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Assessment of the kinetics of oxidation of some steroids and pharmaceutical compounds in water using ozone

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ABSTRACT

Emerging contaminants are present in surface and ground water, generating a potential risk for the public health of surrounding populations that consume contaminated water. However, their elimination using conventional treatment methods has not been an easy task. The aim of this research was the assessment of the kinetics of oxidation of four emerging contaminants in water two steroids: estradiol (E2) and ethynilestradiol (EE2) and two pharmaceutical drugs: naproxen (NPX) and ibuprofen (IBP) – by using an ozonation process. The stoichiometry and the second order rate constants for the four compounds were obtained. The method of competitive kinetics was established to assess the kinetics of oxidation of steroids and NPX and the absolute rate constant under pseudo-first-order conditions method for IBP. The second order rate constants for E2, EE2, NPX were in the order of 10^4 to 10^5 L/(mol s) and for IBP the value was 10^1 L/(mol s). An oxidation kinetic model for the steroids and pharmaceutical drugs at different doses of ozone was obtained from the rate constants, and validated with the experimental values. In addition, the half-life of the selected compounds for each experimental ozone dose was obtained, which serves to predict the behavior of oxidation of emerging contaminants, knowing the initial concentration of ozone. This research is focused toward a project for water treatment with the presence of emerging contaminants on a semi-pilot scale in continuous operation.

Introduction

Anthropogenic activities, in particular those of industry, produce and use a large diversity of emerging contaminants, such as pesticides, alkylphenols, dioxins, bisphenol A, polycyclic aromatic hydrocarbons, styrene, and phthalates, as well as steroids, pharmaceutical drugs and personal care products [1–3]. The presence of emerging contaminants in the environment has awakened interest in investigating the possible adverse effects in human health and aquatic ecosystems [1,4,5] due to the potential hazard that some of them have shown to the endocrine system of living organisms [6–8].

Emerging contaminants at different concentration levels have been detected in wastewater discharged to the environment with or without treatment. Examples include pharmaceutical drugs in concentrations on the order of μg/L [9–12] and also natural and synthetic steroids on the order of ng/L, which are considered the most powerful estrogenic compounds [9,13–16]. Emerging contaminants are recalcitrant; they have a low biodegradability, that is, they are resistant to biological degradation and conventional processes for water treatment. Therefore, they remain in the environment for long periods [17–19,8]. Due to natural infiltrations and runoff, these contaminants pollute surface and ground waters that serve as potable water supplies. This situation generates a risk for the population that consumes this water [4,9,13,14]. The necessity for developing effective treatment processes to degrade emerging contaminants present in water becomes of great importance [20,21]. Some of these treatment processes are advanced oxidation processes (AOPs) based on ozone. An AOP is defined as the coupling of two or more strong oxidant species in order to generate hydroxyl radicals ($HO^{\bullet}$), causing a rapid and complete oxidation of recalcitrant compounds [2,15,20]. Examples of coupling strong oxidant species are O_3/high pH values, O_3/H_2O_2, Fe^{2+}/H_2O_2, O_3/catalyst, H_2O_2/UV, O_3/UV, O_3/H_2O_2/UV, Fe^{2+}/H_2O_2/UV (Photo-Fenton), O_3/catalyst, and O_3/TiO_2/UV [22–26].

AOPs have been useful for the degradation of steroids such as 17β-estradiol (E2) and 17α-ethinylestradiol (EE2) in deionized water using ozone [20], demonstrating the strong dependence between the rate constant with changes in pH and ozone doses. Deborde et al. [27] investigated the oxidation of six emerging contaminants with ozone and obtained removal efficiencies

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greater than 95% for all the compounds at ozone exposures of only $\sim 2 \times 10^{-3}$ (mg min)/L. Huber et al. [28] used ozone for the oxidation of pharmaceutical drugs, reaching 55% oxidation of ibuprofen (IBP) with times of reaction greater than 35 min. At pilot scale, effluents from a wastewater treatment plant containing pharmaceutical drugs and steroids showed that many of these compounds could be efficiently oxidized with ozone [20]. Benítez et al. [29] studied the ozonation of four pharmaceutical drugs in ultra-pure water at a pH range from 2.5 to 9. Nanaboina et al. [21] carried out the ozonation of wastewater containing ibuprofen and naproxen obtaining second order rate constants for both pharmaceutical drugs.

High efficiency of oxidation of the compounds of interest is ensured by choosing the most appropriate process; either ozonization or AOP [23,28,30]. Water treatment with ozone depends mainly on oxidation kinetics and the liquid–gas transfer phenomenon [20]; nonetheless, this research analyzes only the kinetics without discrediting the importance of the second term. Second order kinetic constants have been established for the ozonation of pharmaceutical compounds and steroids, where the direct reaction between ozone and a given emerging contaminant is first-order with respect to ozone and emerging contaminant [21,22,24,25,27–30]. Obtaining the second-order kinetics constants is important in ozonation processes especially for reactor design. For second order kinetic constants, rate constants greater than 1000 L/(mol s) and less than 1000 L/(mol s) can be distinguished. Experimental determination of rate constants more than 1000 L/(mol s) can be analyzed with sophisticated equipment such as stopped-flow and quenched-flow systems. However, those techniques are expensive and limited due to the difficulty of the spectrophotometric analysis of the oxidant (in this case, ozone), the analyte and the oxidation byproducts. There are spectral interferences between those chemical species, particularly with aromatic compounds identified in a near-UV wavelength; therefore an alternative is the *competitive kinetic model* [27–29]. For rate constants less than 1000 L/(mol s), the determination of the *absolute rate constant* is used. It can be performed by two pathways: (i) measuring analyte oxidation and maintaining high and constant ozone concentration and, (ii) measuring ozone consumption at different times while maintaining high analyte concentration under pseudo-first kinetic order [28].

Currently, several studies report oxidation kinetic constants between ozone and organic compounds by absolute and competitive kinetics methods without considering the stoichiometric coefficient for its determination. Nevertheless this coefficient might be important for a system of competitive chemical reactions [26,28]. The stoichiometric coefficients of E2, EE2, NPX, IBP and phenolate reported in the literature are absent for the process of ozonation. Some of the research carried out by Hoigné and Bader [31] report stoichiometric coefficients of 1 for olefin compounds and 2.5 mol O_3/mol for aromatic compounds (including sodium phenolate). Using an overestimated value of stoichiometric coefficient could affect the calculation of the volume of ozone gas required in the design of the reactor by a relative value of 1–1.5 times. Therefore, the use of experimental stoichiometric coefficients in obtaining oxidation kinetics is necessary.

The aim of this work was to determine the kinetic rate constant between ozone and the selected compounds using stoichiometric coefficients in order to obtain a mathematical model for evaluating oxidation kinetics, in particular the half-life of these compounds.

The emerging contaminants used in this work were chosen due to their presence in water bodies used for public consumption. These include the steroids, 17β-estradiol [E2], the most powerful steroid in mammals and 17α-ethinylestradiol [EE2], the most common estrogen used in combined oral contraceptives and pharmaceutical drugs, and naproxen [NPX] and ibuprofen [IBP], used in medical treatments as non-steroidal analgesic and anti-inflammatory medicaments [4,6,9,11,14]. The assessment of reaction kinetics of these compounds will inform a project focused on the design of chemical reactors to treat waters polluted with emerging contaminants.

Experimental

Standards and reagents

The standards of the steroids and pharmaceutical compounds, E2 (98%), EE2 (98%), NPX (98%) and IBP (98%) were acquired in powder form from Sigma–Aldrich and Fluka (USA). Competitive compound (sodium phenolate, 99%), potassium dihydrogen phosphate (KH_2PO_4) and tert-butyl alcohol were acquired from Sigma–Aldrich (USA). Reagent grade KH_2PO_4 (50 mM) without purification was used for the buffers and elution solutions. All solvents used in this investigation were HPLC grade. Acetonitrile was acquired from Tedia (USA), methanol from JT Baker (USA) and ethyl acetate was acquired from Burdick & Jackson (USA). Stock solutions of the selected compounds were prepared with deionized water (Millipore). Tert-butyl alcohol was used as scavenger of $OH^{\bullet}$ radical in the experiments (reagent grade) and without further purification.

The concentrations of the solutions containing steroids and pharmaceutical drugs were limited by their solubility in deionized water. Considering this limitation, the solubilities obtained in this study for E2, EE2 and NPX at pH 6 and 21 °C and for IBP at pH 5 and 21 °C are reported in Table 1. These values are similar to those reported in literature [32–34].

Ozone in liquid phase was obtained by saturating demineralized water with ozone gas produced by passing oxygen through a Pacific Ozone G11 ozone generator. The ozone generator was operated at $T = 20$ °C and produced 18 g/h of ozone gas with a concentration of 0.25 mmol/L in aqueous solution. Larger concentrations of aqueous solutions of ozone (1 mmol/L) were prepared at a temperature of 2 ± 0.5 °C, by means of a thermo-circulator and a bath [28].

Analytical methods

The method of extraction and analysis were based on previous work [35]. Analytical methods included solid phase extraction (SPE) to concentrate the emerging contaminants. Briefly, the C18 cartridges were conditioned before the extraction step using methanol, ethyl acetate, acetonitrile and water. For each kind of compound a different sequence was used. For steroids extraction, conditioning was done by passing 8 mL of acetonitrile through of the phase, then 7 mL of methanol and finally 5 mL of water. For the pharmaceuticals, 3 mL of ethyl acetate, and then 3 mL of methanol and 3 mL of water were used. The mobile phase for steroids separation was prepared by mixing acetonitrile and ultrapure water in a gradient elution. For pharmaceuticals, the mobile phase was prepared by mixing methanol and 50 mM KH_2PO_4 buffer. The chromatographic separations were performed using LiChrospher 100 RP-18, 5 μm, 250 mm × 4.6 mm i.d. column (Agilent Technologies, Waldbronn, Germany) for all compounds, eluted with the mobile phase at a flow rate of 1.0 mL/min. The extracted samples were analyzed by means of high performance liquid chromatography (HPLC) using Varian ProStar 7725 equipment. The detection was carried out with a Varian ProStar 230 diode array detector (DAD) (Walnut Creek, CA) using maximal absorption wavelengths (λ_{max}) of 197 nm for steroids and 220 nm for IBP and 230 nm for NPX, respectively [12,36]. The SPE–HPLC–DAD showed recovery efficiencies greater than 93% and this factor was applied to quantify the residual concentrations of the selected compounds during the ozonation process.