Chemical Engineering Journal 279 (2015) 861–873

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Naproxen abatement by thermally activated persulfate in aqueous systems

Antoine Ghauch *, Al Muthanna Tuqan, Nadine Kibbi

American University of Beirut, Faculty of Arts and Sciences, Department of Chemistry, P.O. Box 11-0236, Riad El Solh, 1107-2020 Beirut, Lebanon

HIGHLIGHTS

- Naproxen is fully degraded in thermally activated persulfate systems.
- Naproxen degradation mechanism is highly dependent on $SO_4^{\cdot-}$ rather than on $OH^{\cdot}$ radicals.
- Naproxen mineralization extent is proportional to persulfate concentration.
- Inorganic ions slightly affect naproxen degradation efficiency in TAP systems.
- TAP systems showed total mineralization of naproxen in highly charged hospital effluent.

ARTICLE INFO

Article history:
Received 4 February 2015
Received in revised form 16 May 2015
Accepted 20 May 2015
Available online 27 May 2015

Keywords:
Naproxen
Advanced oxidation processes
Hospital effluent
Decontamination
Water reuse

ABSTRACT

In this work, we investigated the use of thermally activated persulfate (TAP) as one of the most powerful advanced oxidation processes for the treatment of pharmaceuticals present in effluents. Pilot experiments were carried out on naproxen (NAP) solutions, and the effect of experimental conditions (e.g. inorganic additives, matrix) was assessed so as to better evaluate TAP systems and improve the reaction stoichiometric efficiency. A comparative kinetics study was provided for the removal of NAP vs work previously published using however other classes of pharmaceuticals e.g. bisoprolol, ibuprofen. The activation energy (E_A) calculated was found to be 155.03 (±26.4) kJ mol^{-1}. The best degradation rate was observed at 70 °C and found to be equal to 1.286×10^{-4} mM min^{-1}. Furthermore, experiments were performed on untreated hospital effluents collected from the largest hospital in Beirut and spiked with NAP solution (50 μM). Results showed full mineralization of the pharmaceutical effluent that was achieved and monitored via total organic carbon (TOC) analysis. Liquid and gas chromatography coupled with mass spectrometry were the techniques used for the identification of NAP and its transformation products. A NAP degradation mechanism was proposed and found to be mainly based on the action of sulfate radicals operating by electron abstraction. This study demonstrated once more that TAP systems are a valid and efficient method that can be used for the removal of dissolved pharmaceuticals in water and sewage water.

1. Introduction

In recent years, non-steroidal anti-inflammatory drugs (NSAIDs) have been found in water effluents in increasing concentrations e.g. ng L^{-1} to μg L^{-1} [1,2]. The issue obtained growing interest because of the potential threats that NSAIDs cause to both the ecological system and human beings [3,4]. In this study, we have chosen naproxen (NAP) for its presence in sewage treatment plant effluents and drinking water in significant concentrations 17–313 ng L^{-1} [1]. NAP toxicity was not only reported on bacteria, microcrustaceans and algae, but also on humans [5]. It was also reported that people who ingest trace amounts of NAP for a long time may have a higher risk of having a heart attack or a stroke than people who are not exposed to this medication [6]. In the past few years, several studies have been conducted on the subject of NAP removal from water. These studies used different treatment methods and remediation technologies such as photo-degradation, ozonation, ultra-sonication, gamma irradiation, nanofiltration [7–13]. Benitez et al. [14] showed that O_3/H_2O_2 was the most successful oxidative system for NAP (1 μM) degradation in ultrapure water (UP) with an achieved degradation rate of about 2.64×10^{-4} M^{-1} s^{-1}. Two years later, Marotta et al. [10] investigated the role of oxygen during photo-degradation of NAP solution

* Corresponding author. Tel.: +961 1350 000; fax: +961 1 365 217.
E-mail address: antoine.ghauch@aub.edu.lb (A. Ghauch).

http://dx.doi.org/10.1016/j.cej.2015.05.067
1385-8947/

(1 μM) and found better results in oxic solutions rather than under anaerobic conditions. In 2014, Ma et al. [7] demonstrated that NAP (43 μM) photo-degradation by direct solar photolysis and by self-sensitization via reactive oxygen species was effective. However, the adopted process yielded some intermediate products more toxic than NAP. In 2015, Rein and Welch [15] found that NAP's photo-degradation products were significantly more toxic than NAP itself, and combinations of NAP and its photo-degradation products were particularly toxic. Accordingly, investigations into new methods of NAP's removal become of interest, especially if the resulting transformation products are more biodegradable, totally absent or at least do not represent greater toxicity than NAP, the parent NSAID [15].

Since several methods have been developed to remove pharmaceuticals from water effluents [16], the focus has also been toward efficient and economically viable techniques, especially for large scale treatment and field applications. Persulfate technology emerged in the recent years as part of the advanced oxidation processes (AOPs) to be considered by water treatment specialists [17,18].

In the past decade, TAPs have been significantly applied as powerful in situ chemical oxidation (ISCO) processes for the removal of volatile organic compounds [19], polycyclic aromatic hydrocarbons (PAHs) [20], trichloroethylene [21] and very recently pharmaceuticals [22–25] and dyes [26,27] in water. When used for ISCO processes sodium persulfate (PS) showed very promising results due to its high redox potential (Eq. (1)) and its strongly oxidative sulfate radical $SO_4^{\cdot-}$ (Eq. (2)) that can either be generated thermally or chemically (Eqs. (3)–(5)) [28,29]. In thermally activated systems, increased temperatures result in faster generation of the oxidative $SO_4^{\cdot-}$ [22,23], while in chemically activated systems, excess of activators might jeopardize the oxidation process due to $SO_4^{\cdot-}$ quenching [24,25,30]:

$$S_2O_8^{2-} + 2e \rightarrow 2SO_4^{2-} \text{ with } E^0 = 2.01 \text{ V/SHE} \quad (1)$$

$$SO_4^{\cdot-} + e \rightarrow SO_4^{2-} \text{ with } E^0 = 2.41 \text{ V/SHE} \quad (2)$$

$$S_2O_8^{2-} \rightarrow 2SO_4^{\cdot-} \text{ (Thermal activation) with } 30\,^{\circ}C < T < 99^{\circ} \quad (3)$$

$$S_2O_8^{2-} + Fe^{2+} \rightarrow SO_4^{2-} + SO_4^{\cdot-} + Fe^{3+} \text{ (Chemical activation)} \quad (4)$$

$$SO_4^{\cdot-} + Fe^{2+} \rightarrow SO_4^{2-} + Fe^{3+} \text{ with } k = 4.6 \times 10^9\ M^{-1}\ s^{-1} \quad (5)$$

To our knowledge, no data exists today on the removal of NAP from water in TAP systems especially when it comes to highly charged effluents e.g. hospitals, clinical laboratories, etc. In the present study, TAP systems are adopted in order to investigate NAP degradation in UP water as well as in a hospital effluent (HE). A kinetics study is presented taking into account the reaction rate and reaction stoichiometric efficiencies (RSEs) under controlled temperatures (40–70 °C) and in the presence of inorganic additives at circumneutral pH. Scavenging reactions are performed as well to identify the main oxidative radical ($SO_4^{\cdot-}$ vs $HO^{\cdot}$). The calculated activation energy (E_A) of NAP is determined and compared to that of other pharmaceuticals previously investigated under similar conditions [22,23]. TOC analyses are performed on treated solutions demonstrating full NAP mineralization. At the end, an assessment of TAP systems for the removal of dissolved pharmaceuticals in a real HE collected from the effluent of the largest hospital located in Beirut is presented. NAP transformation products are identified and a degradation mechanism is proposed.

2. Materials and methods

2.1. Chemicals

Pharmaceutical grade naproxen sodium (NAP), sodium persulfate (PS) ($Na_2S_2O_8$, 99+%) and acetic acid glacial (CH_3COOH, 99.5+%) were purchased from Sigma–Aldrich (China), Chem-Lab (Belgium) and Surechem Products LTD (UK), respectively. Sodium dihydrogen phosphate dihydrate ($NaH_2PO_4{\cdot}2H_2O$, 99+%) and disodium hydrogen phosphate (Na_2HPO_4, 99+%) were acquired from Fluka (Netherlands) and Merck (Germany), respectively. Potassium iodide (KI) (puriss, 99–100.5%) and potassium dihydrogen phosphate (KH_2PO_4) were obtained from Riedel-de-Haen (Germany). Acetonitrile (CH_3CN) and methanol (CH_3OH) were both of HPLC grade and purchased from Sigma (USA).

2.2. Chemical analysis

2.2.1. HPLC/DAD/FLD/MSD

NAP was analyzed using an Agilent 1100 Series high pressure liquid chromatography (HPLC). The HPLC system is composed of a quaternary pump equipped with a vacuum degasser, thermostated autosampler and column compartment in addition to a diode array detector (DAD) and a fluorescence detector (FLD). Both were placed in series with an ion-trap mass spectrometry detector (MSD). A C_{18} reverse phase column (5 μm; 4.6 i.d. × 250 mm long) attached to a pre-column guard HS C_{18} (5 μm; 4.6 i.d. × 20 mm long, Discovery, Supleco, USA) was used for the separation of pharmaceutical molecules and all derivatives. Both column and column guard were maintained at 30 °C throughout the analysis. The mobile phase consisted of acetonitrile (55%) and 0.04% (v/v) acetic acid glacial (45%) percolating through the column in an isocratic mode with a flow rate of 1.0 mL min^{-1}. The sample injection volume was about 50 μL. The whole chromatography system was controlled by Agilent ChemStation software for LC and LC/MS systems version A.09.0.

For HE samples, the same HPLC system was used however with gradient elution in order to better separate dissolved organic molecules inside. The mobile phase was composed of (A) 50 mM KH_2PO_4 and (B) acetonitrile. The gradient was run as follows: at time 0–4.5 min, 85% of (A) and 15% of (B); at t = 12.5 min, 80% of (A) and 20% of (B); at t = 18 min, 75% of (A) and 25% of (B); finally at t = 27–45 min, 55% of (A) and 45% of (B).

2.2.2. GC/MS

MS analyses were performed on a thermo scientific GC/MS equipped with a POLARIS Q Ion Trap MS detector, a Thermo Finnigan autosampler and XCalibur software (USA) in order to identify NAP transformation products. The conditions were as follows: EI = 70 eV, manifold temperature 473 K, dwell time 100 μs and scan range of 50–500 m/z. Separation was done on Agilent DB-23 column (30 m length, 0.25 mm internal diameter and 0.25 μm film thickness) flushed with Helium as carrier gas. The injection volume was about 2 μL. System temperature was programed to start at 373 K for 2.5 min followed by a 6 K/min increase up to 523 K then held for 15 min.

2.2.3. Persulfate analysis

Persulfate anion concentration was determined on a Nanodrop 2000c UV–vis spectrophotometer (Thermo scientific) as per the procedure developed by Liang et al. [31]. The absorbance of the complex was measured at λ = 352 nm. PS calibration curves were performed with a range of concentrations of 5–1000 μM (Fig. 1S). The limit of detection of PS under these conditions was less than 5.0 μM [22,23].