar 3000 V6.08 A through the Barret-Joyner-Halenda (BJH) method). Fig. 1 shows the SEM micrographs of the clay, and Table 1 shows the percentage by weight of the detected elements in the

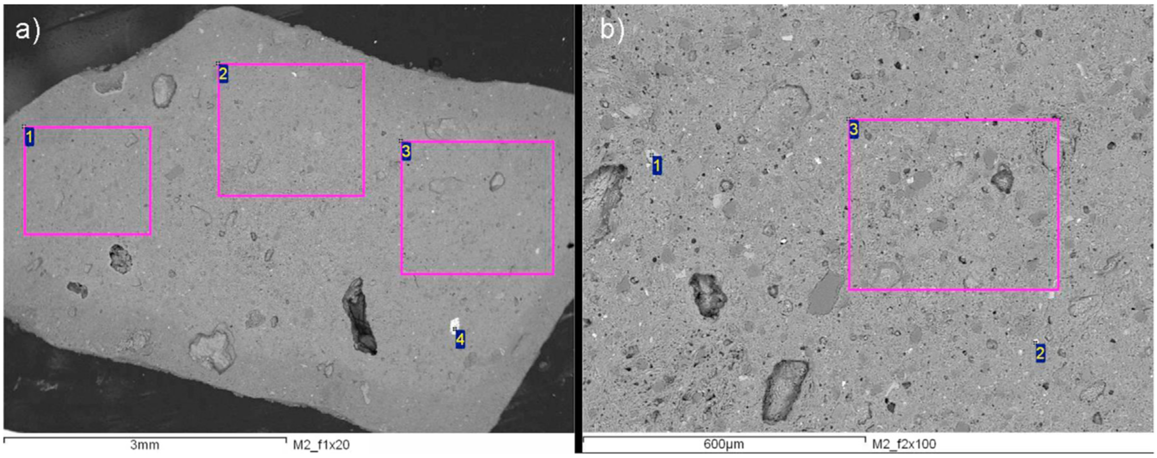

Fig. 1. SEM micrograph of clay: a) × 20; b) × 100 zoom.