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Fate of iron oxalates in aqueous solution: The role of temperature, iron species and dissolved oxygen

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ABSTRACT

The effect of temperature (up to 120 °C) and the iron species (Fe^{2+} or Fe^{3+}) as well as dissolved oxygen on the degradation of oxalic acid in aqueous solutions was studied. The results obtained showed that the fate of oxalate depends on the concentration of ferric ions, which are involved in the formation of oxalate complexes, and the presence of oxygen which oxidizes iron species. By increasing the temperature (120 °C), the ferric oxalate complexes undergo a ligand-to-metal electron-transfer reaction, leading to the homolytic cleavage of a Fe^{III}–O coordination bond of the oxalate anion ligand giving rise to ferrous ion, oxalate anion and oxalate radical. The presence of dissolved oxygen enhances the degradation of oxalic acid by oxidizing Fe^{2+} to Fe^{3+}.

This explains the fact that oxalic acid is easily mineralized by Fenton oxidation at high temperature (above 100 °C), whereas it proves refractory at lower temperatures. Experiments with a radical scavenger were also carried out to learn about the role of $^{\bullet}OH$ radicals.

Introduction

Oxalic acid is commonly found among the byproducts of the oxidative degradation of a large variety of organic compounds [1]. In particular, it is fairly resistant to mineralization under the operating conditions of the conventional Fenton process [2], one of the most frequently-used advanced oxidation techniques. In spite of its low ecotoxicity it has shown a poor response in biodegradability tests and therefore further abatement with biological treatment appears unlikely [3].

In the Fenton process, oxalic acid can deactivate the iron cations through the formation of highly stable complexes. The formation of iron oxalates and their photo-activity has been widely researched, since the breakdown of oxalates is strongly enhanced in photo-assisted AOP [5–7]. Depending on the pH and the concentrations of Fe and oxalate ions, complexes with one, two or three ligands in the coordination sphere of Fe can exist in aqueous solution (Reactions (1)–(6)) [6].

$$Fe^{2+} + C_2O_4^{-2} \leftrightarrow Fe^{II}\left[(C_2O)_4\right] \tag{1}$$

$$Fe^{II}(C_2O_4) + C_2O_4^{-2} \leftrightarrow Fe^{II}(C_2O_4)_2^{2-} \tag{2}$$

$$Fe^{3+} + C_2O_4^{2-} \leftrightarrow Fe^{III}(C_2O_4)^{+} \tag{3}$$

$$Fe^{III}(C_2O_4)^{+} + C_2O_4^{2-} \leftrightarrow Fe^{III}(C_2O_4)_2^{-} \tag{4}$$

$$Fe^{III}(C_2O_4)_2^{-} + C_2O_4^{2-} \leftrightarrow Fe^{III}(C_2O_4)_3^{3-} \tag{5}$$

$$Fe^{III}(C_2O_4)_3^{3-} + Fe^{3+} \leftrightarrow Fe_2^{III}(C_2O_4)_3 \tag{6}$$

The mineralization of oxalic acid by photocatalytic, ultrasonic, electrochemical and wet air oxidation has been studied [8–12], although they suffer from important technical and economic drawbacks [13].

In a recent work, we demonstrated that oxalic acid or oxalate could be readily mineralized using Fenton oxidation by increasing the temperature, even after total consumption of H_2O_2 [14], unlike what occurs at near-room temperature. This study has the double objective of elucidating the fate of ferrous and ferric oxalates in aqueous solution at high temperature (120 °C) in the presence and

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absence of dissolved oxygen and to address the mineralization of oxalic acid by $^{\bullet}OH$ radicals in high-temperature Fenton oxidation.

Materials and methods

Chemicals

Oxalic acid (O_xAc), +99%; ferrous sulphate ($FeSO_4\cdot 7H_2O$), and ferric nitrate ($(FeNO_3)_3\cdot 9H_2O$), were purchased at Sigma–Aldrich. Hydrogen peroxide (H_2O_2), analytical grade, $w = 30\%$ was supplied by Panreac.

Experimental procedure

The experiments were carried out in a 500 mL stoppered glass reactor (Büchi, inertclave Type I) equipped with a backpressure controller. The reactor was initially loaded with 380 mL of oxalic acid solution (105.3 mg/L, to complete 100 mg/L when all the reactants were added). Once the testing temperature (120 °C) was reached, 20 mL of iron aqueous solution were injected. The behaviour of the different iron oxalate complexes was checked by using Fe^{2+} or Fe^{3+}, either under N_2-saturated atmosphere conditions (continuous N_2 flow of 50 NmL/min) or in the presence of oxygen ($Q_{O2} = 50$ NmL/min). Iron doses were varied within the range of 10–100 mg/L.

In the Fenton oxidation experiments, 10 mL of the hydrogen peroxide solution and 10 mL of the iron aqueous solution were injected into the reactor once the temperature was equilibrated. The initial concentrations of H_2O_2 and Fe^{3+} were 500 and 10 mg/L, respectively. The experiments in presence of a radical scavenger were conducted by adding 5 mL of 20 mM *tert*-butanol (Bu^tOH) solution. In these experiments, N_2 was continuously bubbled into the reactor at 50 NmL/min. The initial pH was around 3 in all cases and was not controlled throughout the experiments. Nevertheless, significant pH alterations were never observed during the experiments. Samples were taken periodically from the reactor and analysed immediately thereafter. Oxidation runs were carried out by triplicate, the standard deviation being less than 5% in all cases. Blank experiments with oxalic acid in the presence and in the absence of O_2 or H_2O_2 were also performed.

Analytical methods

Total organic carbon (TOC) was measured by a Shimadzu model VSCH TOC analyser. Oxalate anions were analysed by ion chromatography with chemical suppression (Metrohm 790 IC) using a conductivity detector. A Metrosep A Supplementary 5-250 column (25 cm length, 4 mm internal diameter) was used as stationary phase and a 3.2 mM Na_2CO_3 aqueous solution as the mobile phase. The total amount of iron ($\sum Fe^{n+}$) was measured by colourimetric titration using the *o*-phenantroline method. The concentration of hydrogen peroxide during the Fenton experiments was determined by the colourimetric $TiOSO_4$ method [15].

Results and discussion

Fate of iron oxalate complexes at high temperature

The speciation of dissolved iron in aqueous solution in the presence of oxalic acid depends on the competition between the formation of iron–hydroxo and iron–oxalate complexes [4]. Zuo and Hoigne [5] reported that under acidic conditions (pH range 3–5), Fe^{2+} mainly occurs as the hydrated cation $[Fe(OH)_x]^{2-x}$, whereas Fe^{3+}–oxalate complexes could be the predominant dissolved species. This latest can be easily confirmed by a spectrophotometer measurement since Fe(III)–oxalate complexes have absorption bands that extend into the 290–570 nm, being the maximum absorbance at 274 nm [5].

The authors of the above mentioned paper also reported that the amount of oxalic acid oxidized to CO_2 was proportional to the amount of Fe^{2+} in solution, reduced under UV light and inert conditions, according to the following overall Reaction (7):

$$2Fe(C_2O_4)_n^{(3-2n)+} \xrightarrow{h\nu} 2Fe^{2+} + (2n-1)C_2O_4^{2-} + 2CO_2 \qquad (7)$$

This reaction, though thermodynamically favourable, requires high activation energy. Thus, the reaction can be promoted by photons ($h\nu$) or by thermal energy, i.e. increasing the temperature.

Fig. 1 shows the effect of Fe^{II} and Fe^{III} on the evolution of TOC (corresponding to 100 mg/L of starting oxalic acid) at 120 °C under N_2 or O_2 atmosphere. Previously, those runs were carried out at 50 °C and 90 °C but the TOC reduction was negligible in all cases (data not shown). The thermal stability of oxalic acid was confirmed in blank experiments at 120 °C in the absence of iron. As can be observed, under N_2 atmosphere, complexation between Fe^{2+} and oxalic acid does not occur and the TOC remained unchanged. Contrariwise, with ferric ions up to 55% TOC reduction was observed due to the decomposition of ferric oxalates by Reaction (7). In the presence of O_2, the degradation of oxalic acid was significantly enhanced in the case of both iron species. Under these conditions, Fe^{2+} is oxidized to Fe^{3+} (Reaction (8)) [15] which would form new complexes, allowing the degradation cycle of ferric oxalate complexes to continue.

$$Fe^{2-} + O_2 \rightarrow Fe^{3+} + O_2^{\bullet -} \qquad (8)$$

Hence, the degradation of ferric oxalates at high temperature proceeds through a thermal/chemical cycle involving Fe^{3+}, oxalic acid and O_2. Increasing the temperature promotes an electro-transfer from a complexing oxalate ligand to the central ferric ion, leading to the homolytic breaking of a Fe^{III}–O coordination bond of the oxalate ligand giving rise to ferrous ion, oxalate anion and oxalate radical anion, according to Reaction (9) [5]. Then, the oxalate radical can reduce another Fe^{III}–oxalate complex according to the Reaction (10). Therefore, the overall mechanism for oxalate mineralization (Reaction (7) can be summarized as the sum of these two Reactions ((9) and (10)).

$$Fe(C_2O_4)_n^{(3-2n)+} \xrightarrow{T^{a}} Fe^{2+} + (n-1)C_2O_4^{2-} + C_2O_4^{\bullet -} \qquad (9)$$

$$Fe(C_2O_4)_n^{(3-2n)+} + C_2O_4^{\bullet -} \rightarrow Fe^{2+} + nC_2O_4^{2-} + 2CO_2 \qquad (10)$$

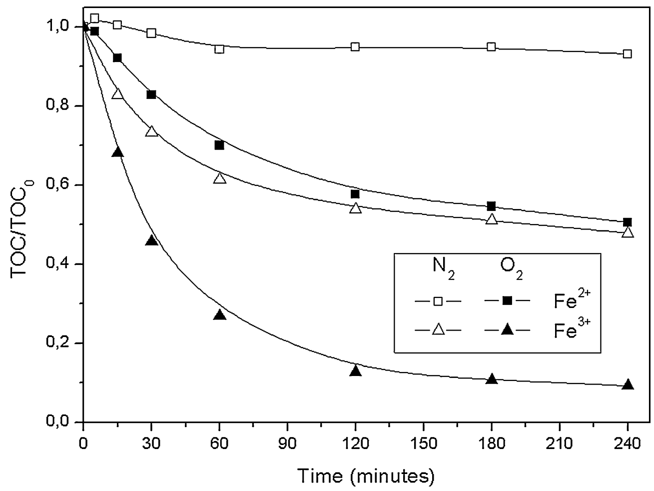

Fig. 1. Effect of iron species and dissolved oxygen on the mineralization of oxalic acid ($[O_xAc]_0 = 100$ mg/L; $[Fe^{n+}]_0 = 100$ mg/L; $pH_0 \approx 3$; $T_0 = 120$ °C; $Q_{N2/O2} = 50$ N mL/min).