Effects of oxalate and persulfate addition to Electrofenton and Electrofenton-Fenton processes for oxidation of Ketoprofen: Determination of reactive species and mass balance analysis

Mohammad Alizadeh Fard[*], Brian Barkdoll

Department of Civil and Environmental Engineering, Michigan Technological University, 1400 Townsend Dr., Houghton, MI 49931, USA

ABSTRACT

Electrofenton (EF) has been widely used to remove contaminants from aqueous solution, while Electrofenton-fenton (EFF), is a two stage process that employs partial electrolysis, needs further study. In addition, a combination of oxalate and persulfate with these systems (EF-Oxalate, EFF-Oxalate, EF-Persulfate, and EFF-Persulfate) could improve the oxidation capacity. This study assessed the applicability of these systems for degradation of Ketoprofen as an emerging contaminant. Under batch experiments, results showed that the order of oxidation capacity and mineralization is EF-Persulfate > EFF-Persulfate > EF-Oxalate > EFF-Oxalate > EFF > EF. Radical scavenger experiments indicated that $^{•}OH$ is the dominant radical species in EF, EFF, EF-Oxalate, and EFF-Oxalate systems. However, both $^{•}OH$ and $^1O_2$ participated in oxidation of Ketoprofen in both EF-Persulfate and EFF-Persulfate processes. Fe(II)/Total Fe ratios in both solution and sludge samples decreased as oxidation capacity enhanced. Solution and sludge analyses revealed that the amount of Ketoprofen and oxidation byproducts increased in sludge over time. Carbon mass balance calculations showed that EF-Persulfate leaves the lowest amount of oxidation by-products in the system. BOD_5/COD ratio analyses demonstrated that all studied systems improved biodegradability of the raw wastewater. EFF and EF-Persulfate systems had the lowest and highest operational costs, respectively. Competitive maps were developed to compare all six processes by Ketoprofen removal efficiency, mineralization capacity, and operational costs. Results confirmed that addition of oxalate and persulfate to EF and EFF systems provide good solutions to decrease the load and risk posed by Ketoprofen to water systems.

© 2018 Elsevier Ltd. All rights reserved.

1. Introduction

Rapid population growth and Industrial development have resulted in many synthetic organic compounds being released in drinking water resources [1—3]. Over the last decades, the existence of emerging contaminants in aquatic environments has been reported as a serious environmental problem [4—6]. Compounds such as pesticides, herbicides, pharmaceuticals, and hormones can cause toxicological concerns in aquatic ecosystems, and consequently to human health [7]. Nonsteroidal anti-inflammatory drugs (NSAIDs) are persistent so they can last in the environment for a long time [8]. The persistent nature of these compounds means that if released into the environment they will persist in the soil and possibly reach the groundwater. Ketoprofen, as one of the NSAIDs, is a pharmaceutically active compound that is highly hydrophilic (pK_a of 4.45). This makes its elimination relatively inefficient by sorption processes in wastewater treatment plants (WWTPs). Its removal is mainly dependent on the chemical or biological process(es) applied [9].

Various treatment methods have been proposed and studied to remove emerging contaminants from aqueous solutions [9,10]. However, advanced oxidation processes (AOPs) that are based on generation of hydroxyl radicals and/or other strong oxidant species have received more attention [11—13]. As such, AOPs are powerful, promising, and environmentally friendly methods for degradation of emerging contaminants and their residues in water. Among AOPs, electrochemical advanced oxidation processes (EAOPs), have been considered to be reliable treatments that are able to eliminate contaminants even in low concentrations. These processes are able to generate strong oxidizing agents either by direct oxidation of

---

water (anodic oxidation) or in the homogeneous electrochemically generated Fenton's reagent (Electrofenton (EF) process). The generated oxidant species can degrade organic pollutants to their ultimate oxidation state, i.e., mineralization to carbon dioxide and water [14].

Recently, Fard et al. [15] suggested running the EF process for a few minutes, then cut the electrical current and let the system proceed under the Fenton process. They called this two-stage process Electrofenton-Fenton (EFF). Results showed that this system has better performance than EF, in addition to lower operational costs, as it consumes less energy than EF. This can result in a significant benefit in practice as electrolysis time directly relates to the treatment cost [15].

Studies have been done to combine EF with chemicals to enhance the treatment efficiency. Addition of oxalic acid to the system can lead to creation of ferrous oxalate and ferrioxalate complexes, which can make the oxidation system faster and more efficient than the simple Fenton process. Kwan and Chu [16] demonstrated that oxalate ($C_2O_4^{2-}$) is the best organic ligand compared to others such as EDTA or citrate. A ferrous-oxalate complex improved the production of •OH. In addition, oxalate can react with O_2 to form superoxide radicals that are likely to produce hydrogen peroxide [16].

On the other hand, persulfate ($S_2O_8^{2-}$) has been investigated as a potentially feasible chemical oxidant for organic pollutants [17]. This strong and non-selective oxidant is relatively stable at room temperature and can be activated by UV irradiation, heat, or transition metal ions to form sulfate radicals which are even stronger [18]. In this system, hydroxyl radicals can also be generated to participate in the degradation process [19].

In this study, first EF, EFF, EF-Oxalate, EFF-Oxalate, EF-Persulfate and, EFF-Persulfate systems were optimized for maximum Ketoprofen removal efficiency through different contributing factors. Then, the existence of common radical species were studied in each system. Next, the dominant iron species and mineralization capacity of each system were studied. Finally, operational costs were calculated and competitive maps, as decision making tools, were developed.

2. Materials and methods

2.1. Reagents and chemicals

Sodium hydroxide, sulfuric acid (98%), hydrogen peroxide (30%), and methanol were obtained from Merck (Germany) and used as received. Potassium persulfate (KPS), oxalic acid, superoxide dismutase (SOD), sodium sulfate, sodium azide (SA), and Ketoprofen were purchased from Sigma-Aldrich (USA).

2.2. Analysis methods

Ketoprofen concentration measurements were performed by a gas chromatography-mass spectrometry (GC/MS) which was equipped with a fused capillary column (TRB-5, 60 m, 0.32 mm ID). The apparatus was operated under the internal ionization mode in which a capillary column SGE (30 m $\times$ 0.25 mm), was used at the scan speed of 1000 Hz, electron energy of 60 eV and transfer-line temperature of 200 °C. Total organic carbon (TOC) was measured with a Shimadzu TOC analyzer. The concentration of hydrogen peroxide residual was determined using ammonium metavanadate. COD and BOD were analyzed using standard methods [20].

Ferrous iron and total iron concentrations were measured by the ferrozine method [21]. A 1-mL sample was added to a 60-mL aliquot of 50-mM ferrozine to bind ferrous iron. The absorbance

of ferrous-ferrozine complex was determined at 562 nm using a Hach spectrophotometer (DR 5000). Total iron concentration was measured by adding 180 mL hydroxylamine hydrochloride stock solution into the mixture containing the sample and ferrozine and letting the mixture rest for 20 min proceeding the reaction. After reducing any ferric species to ferrous form, the mixture were tested by colorimetric determination.

Reactive species were determined using radical scavengers. Methanol (MeOH) was used as a scavenger for sulfate and hydroxyl radicals [22]. The existence of singlet oxygen was determined using sodium azide (SA) [23]. Superoxide dismutase (SOD) was also used for determination of superoxide radicals [22].

Sludge analysis were done by re-dissolving the sludge using nitric acid. First, each sample was centrifuged (10,000 rpm, 5 min) and the supernatant was removed. Then, sludge pellets were re-dissolved with concentrated nitric acid (5 mL) for 30 min. The sample was diluted with ultrapure water and used for the determination of Ketoprofen, TOC, and iron species.

2.3. Experimental procedure

Batch oxidation experiments were done to determine the parameters affecting each process. A synthesized sample of 750 mL was batch-treated in a 1000 mL beaker, equipped with 2 iron electrodes (with a total effective area of 60 cm^2). Sodium sulfate was added to the reactor as electrolyte (0.03 M) and the initial pH of the solution was adjusted to a preferred pH value. The distance between electrodes was set to 2.5 cm in all experiments [15,24]. The current (300 mA) and voltage (40 V) were kept constant in all experiments. The initial concentration of Ketoprofen was 10 μM in all experiments except those related to BOD$_5$ and COD, in which it raised to 100 μM.

3. Results and discussion

3.1. Optimization of reaction parameters

Ketoprofen was used as a probe compound to test the reactivity of the treatment processes. Batch experiments were performed to study the effects of initial solution pH on the Ketoprofen removal efficiency for each process (Fig. 1 (a)). The initial pH values were set in the range of 3.0—9.0 and experiments were done for 20 min. It has been demonstrated that pH is an important parameter influencing the performance of electrofenton process [25,26]. In both EF and EFF systems, the removal efficiency declined at pH values higher than 3.0. This could be due to the domination of ferric hydroxide and other ferric ion species; the generation of these species causes quick decomposition of hydrogen peroxide to water and oxygen, resulting in less oxidation capacity [24]. Furthermore, the precipitation of Fe^{3+} in the form of $Fe(OH)_3$, can prevent the reaction between Fe^{3+} and H_2O_2 which consequently hinders the regeneration of ferrous ion [27]. At a pH value of 9.0, $Fe(OH)_4^-$ becomes dominant between ferric species, leading to the generation of flakes that decreases the oxidation capacity [24].

For EF-Oxalate and EFF-Oxalate processes, the results were similar to those of EF and EFF systems; the Ketoprofen removal efficiency was dropped by increasing solution pH. At pH 3.0 the degradation rates were 84 and 79% for EF-Oxalate and EFF-oxalate systems, respectively. However, these systems were able to remove 35 and 31% of Ketoprofen at pH 9.0. These results could be due to the fact that pH controls the ferrous ion speciation. This is in accordance with the results that Balmer and Sulzberger 1999 [28], were reported. They found the highest Atrazine degradation in acidic pH values in an irradiated iron/oxalate like system [28].

Unlike other studied systems, EF-Persulfate and EFF-Persulfate