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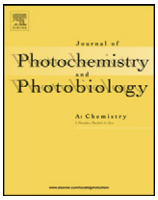

Development of a new homogenous photo-Fenton process using Fe(III)-EDDS complexes

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ABSTRACT

We report for the first time the use of Fe(III)-EDDS (EDDS: ethylenediamine-*N*,*N*′-disuccinic acid) complex as an iron source in a homogeneous photo-Fenton system. The performance of this system was followed through the formation of the $^{\bullet}OH$ and the degradation of 2,2-bis-(4-hydroxyphenyl)propane (BPA). It was observed that Fe(III)-EDDS can enhance the efficiency of both $^{\bullet}OH$ formation and BPA degradation especially near neutral pH. The effect of H_2O_2 concentration, Fe(III)-EDDS concentration, pH value and oxygen concentration on the BPA degradation during this photo-Fenton system was investigated. It was observed that O_2 is an important parameter affecting the efficiency of this process not only due to its reactivity with BPA but also because of its effect on the iron species present in solution. Comparison with iron complexes of oxalate, citrate and EDTA have demonstrated that Fe(III)-EDDS is a very efficient iron source for this photo-Fenton process. This work also demonstrates that Fe(III)-EDDS plays a positive role in the photo-Fenton system, especially at higher pHs, and makes this system an encouraging method for the treatment of organic pollutants in the natural environment.

1. Introduction

The reaction between H_2O_2 and Fe(III)/Fe(II) is a well known method for the generation of the hydroxyl radical ($^{\bullet}OH$), and the use of this method in the Fenton (Fe(II)/H_2O_2), Fenton-like (Fe(III)/H_2O_2) and photo-Fenton (UV/Fe(III)/H_2O_2) reactions is of great interest for research into wastewater treatment. For the photo-Fenton process in particular, the use of sunlight energy should be taken into account, since it is environmentally friendly and conserves energy. The main conversion sequence from H_2O_2 into the hydroxyl radical ($^{\bullet}OH$) is shown in reactions (I)–(III):

$$Fe^{3+} + h\nu + H_2O \rightarrow Fe^{2+} + {}^{\bullet}OH + H^+ \tag{I}$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^- \tag{II}$$

$$H_2O_2 + h\nu \rightarrow 2{}^{\bullet}OH \tag{III}$$

The photo-Fenton process has been proved to be an efficient method for the removal of many kinds of contaminants including pesticides [1,2], dyes [3,4], insecticides [5], pharmaceuticals [6], nitrobenzene [7], chlorophenols [8] and PCBs [9]. However, there are some defects in the traditional photo-Fenton process. Firstly, low efficiency is usually observed when the photo-Fenton process is taking place at neutral or alkaline pH. Secondly, high concentrations of iron salts and peroxide are necessary to achieve an efficient rate of removal of substrate. In fact, most of the iron in natural waters exists in the form of insoluble ferric oxides and (hydr)oxides [10]. Due to the insolubility of Fe(III) in neutral pH, the photo-Fenton system is unstable, which results in low generation of hydroxyl radical in the presence of H_2O_2.

Polycarboxylates such as oxalate and citrate, which are common constituents of precipitation, fog, surface waters and soil solutions [11–14], have been used as ligands for the iron complex in the photo-Fenton process [15]. It is known that a strong complex forms between Fe(III) ion and polycarboxylate, which can enhance the dissolution of iron in natural water through photochemical reduction of Fe(III) to Fe(II). At the same time, oxidative species (such as H_2O_2, $O_2^{\bullet -}/HO_2^{\bullet}$ and $^{\bullet}OH$, etc.) can be formed due to the rapid photochemical reactions of iron-polycarboxylate complexes in the presence of dissolved oxygen [16,17].

Similar complexes may be formed between iron and aminopolycarboxylic acids (APCAs), of which the most typical and widely used

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example of these complexing agents is ethylenediaminetetraacetic acid (EDTA). Aminopolycarboxylic acids can also dissolve and inactivate metal ions by complex formation [18]. It is demonstrated that Fe(II)/Fe(III)-EDTA complexes have a significant role in producing harsh oxidants from dissolved oxygen [19]. Zhou and coworkers [20] reported that the Fenton-like system with Fe(III)-EDTA should be efficiently used over a wider pH range and the main advantage was the solubilization and so the stabilization of iron in the solution under neutral and basic pH. It is known from previous research that the degradation of malathion [19], 4-chlorophenol, polychlorophenol [21] and reduction of heavy metals [22] were achieved in neutral pH conditions. However, neither conventional chemical nor biological wastewater treatment can effectively removes EDTA [23], so it is not so easy to remove it from aqueous solution.

As a structural isomer and safe and environmental friendly replacement for EDTA, ethylenediamine-*N*,*N*′-disuccinic acid (EDDS), has attracted our interest recently. Our group is now using EDDS as a new complexing agent for iron and investigating the effect of EDDS on photochemical processes using iron. EDDS forms three stereo isomers, namely [S,S]-EDDS, [R,R]-EDDS and [R,S/S,R]-EDDS. Of these, [S,S]-EDDS is readily biodegradable. Under irradiation, Fe(III)-EDDS is easily photolyzed and the quantum yield of the •OH radical formation was higher at higher pH values in the range 3.0–9.0, which demonstrates that this complex is stable in aqueous solution at neutral pH and is photochemically efficient [24].

Bisphenol A (BPA), 2,2-bis-(4-hydroxyphenyl)propane, which is known as an emerging pollutant, causes not only endocrine disruption [25], but also cancer [26,27]. In summary, the treatment of BPA in the environment is of great importance. In fact, the removal of BPA from water using AOPs has been widely reported, using methods including UV-A irradiation with iron oxide [28–30], ultrasound-Fe(II)-UV [31], Fenton/Sono-Fenton [32], UV-TiO_2 [33,34] and ozonization [35].

To summarize the previous comments, the main aim of this paper is to investigate the efficiency of the photo-Fenton process using Fe(III)-EDDS complex/H_2O_2 system through hydroxyl radical (•OH) generation and the degradation of BPA. The effects of parameters such as pH and the concentrations of H_2O_2, Fe(III)-EDDS complex and oxygen were studied. The effects of Fe(III)-oxalate, Fe(III)-citrate and Fe(III)-EDTA complexes were also measured and compared with those of the Fe(III)-EDDS complex.

2. Experimental

2.1. Chemical

Bisphenol A (BPA), *S*,*S*′-ethylenediamine-*N*,*N*′-disuccinic acid trisodium salt (EDDS-Na) solution (35% in water) and 2-propanol were obtained from Sigma, France. Ferric perchlorate ($Fe(ClO_4)_3 \cdot 9H_2O$), nitrobenzene and hydrogen peroxide (H_2O_2) (30% in water) were from Fluka, France. Chloroform was purchased from Carlo Erba, France. Perchloric acid ($HClO_4$) and sodium hydroxide (NaOH) were used to adjust the pH of the solutions. All chemicals were used without further purification.

2.2. Preparation of complex

The Fe(III)-EDDS complex solution was prepared by mixing appropriate amounts of ferric perchlorate and EDDS salt solutions with 1:1 stoichiometry. The complex was freshly prepared before each experiment and stability was checked by means of UV–vis spectroscopy. Using a starting solution of Fe(III) (0.3 mM), additions of EDDS showed the complex formation through the increase of absorption. The complex absorption investigated at 340 nm showed a maximum at 0.3 mM of EDDS reaching a plateau up to 1 mM demonstrating that EDDS (hexadentate ligand) forms a 1 to 1 stable complex with Fe(III) [36].

2.3. Irradiation experiments

Photo-Fenton experiments were carried out in a home-made Pyrex photoreactor placed in a cylindrical stainless steel container. Around the reactor, four fluorescent tubes (Philips TL D 15W/05), with a continuous emission in the 300–500 nm range, were placed. Fig. 1 displays the measured spectral irradiance of the four tubes used during these experiments, as well as a UV–vis spectrum of BPA and Fe(III)-EDDS in water solution (taken with a Cary 300 UV-visible spectrophotometer) to show the spectral overlap. The emission spectrum reaching the solution was measured with an Ocean Optics SD 2000 CCD spectrophotometer (calibrated using a DH-2000-CAL Deuterium Tungsten Halogen reference lamp) and normalized to the actinometry results using *p*-nitroanisole (PNA)/pyridine actinometer [37]. Over the wavelength range 300–390 nm, a total flux of 530 W m^{-2} was measured.

The solutions were magnetically stirred with a magnetic bar during irradiation. An appropriate amount of BPA solution was mixed with the Fe(III)-EDDS complex solution and the pH value was adjusted using a Cyberscan 510 pH meter. The reaction started when an appropriate amount of H_2O_2 was added to the solution. At the same time the pH value was measured again, and it was found that the variation of pH value before and after adding H_2O_2 was less than 0.1. All the experiments were carried out at room temperature (293 ± 2 K). Samples were taken from the reaction flask at fixed intervals. The direct photolysis of BPA was checked and the results showed its stability under the irradiation conditions used.

2.4. Hydroxyl radical quantification

The detection of •OH during the photo-Fenton processes was performed using nitrobenzene (NB) as the trapping molecule. Nitrobenzene reacts directly with •OH to produce different nitrophenols and 1,3-dinitrobenzene [38].

The concentration of remaining nitrobenzene in the aqueous solution was determined by Alliance high performance liquid chromatography (HPLC) equipped with a dual λ absorbance detector (Waters 2487) and Waters 2695 separations module. The experiments were performed by UV detection at 210 nm. The flow rate was 1 mL min^{-1} and the mobile phase was a mixture of water and acetonitrile (50/50, v/v). The column was a Zorbax C8 of 150 mm × 4.6 mm, particle size 5 μm. In such conditions the column dead time was 0.9 min and the NB retention time was 4.6 min.

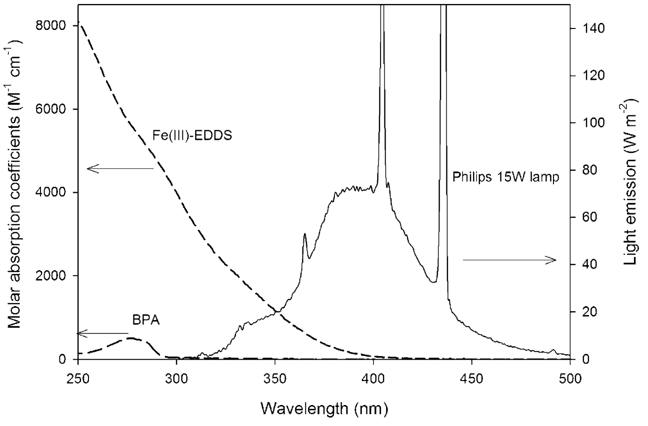

Fig. 1. Emission spectrum of the four Philips TL D 15 W tubes and the molar absorption coefficients of the aqueous solutions of BPA and Fe(III)-EDDS.