



## Green Fenton-like magnetic nanocatalysts: Synthesis, characterization and catalytic application



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### ABSTRACT

Five iron oxalate core-shell magnetite nanoparticles catalysts are evaluated as magnetic heterogeneous materials. Simple and efficient procedures for the preparation of magnetic iron oxalate coated nanoparticles are presented. The catalysts are fully characterized using various investigation techniques. Additionally, the formation of photo-sensitized oxygen by spin-trapping using electron spin resonance is investigated. The catalytic activity of two model substrates (carbamazepine and bisphenol A) is also evaluated. The effect of operational parameters (catalyst and H<sub>2</sub>O<sub>2</sub> concentration, UVA light) on the degradation performance of the oxidation process is investigated. The obtained reaction rates depend on the nature of the compound and increase with iron oxide shell thickness of the catalyst. Moreover, these materials show a significant activity during two consecutive tests. The optimum experimental parameters are found to be 1.0 g L<sup>-1</sup> of catalysts, 10 mM H<sub>2</sub>O<sub>2</sub>, under UVA irradiation. More than 99% of both substrates are removed after 30 min of reaction time under the experimental conditions given above. The results obtained show that the catalysts are suitable candidates for the removal of pollutants in wastewaters by means of the Fenton heterogeneous reaction.

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### 1. Introduction

A wide variety of chemicals, that are not easily biodegradable, are known to bio-accumulate in water organisms, especially in their fatty tissues, and therefore produce serious detrimental reproductive effects on wildlife and humans [1]. Bisphenol A (BPA) is widely used as a raw material for polycarbonate and epoxy resins and is known to accumulate in nature without decomposition. BPA causes reproductive damage to a variety of animal species and has been found to be weakly estrogenic [2]. Carbamazepine (CBZ), an anticonvulsant and mood-stabilizer, has been reported as an anthropogenic marker of urban pollution [3]. One of the most important concerns about the presence of CBZ in the aquatic environment is its potential for bioaccumulation in aquatic biota. The removal of both micropollutants by conventional biological, physical and chemical methods is difficult and costly. The emerging methods for treating water that contains biorefractory organic

pollutants are advanced oxidation processes (AOP), which imply generation and subsequent reaction of hydroxyl radicals, the most powerful oxidizing species after fluorine [4]. However, the high consumption of expensive oxidants, the generated sludge and high operating costs limit the application of the AOPs. Fenton-like processes have been used as a powerful source of hydroxyl radicals from H<sub>2</sub>O<sub>2</sub> in the presence of a homogeneous or a heterogeneous catalyst based on a transitional metal cation, under mild reaction conditions and possibly a source of light. Although the homogeneous systems offer a cost-effective source of hydroxyl radicals, there are two major drawbacks that limit the industrial application of this technology: (i) the tight range of pH in which the reaction proceeds and (ii) the need for recovering the precipitated catalyst after the treatment. The resulting sludge may contain organic substances as well as heavy metals and has to be treated further, thus increasing the overall costs. With respect to the weaknesses that the above methods are confronted with, heterogeneous catalytic and photocatalytic processes for wastewater treatment do not have these limits, while offering several advantages and potential benefits. They can be performed under milder conditions (temperature and pressure). Another advantage is the possibility to treat a

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single or a group of similar pollutants selectively [5]. Post- or pre-treatment by photocatalysis is an economically feasible possibility to reduce recalcitrant wastewater compounds and achieve a water quality sufficient for reuse. Such an alternative method could be the application of heterogeneous solid Fenton-like catalysts.

The use of magnetic materials as adsorbents or heterogeneous catalysts in water cleanup has attracted increasing attention [6]. Iron oxide magnetic nanoparticles encapsulated in carbonaceous materials, silica, mesoporous silicas or by combining  $\text{WO}_3$  [7], have been tested as catalysts in Fenton-like reactions. These materials can be easily removed from water by the simple use of a magnetic field.

Ferrimagnetic catalysts are also known to activate molecular oxygen in air or water and produce reactive oxygen species (ROSS), including hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), superoxide radical ( $\cdot\text{O}_2^-$ ), singlet oxygen ( $^1\text{O}_2$ ) and hydroxyl radical ( $\cdot\text{OH}$ ), which are capable of oxidizing contaminants that cannot be removed [6,8][6b,c,8]. Obviously, the combination of abundant iron and molecular oxygen is highly desirable for pollutant control and environmental remediation in view of economic and environmental issues and, therefore, attracts much attention. Several authors reported that unprotected iron oxide nanoparticles could release  $\text{Fe}^{2+}$  ions into an aqueous phase, promoting in this way the ROS production through Fenton/Haber–Weiss reactions [8]. However, according to other studies, the surface of iron oxide nanoparticles could also play a role in the catalytic ROS production [6][6b]. The rate of the reaction between  $\text{O}_2$  and  $\text{Fe}^{2+}$  ions absorbed onto a mineral was found to be much higher in solution. Moreover, the enormously high surface-to-volume ratio of magnetite is expected to intensify the role of chemical reactions occurring at the surface [8].

A series of studies revealed some adverse effects of iron oxide nanoparticles both *in vivo* and *in vitro* [9]. Some of these adverse effects can be effectively reduced by coating the iron oxide nanoparticles with organic ligands. Uncoated magnetite adsorbs oxygen to form maghemite and/or amorphous iron (III) oxide, losing its susceptibility and catalytic activity with time. In addition, the nanosized particles of maghemite form less stable systems, determining their agglomeration. To prevent agglomeration and iron loss, the surface coating of a particle is essential for having stable colloidal dispersion over a wide pH range. The adsorption layer can also enhance the resistance against oxidation of magnetite into maghemite. In this study, in order to improve the stability of iron nanoparticles against aggregation, iron oxalate was chosen. Iron oxalate could be a good candidate to diminish these disadvantages; it is used as a reducing reagent to provide the reducing atmosphere for the synthesis system as well as a coordination ligand to reduce the concentration of free iron ions in aqueous solution. Analogous to previous reports for citrate [10,11] and iron/iron oxide core–shell nanoparticles [12–13], iron oxalate ions could form a shell around each magnetite particle, raising in this way the energy required for the particles to agglomerate, and, consequently, stabilizing the corresponding colloidal suspension.

However, to our knowledge, no study has been carried out on the degradation of BPA and CBZ by iron oxalate coated magnetite. Here we present the characterization and application of five magnetic heterogeneous Fenton catalysts, synthesized by different

procedures. The specific objective of this paper is to investigate the removal efficiency of BPA and CBZ in the presence of magnetite-iron oxalate core–shell nanoparticle catalysts using heterogeneous Fenton-like oxidation and the effects of several parameters such as catalyst loading,  $\text{H}_2\text{O}_2$  dosage, UV light and behavior of the mixed micropollutants on the oxidation of selected compounds.

## 2. Experimental

### 2.1. Reagents and materials

High purity reagents (Sigma–Aldrich) were used in all experiments as purchased without additional purification. Ultrapure water ( $18.2\text{ M}\Omega\text{ cm}^{-1}$ ), obtained with a Barnstead EASYpure®II Ultrapure Water System, was used throughout all synthesis procedures.

### 2.2. Synthesis of magnetic catalysts

Five magnetic nanocatalysts, based on a magnetite core and a ferrous oxalate shell, were prepared by varying certain parameters during synthesis in order to test their performance depending on their physico-chemical properties (Table 1).

In a first stage,  $\text{Fe}_3\text{O}_4$  nanoparticles were synthesized using the wet chemical approach (modified co-precipitation method). During the experimental procedure (performed at room temperature), three solutions of  $\text{FeCl}_3 \times 6\text{H}_2\text{O}$  (134 mM),  $\text{FeSO}_4 \times 7\text{H}_2\text{O}$  (67 mM) and NaOH (2 M) were prepared in distilled deionized water (DDW). Subsequently, the iron salt solutions (in the stoichiometric ratio of 2:1 of  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  salts) were mixed together and allowed to reach equilibrium under constant stirring and heating. Precipitation of the iron precursors was immediately initiated by adding dropwise the alkaline precipitation agent (NaOH solution) until pH was 12, into the homogeneous mixture with simultaneous constant heating ( $75^\circ\text{C}$ ) and vigorous magnetic stirring. The formation of NP was marked by the appearance of an intense black precipitate. The resulted mixture was then allowed to settle and cool down onto a permanent magnet followed by repeated washing with DDW in order to remove residual products; the last washing step was carried out with absolute ethylic alcohol for the final product purification. The resulting magnetic slurry was dried in an oven under vacuum at  $50^\circ\text{C}$ .

In the next stage, the magnetic nanocatalysts based on magnetite core surrounded by a ferrous oxalate shell were prepared in a post-synthesis procedure. The nanocatalyst samples were prepared as follows:

During the synthesis protocol,  $\text{Fe}_3\text{O}_4$  dried powder was resuspended in DDW with constant mechanical stirring and heating up to  $75^\circ\text{C}$ ; separately, ferrous oxalate ( $\text{FeC}_2\text{O}_4 \times 2\text{H}_2\text{O}$ ) powder was also dissolved in DDW. For the FF1 catalyst, the  $\text{Fe}_3\text{O}_4$  suspension was added slowly into the  $\text{FeC}_2\text{O}_4 \times 2\text{H}_2\text{O}$  solution (at  $75^\circ\text{C}$ ) with continuous mechanical stirring for two hours. For the second nanocatalyst (FF2), the ferrous oxalate was added in four steps (0.06 g every 15 min) to the  $\text{Fe}_3\text{O}_4$  suspension (at  $75^\circ\text{C}$ ) with continuous mechanical stirring for two hours. Three more samples (FF3–FF5) were prepared in a similar manner as the FF2, by

**Table 1**  
Synthesized catalysts.

Catalysts	$\text{Fe}_3\text{O}_4:\text{FeC}_2\text{O}_4 \times 2\text{H}_2\text{O}$ ratio	Synthesis approach
FF1	1:0.310	$\text{Fe}_3\text{O}_4$ suspension added to $\text{FeC}_2\text{O}_4$ , slowly in one step
FF2	1:0.120	$\text{FeC}_2\text{O}_4$ added slowly in four steps, every 15 min
FF3	1:0.090	$\text{FeC}_2\text{O}_4$ added slowly in one step
FF4	1:0.067	$\text{FeC}_2\text{O}_4$ added slowly in one step
FF5	1:0.045	$\text{FeC}_2\text{O}_4$ added slowly in one step

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