



Ultrasonic degradation of acetaminophen in water: Effect of sonochemical parameters and water matrix



Erica Villaroel^a, Javier Silva-Agredo^b, Christian Petrier^{c,d}, Gonzalo Taborda^a, Ricardo A. Torres-Palma^{b,*}

^a Grupo de Investigación en Cromatografía y Técnicas Afines, Facultad de Ciencias Exactas y Naturales, Universidad de Caldas, A.A. 275, Manizales, Colombia

^b Grupo de Investigación en Remediación Ambiental y Biotecnología, Instituto de Química, Facultad de Ciencias Exactas y Naturales, Universidad de Antioquia, A.A. 1226, Medellín, Colombia

^c Laboratoire Rhéologie et Procédés, Grenoble, France

^d King Abdulaziz University, Jeddah, Saudi Arabia

ARTICLE INFO

Article history:

Received 3 October 2013

Received in revised form 5 April 2014

Accepted 5 April 2014

Available online 15 April 2014

Keywords:

Paracetamol

Acetaminophen

Pharmaceutical products

Sonochemical degradation

Water treatment

Advanced oxidation processes

ABSTRACT

This paper deals about the sonochemical water treatment of acetaminophen (ACP, N-acetyl-*p*-aminophenol or paracetamol), one of the most popular pharmaceutical compounds found in natural and drinking waters. Effect of ultrasonic power (20–60 W), initial ACP concentration (33–1323 $\mu\text{mol L}^{-1}$) and pH (3–12) were evaluated. High ultrasonic powers and, low and natural acidic pH values favored the efficiency of the treatment. Effect of initial substrate concentration showed that the Langmuir-type kinetic model fit well the ACP sonochemical degradation. The influence of organic compounds in the water matrix, at concentrations 10-fold higher than ACP, was also evaluated. The results indicated that only organic compounds having a higher value of the Henry's law constant than the substrate decrease the efficiency of the treatment. On the other hand, ACP degradation in mineral natural water showed to be strongly dependent of the initial substrate concentration. A positive matrix effect was observed at low ACP concentrations (1.65 $\mu\text{mol L}^{-1}$), which was attributed to the presence of bicarbonate ion in solution. However, at relative high ACP concentrations a detrimental effect of matrix components was noticed. Finally, the results indicated that ultrasonic action is able to transform ACP in aliphatic organic compounds that could be subsequently eliminated in a biological system.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

The presence of pharmaceutical compounds in the ecosystem is nowadays a big concern. N-acetyl-*p*-aminophenol or paracetamol, commercially available as acetaminophen (ACP) is a mild analgesic, currently used for the relief of headaches and other minor aches and pains. It is a major ingredient in numerous cold and flu remedies. In combination with opioid analgesics, paracetamol can also be used in the management of more severe pain such as post-surgical pain and providing palliative care in advanced cancer patients. ACP is not completely removed in municipal wastewaters, and it is nowadays one of the most popular compounds found in natural and drinking waters [1]. In fact, it has been recognized as the pharmaceutical compound with a higher presence in rivers in France [2]. ACP concentrations in effluents leaving several treatment plants are reported [3] to be higher than 65 $\mu\text{g L}^{-1}$. Thus, ACP represents a serious risk for the environment.

Ultrasound is an advanced oxidation process having an increased interest in the last years [4,5]. Central events during ultrasonic action are based on acoustic cavitation, which can be defined as the cyclic formation, growth and collapse of microbubbles. In the final step of the collapse, temperature and pressure can reach higher values than 2000 K and 200 atm, respectively. When dissolved gas, water vapor and volatile compounds are exposed to such extreme conditions, bond rupture occurs. Therefore, upon ultrasound action hydroxyl and perhydroxyl radicals are generated from water and oxygen dissociation [6]:



* Corresponding author. Tel.: +57 4 219 56 69; fax: +57 4 219 56 66.

E-mail address: rtorres@matematicas.udea.edu.co (R.A. Torres-Palma).

The formed radicals that do not react with the substrate can also be diffused into the solution to produce hydrogen peroxide:



Thus, comparison of hydrogen peroxide determination during acoustic cavitation, in presence and in absence of substrate, is a suitable method to estimate the radical production rate for specific sonochemical conditions.

Sonolysis of organic pollutants may occur by two different mechanisms. Compounds may be degraded via thermal decomposition, inside the bubble and/or in the interface, or by reactions with radicals and hydrogen peroxide at the interface and/or in the liquid bulk.

Quesada-Peñate et al. [2], reported the sonochemical ACP degradation. They found that ~600 kHz is the best frequency for ACP removal. Additionally, ·OH radical attack was reported to be the main degradation pathway. More recently, Jagannathan et al. [7] demonstrated that ACP mineralization is possible by using ultrasound combined to photochemical systems.

It is well known that chemical composition of waters has a strong effect on the efficiency of treatment systems [6]. However, because neither the influence of water matrix components (inorganic and organic compounds) nor the initial pH solution was evaluated, the feasibility of the ultrasonic system for the treatment of ACP solutions cannot be estimated from previous works.

Therefore, herein, the viability of acoustic cavitation to the treatment of water contaminated with ACP was investigated. The effect of ultrasonic power, ACP concentration and initial pH of solution was evaluated. Additionally, the influence of water matrices containing organic compounds with different chemical properties (oxalic acid, glucose, hexanol and isopropanol) was studied. Finally, the degradation of the substrate contained in mineral natural water was also evaluated.

2. Materials and methods

2.1. Reagents

Acetaminophen (molecular formula $\text{C}_8\text{H}_9\text{NO}_2$, FW 151.17 g mol^{-1}) was obtained from LAPROFF® S.A. and used without further purification. Methanol, propan-2-ol, hexan-1-ol, potassium dichromate, glucose, potassium phthalate and sodium hydroxide were obtained from Merck. Phosphoric acid, ferrous sulfate, ammonium heptamolybdate and potassium iodide, were obtained from Riedel-de Hanën. Oxalic acid was obtained from Panreac; while sulfuric acid was obtained from Carlo Erba.

2.2. Acetaminophen solutions

The solutions of ACP were obtained by dissolving the corresponding quantity of substrate into deionized or mineral water, then pH was adjusted (using phosphoric acid or sodium hydroxide) as required (to 3.0, 5.6, 9.5, 11.0, 12.0) and the solutions were finally filtered through membrane filter (0.45 μm).

2.3. Apparatus

The source of ultrasonic waves was a piezoelectric disk (diameter 4 cm) fixed on a Pyrex plate (diameter 5 cm) in the bottom of a batch homemade reactor of 500 mL of capacity, which was filled with 300 mL of the ACP solution. Applied ultrasonic power was adjusted as needed between 20 and 60 W; while frequency was fixed to 600 kHz. The cylindrical sonochemical reactor was

thermostated by a water jacket at 20 ± 1 °C. Ultrasonic energy dissipated in the reactor (~58% of electrical power input) was estimated by calorimetric method [8].

2.4. Analysis

Total Organic Carbon (TOC) removal was followed in a (LABTOC analyzer), using a solution of potassium phthalate as the calibration standard. Quantitative analysis of ACP, aromatic and aliphatic by-products was done by HPLC in a Agilent 1100 Series with a mobile phase water/methanol (70/30 v/v) at flow rate 1.0 mL min^{-1} on LiChrospher® 100 RP-18 column (5 μm , $250 \times 4 \text{ mm}$) and a tunable UV detector set a 243 nm. Chemical Oxygen Demand (COD) was measured using a dichromate solution as the oxidizer in a strong acidic medium. Test solution (2 mL) was transferred into dichromate reagent and digested at 150 °C for 2 h [9]. The optical density for the color change of dichromate solution was measured at 445 nm with a Spectrophotometer SPECTRONIC® 20 GENESYS™. Hydrogen peroxide concentrations were determined iodometrically: aliquots taken from the reactor were added in the sample quartz cuvette of the Spectrophotometer SPECTRONIC® 20 GENESYS™ containing the reagent (potassium iodide, 0.1 M and ammonium heptamolybdate, 0.01 M). Absorbance was recorded at 5 min.

3. Results and discussion

3.1. Effect of initial pH

It is well known that pH of solutions markedly influence the sonochemical degradation of organic pollutants [5,10,11]. Hence the effect of this parameter on the sonochemical degradation rate of ACP was investigated. Different initial pH values ranged between 3.0 and 12.0 were tested at $82.69 \mu\text{mol L}^{-1}$ of substrate concentration, 600 kHz, 60 W and 20 °C. The results showed in Fig. 1A indicated that ultrasonic degradation in acidic medium (pH 3.0–5.6) is higher than those obtained in basic aqueous solutions (pH 9.5–12.0). In fact, ACP initial rate is ~80% lower at pH 12.0 than the observed at pH 3.0 or 5.6. Thus, acidic conditions are propitious to the ultrasonic degradation of ACP. As can be observed in Fig. 1B, initial pH values between 3 and 11, does not affect significantly the sonochemical accumulation rate of hydrogen peroxide in absence of substrate ($\sim 1.63 \mu\text{mol L}^{-1} \text{ min}^{-1}$ in all of cases) and then, between this pH range, the hydroxyl radical formation rate is independent of the initial pH. Thus, the influence of pH during the ultrasonic degradation of ACP is probably due to the chemical structure and properties of ACP. It has been shown that hydrophobicity of the pollutant is one of the most important factors to predict the sonochemical reaction pathway. ACP degradation would be increased if its hydrophobicity is favored. Since ACP molecule is a polar substrate, having at high solubility (12.5 mg mL^{-1}) with a value of the Henry's law constant ($6.42 \times 10^{-11} \text{ atm m}^3 \text{ mol}^{-1}$) [12] as low as bisphenol A ($1.10 \times 10^{-11} \text{ atm m}^3 \text{ mol}^{-1}$) [4], it cannot enter inside the bubble. However, as reported previously [1], it is mainly eliminated by ·OH radicals at the solution bulk or at the surface of the bubble. The degradation rate as a function of pH is also related to the pK_a value of organic pollutants. pK_a value of ACP is 9.5; accordingly, in aqueous acid solutions (pH 3.0, 5.6) ACP is mostly found in its molecular form. Under such conditions, his hydrophobicity is favored, and it accumulates at the interface of the cavitation bubbles, where a relatively elevated concentration of ·OH radicals is present. As the pH increases higher than the pK_a of ACP, the hydroxyl group of the substrate structure is ionized, its hydrophobicity is reduced and ACP degradation takes place at the solution-bulk where a lower

Download English Version:

<https://daneshyari.com/en/article/1266102>

Download Persian Version:

<https://daneshyari.com/article/1266102>

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