



Degradation of naproxen by ferrous ion-activated hydrogen peroxide, persulfate and combined hydrogen peroxide/persulfate processes: The effect of citric acid addition



Niina Dulova*, Eneliis Kattel, Marina Trapido

Department of Chemical Engineering, Tallinn University of Technology, Ehitajate tee 5, Tallinn 19086, Estonia

HIGHLIGHTS

- Addition of CA showed promoting effect on NPX degradation by all systems at $\text{pH}_0 > 3$.
- $\text{S}_2\text{O}_8^{2-}/\text{Fe}^{2+}/\text{CA}$ proved the most effective in NPX degradation at a wide range of pH.
- Non-purgeable organic carbon was degraded gradually during the NPX mineralization.
- HO^\cdot was proposed as the predominant radical in activated $\text{H}_2\text{O}_2/\text{S}_2\text{O}_8^{2-}$ systems.
- NPX transformation products were identified in all CA-Fe^{2+} -activated systems.

ARTICLE INFO

Article history:

Available online 4 July 2016

Keywords:

Naproxen
Chelating agent
Fenton process
Ferrous ion-activated persulfate
In situ chemical oxidation

ABSTRACT

Naproxen (NPX), a widely used non-steroidal anti-inflammatory drug, has been detected extensively in different environmental systems at concentrations ranging from ng/L to $\mu\text{g/L}$, which may have a detrimental effect on human health and natural ecosystems. In this study, the degradation of NPX by citric acid (CA) chelated ferrous ion-activated hydrogen peroxide, persulfate and an innovative combined hydrogen peroxide/persulfate system was evaluated. The addition of CA at an appropriate complexation ratio considerably improved the target compound decomposition by the applied systems. Among the studied processes, the $\text{S}_2\text{O}_8^{2-}/\text{Fe}^{2+}/\text{CA}$ system showed the highest performance in NPX degradation at a wide range of pH followed by the combined $\text{H}_2\text{O}_2/\text{S}_2\text{O}_8^{2-}/\text{Fe}^{2+}/\text{CA}$ process. Limited elimination of non-purgeable organic carbon (NPOC) was observed during the mineralization of NPX by the examined systems. The results of radicals scavenging experiments indicated that both HO^\cdot and SO_4^\cdot contributed to the overall oxidation performance in the activated $\text{S}_2\text{O}_8^{2-}$ and $\text{H}_2\text{O}_2/\text{S}_2\text{O}_8^{2-}$ systems, but the former was the principal radical in the combined process. Transformation products (TPs) were identified using LC–MS analysis in the CA-Fe^{2+} -activated systems. Potential NPX degradation mechanism was subsequently proposed revealing hydroxylation with the subsequent decarboxylation or demethoxylation as the main step of the TPs formation. The findings of this study strongly suggest that the CA-Fe^{2+} -activated $\text{S}_2\text{O}_8^{2-}$ and combined $\text{H}_2\text{O}_2/\text{S}_2\text{O}_8^{2-}$ oxidation are promising treatment technologies for the abatement of NPX pollution in natural aqueous matrices.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

The introduction of non-steroidal anti-inflammatory drugs (NSAIDs) into natural matrices such as drinking water, surface water, groundwater, seawater, sediments and soil is an emerging problem due to their potential harmful effect on human health and natural ecosystems [1–4]. Most of NSAIDs are not fully

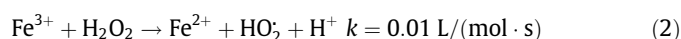
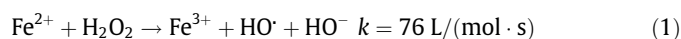
metabolized after application, only partially oxidized by conventional treatment processes used in wastewater treatment plants, and as a result found in the environment in an unchanged or slightly modified active form [5]. Naproxen (NPX) is a non-steroidal anti-inflammatory drug with analgesic and antipyretic properties, widely used for the treatment of rheumatoid arthritis as well as in the veterinary medicine. Similarly to other NSAIDs, NPX and its intermediates have been detected in different environments at concentrations ranging from ng/L to $\mu\text{g/L}$ [6–8]. Therefore, the development of effective remediation technology for

* Corresponding author.

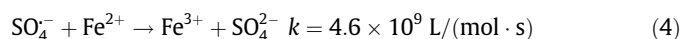
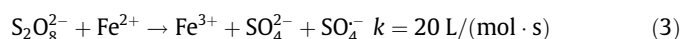
E-mail address: niina.dulova@ttu.ee (N. Dulova).

elimination of NSAIDs, including NPX, from natural matrices, such as groundwater, is of great scientific and public interest.

Among the various chemical, physical and biological technologies used in the remediation of organically contaminated groundwater, in situ chemical oxidation (ISCO) is the most promising one due to its feasibility to degrade a wide range of bio-recalcitrant contaminants, relatively fast treatment and cost-effectiveness as well as potentially enhanced post-oxidation microbial activity [9,10]. The ISCO is typically implemented by the application of systems based on hydrogen peroxide (H_2O_2), permanganate (MnO_4^-), ozone (O_3), persulfate ($\text{S}_2\text{O}_8^{2-}$), or a combination of them [9,11,12]. The Fenton treatment is widely studied and used technology for in situ groundwater and soil remediation based on the generation of hydroxyl radicals (HO^\cdot) from iron-activated hydrogen peroxide decomposition [13]. The commonly accepted Fenton mechanism consists of a chain reaction, where Eq. (1) is known as the Fenton reaction implying the oxidation of ferrous iron ions (Fe^{2+}) to decompose H_2O_2 into HO^\cdot and Eq. (2) is so-called Fenton-like reaction representing the activator regeneration by H_2O_2 decomposition into hydroperoxyl radical (HO_2^\cdot) [14,15]:



Persulfate is an alternative ISCO oxidant, which has the potential to overcome some limitations associated with activated hydrogen peroxide environmental applications [16–19]. The activation of persulfate by heat, UVC light or ultrasound (US), transition metal, base, peroxide or ozone leads to the generation of sulfate radicals (SO_4^\cdot) [12,20,21]. Among different transition metals used in persulfate activation [22], iron in its ferrous form is the most frequently studied activator for ISCO applications [12,16,18]. However, ferrous ion-activated persulfate oxidation has its limitations related mainly to the fast conversion of Fe^{2+} into Fe^{3+} via Eq. (3) leading to the rapid termination of persulfate activation and the fast scavenging of SO_4^\cdot by excessive Fe^{2+} through Eq. (4) eventually causing the reduction in treatment efficacy [16,23,24]:



Moreover, in the both above-mentioned ISCO technologies iron is used initially in a soluble Fe^{2+} form to activate oxidant; however aqueous iron is relatively insoluble at the ambient $\text{pH} \geq 5$ of most natural aquifer systems and tend to precipitate in the form of amorphous ferric oxyhydroxides [25]. Thus, to adjust the availability of Fe^{2+} and to stabilize its amount in aqueous matrices at natural pH values, chelating agents such as ethylenediaminetetraacetic acid (EDTA) [17,26], ethylenediaminedisuccinate (EDDS) [27–29], sodium polyphosphates (STPP, TSPP) [17,27], oxalic acid (OA) [26,29], tartaric acid [26,29] and citric acid/citrates (CA) [17,27,29] could be employed in ISCO applications. The latter, CA, proved to be the most feasible chelating agent both for Fe^{2+} -activated hydrogen peroxide and persulfate oxidation of chlorophenols [27] and the most efficient one for aniline decomposition by Fe^{2+} -activated persulfate system [29].

Therefore, in the present study the potential of $\text{H}_2\text{O}_2/\text{Fe}^{2+}/\text{CA}$, $\text{S}_2\text{O}_8^{2-}/\text{Fe}^{2+}/\text{CA}$ and combined $\text{H}_2\text{O}_2/\text{S}_2\text{O}_8^{2-}/\text{Fe}^{2+}/\text{CA}$ systems in NPX decomposition was assessed. According to the available literature, the application of radical-based advanced oxidation technologies (AOTs), including UVC/ H_2O_2 system [30,31], $\text{O}_3/\text{H}_2\text{O}_2$ and O_3/UVC processes [32], O_3/TiO_2 oxidation [32], sonolysis and combined US/Fenton/ TiO_2 system [33], photo-Fenton and photo-Fenton-like systems [31,34], photocatalysis [32], and thermally activated persulfate oxidation [35], proved to be a promising solution for NPX

degradation in aqueous matrices. However, the application of Fe^{2+} -activated persulfate and combined hydrogen peroxide/persulfate systems for NPX decomposition in aqueous solution was not previously evaluated.

The main objective of this study was to investigate and compare the degradation of NPX by citric acid chelated ferrous ion-activated hydrogen peroxide, persulfate and innovative combined hydrogen peroxide/persulfate systems. The effect of pH and different initial oxidant, activator and chelating agent concentrations were evaluated. The consumption of hydrogen peroxide and persulfate as well as mineralization and degradation mechanism of NPX were also studied. It is expected that the results of this study can provide valuable information on the degradation of NPX by these radical-based AOTs applied as an ISCO approach for groundwater remediation.

2. Materials and methods

2.1. Chemicals and materials

All chemicals were of the highest purity commercially available and used without further purification. Naproxen (Fig. 1; $\text{C}_{14}\text{H}_{14}\text{O}_3$, $\geq 98\%$, molecular weight 230.26 g/mol, $\text{pK}_a = 4.45$ [36], hydrogen peroxide (H_2O_2 , PERDROGENTM, $\geq 30\%$), sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$, $\geq 99\%$), ferrous sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, $\geq 99\%$), citric acid monohydrate ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$, $\geq 99\%$), sodium sulfite (Na_2SO_3 , $\geq 98\%$), sodium hydroxide (NaOH , $\geq 98\%$), and sulfuric acid (H_2SO_4 , 95–98%) were purchased from Sigma-Aldrich. Acetonitrile (CH_3CN , LiChrosolv[®]), ethanol ($\text{C}_2\text{H}_6\text{O}$, EtOH, 99%), formic acid (CH_2O_2 , 99%), and tertiary butanol ($(\text{CH}_3)_3\text{COH}$, *t*-BuOH, $\geq 99\%$) were purchased from Merck KGaA. Ultrapure water, generated by a Millipore Simplicity[®] UV System, was used for the preparation of all solutions used in the non-activated and activated hydrogen peroxide, persulfate and combined hydrogen peroxide/persulfate oxidation experiments.

2.2. Experimental procedure

The laboratory-scale experiments of the activated hydrogen peroxide (H_2O_2), persulfate ($\text{S}_2\text{O}_8^{2-}$) and combined $\text{H}_2\text{O}_2/\text{S}_2\text{O}_8^{2-}$ systems were performed in batch mode at ambient room temperature ($22 \pm 1^\circ\text{C}$). No buffer solution was used to avoid any interference related to potential reactions between hydroxyl and sulfate radicals and buffer species. NPX solutions (75 μM , 0.4 L) were treated in a 0.6-L cylindrical glass reactor with a permanent agitation speed (400 rpm) for a period of 3 h. The pH of the samples was adjusted to 3, 5, 7 or 9 by NaOH or H_2SO_4 aqueous solutions. The activator ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, Fe^{2+}) or activator/chelating agent ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$, CA) was added, and after complete dissolution of the activator or chelated activator, the oxidation was initiated by adding hydrogen peroxide and/or sodium persulfate. In the case of combined $\text{H}_2\text{O}_2/\text{S}_2\text{O}_8^{2-}$ system, both oxidants were added simultaneously. Samples were withdrawn at pre-determined time intervals, corresponding to 0, 1, 5, 10, 15, 30, 60, 120 and 180 min. The oxidation quenching was done by the addition of Na_2SO_3 at a $[\text{oxidant}]_0/\text{SO}_3^{2-}$ molar ratio (m/m) of 1/10 or by the addition of 1 M NaOH solution to adjust the pH to ~ 9 . The experiments on NPX oxidation with non-activated

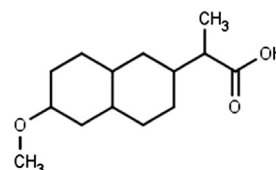


Fig. 1. Molecular structure of NPX.

Download English Version:

<https://daneshyari.com/en/article/6466288>

Download Persian Version:

<https://daneshyari.com/article/6466288>

[Daneshyari.com](https://daneshyari.com)