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Elimination of the iodinated contrast agent iohexol in water, wastewater and urine matrices by application of photo-Fenton and ultrasound advanced oxidation processes

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ABSTRACT

The use of ultrasound and photo-Fenton advanced oxidation processes has been investigated for the treatment of aquatic media contaminated with the iodinated contrast agent Iohexol. Iohexol is primarily introduced in the water network from hospitals discharging the urine of patients submitted to medical imaging. Treatment options have been considered for eliminating either highly concentrated solutions (up to 6 g L^{-1}) at the hospital source (in urine) or highly diluted (in the mg L^{-1} range) within municipal wastewater. Although the efficiency of ultrasound was shown to be low, complete Iohexol removal was achieved by application of photo-Fenton in diluted urine, Advantages and disadvantages of each option are discussed and the biodegradability of solutions subjected to the treatment has been evaluated.

Introduction

Iodinated X-ray contrast media (ICM) are pharmaceutical compounds widely used for medical imaging applications, with an estimated worldwide consumption of 3.5×10^6 kg $year^{-1}$[1]. They are administered to patients prior to X-ray imaging in order to better visualize internal organ structures. They subsequently pass through the body and are excreted, largely unchanged, with the patient's urine. Considering that an average Iodine dosage for typical screening applications is around 2.8 g, it corresponds to an amount of 6.2 g of Iohexol. Assuming normal urinary output (between 800 and 2000 mL 24 h) and high Iohexol clearance (in excess of 80% in 24 h), its concentration in urine can be roughly approximated between 3 and 6 g L^{-1}. However, they are not effectively degraded by conventional wastewater treatment processes [2–4], resulting in μg L^{-1} levels being detected in urban wastewater. One possible reason is poor adsorption and binding to activated sludge, as demonstrated in the case of diatrizoate and iopromide [5,6]. Although the toxicological impact of ICM and their degradation intermediates is unclear, the low toxicity of the parent compounds do not in any way mean that there is no risk associated with their transformation products [7]. To compensate for the limited biodegradability, advanced oxidation processes (AOPs) have been considered as an alternative. These are processes that are able to generate potent reactive oxygen species (ROS) capable of degrading recalcitrant organic contaminants [8] and have been studied as an option for treating many types of industrial and municipal wastewater [9,10]. Jeong et al. [11] have shown that they can also be efficient for the destruction of ICM. Among the studied processes were ozonation [12], UV/TiO_2 [13,14], UV/H_2O_2 [15], $sonolysis/O_3/H_2O_2$ [16], zero-valent iron [17], BDD electrode oxidation [18]. Different ICM were treated with the aforementioned processes such as iomeprol, iopromide, iohexol and diatrizoate. With varying degrees of success, most of these processes could eliminate the ICM, although mineralization was only partial. This work aims to apply the photo-Fenton and ultrasound AOPs (separately and in combination) for the treatment of the ICM Iohexol. To the best of our knowledge, these processes have never been used for ICM compounds.

Photo-Fenton (pF) is among the most widely-studied AOPs, based on the formation of reactive oxygen species following the oxidation of ferrous iron by hydrogen peroxide [19], as per Reaction (R1).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{\bullet} + OH^{-} \qquad (R1)$$

The aqua-Fe(III) species formed when $2.8 < pH < 3$ (mainly $Fe(H_2O)_5(OH)]^{2+}$ are photoactive in the UV–vis part of the solar spectrum, so that application of light can lead to Fe^{2+} regeneration [20], as per Reaction (R2).

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$$Fe(H_2O)_5(OH)]^{2+} + h\nu \rightarrow Fe^{2+} + HO^{\bullet} + H^{+} \qquad (R2)$$

Ultrasonic (US) treatment is based on acoustic cavitation phenomena occurring within a liquid medium by application of ultrasound frequencies. Cavitation bubbles are formed which are subjected to a series of compression and expansion cycles, before violently collapsing [21]. During the collapse, very high temperature and pressure gradients are generated locally which can lead to $HO^{\bullet}$ radical formation via the dissociation of water and/or H_2O_2 present in solution [22,23]. However, as $HO^{\bullet}$ is generated exclusively in the vicinity of the gaseous cavitation bubble, it preferentially reacts with hydrophobic compounds that are expected to be found at the bubble–liquid interface, Compounds found in the immediate vicinity may also be subjected to direct pyrolysis. Nevertheless, as stated below, there are possible advantages for the treatment of hydrophilic compounds, justifying the application of ultrasound.

Applying photo-Fenton in the context of municipal wastewater is a challenge, as pH adjustment and reagent consumption for such high volumes of water make it economically unfeasible. Additionally, one of the most significant problems when treating real water with photo-Fenton is the presence of inorganic salts (e.g., CO_3^{2-}, HCO_3^{-}, PO_4^{3-}) which act as either radical scavengers on $HO^{\bullet}$ or sequester iron and inhibit degradation. Application of ultrasound, admittedly costly itself, may be able to circumvent some of these problems. pH adjustment and iron addition are not necessary, and its partially pyrolytic action occurring at the bubble–liquid interface should not be as strongly affected by the presence of radical scavengers. Additionally, previous research [24] has shown that bicarbonate ions may enhance sonochemical degradation due to the generation of carbonate radicals. While $CO_3^{-\bullet}$ have a significantly lower redox potential than $HO^{\bullet}$ (1.78 in comparison with 2.31) [25], they have a half-life of about 3 ms, about 3000 times greater than that of $HO^{\bullet}$ [26]. They could therefore aid US degradation of hydrophilic compounds like ICM in natural waters.

However, as the primary source of ICM pollution is hospitals, it is of interest to examine the possibility of treatment before discharging into the urban sewer network. The costs associated with photo-Fenton or US would be comparatively low when applied at this scale. Establishing a protocol for the collection and treatment of patient urine following ICM administration could be feasible, provided the treatment leads to biodegradable byproducts.

The efficiency of ultrasound and/or photo-Fenton treatment options for the elimination of Iohexol has been evaluated in the following media: (1) distilled water (in order to understand the interactions between Iohexol and the process without complicating factors such as salts or organic matter) (2) municipal wastewater treatment plant (MWTP) effluent, (3) synthetic urine and (4) real urine.

Materials and methods

Reagents

Omnipaque Iohexol ($C_{19}H_{26}I_3N_3O_9$) solution (300 mg Iodine mL^{-1}) was acquired from GE Healthcare Inc. Sodium sulfate (Reacto Lab). Hydrogen peroxide 30% (w/v) (Fluka Chemicals). Sodium carbonate (99.8%, ACROS Organic). 99.5 percent NaCl acquired from ACROS Organic. $NaNO_3$ from Axon Lab Applichem. KCl from Fluka Chemicals. Urea (98%) from ABCR GmbH & CoKG). Creatinine from ABCR GmbH &CoKG. HPLC gradient grade methanol was from Fisher Scientific. Formic acid (98–100%) was from Merck. Titanium (IV) Oxysulfate and H_2SO_4 for pH control was from Fluka analytical. All the chemicals were used without further purification.

Analytical methods

Iohexol concentration was monitored by an Agilent 1100 series HPLC system equipped with a Nucleosil C18 column (28 cm, 4.6 mm, 5 μm particle size). The mobile phase consisted of 5% methanol—95% deionized water acidified by 0.1% (v/v) formic acid. Flow rate was 0.8 mL min^{-1}. Injection volume was 40 μL. The UV detector was set at a wavelength of 254 nm. Retention time was 15.6 min.

Total organic carbon and inorganic carbon were measured by a Shimadzu TOC-V_{CSN} analyzer equipped with an ASI-V automatic sampler.

pH was measured with a Mettler-Toledo SevenEasy pH meter. Iron was monitored with the ferrozine method. 5 mL of sample were filtered with a 0.2 mm nylon filter. 0.2 mL of acetate buffer at pH 4.65, 0.2 mL of hydroxylamine hydrochloride and 0.1 mL of 10 mM ferrozine solution were added. The absorbance of the resulting magenta-colored solution was measured at 562 nm.

H_2O_2 was monitored spectrophotometrically by adding 0.5 mL of Ti(IV) oxysulfate solution to 5 mL of sample and measuring the absorbance at 410 nm (DIN 38402H15). Due to color interference, H_2O_2 in urine experiments was followed by Merck Millipore Peroxide test strips.

Water matrices

Distilled water was acquired with use of a Merck Millipore Water purification system.

Wastewater was collected from the Lausanne municipal wastewater treatment plant (MWTP), downstream of the secondary biological treatment.

Synthetic urine was prepared with the following recipe: 9.7 g L^{-1} urea, 0.67 g L^{-1} creatinine, 1.17 g L^{-1} NaCl, 0.75 g L^{-1} KCl dissolved in distilled water [27].

Urine was provided by volunteers participating in this study. It was collected in a non-transparent container to protect light sensitive components and stored under refrigeration at 4–6 °C. All experiments were conducted within one day of collection.

Experimental set-up

A 400 mL cylindrical water-jacketed ultrasound reactor was used for the ultrasound experiments. US frequency was set at 297 kHz emitted from a piezoelectric disk (d = 4 cm) fixed on a Pyrex plate (d = 5 cm) at the bottom of the reactor.

The solar simulator used was an Atlas XLS model, providing constant illumination from a Xenon lamp. The lamp has a spectral distribution of about 0.5% of emitted photons at wavelengths shorter than 300 nm and 7% between 300 and 400 nm. For wavelengths between 400 and 800 nm the emission spectrum simulates solar radiation. 30 W m^{-2} of UV irradiance were used, which is a typical solar UV power during a sunny day. UV radiation was measured with a Kipp & Zonen CUV3 radiometer placed within the solar simulator.

Coupled ultrasound/ photo-Fenton experiments (US/pF) were carried out in a system of the above ultrasound reactor and a series of three 75 mL Pyrex glass vessels placed (225 mL illuminated volume) placed within the solar simulator (Fig. 1). Ultrasound was emitted at 297 kHz from a piezoelectric disk (4 cm diameter) fixed on a Pyrex plate (5 cm diameter) at the bottom of the reactor. Taking into account the tubing connecting the system components, the total volume was 700 mL. A peristaltic pump was used to recirculate the solution at a flow rate of 100 mL min^{-1}.

Zahn–Wellens biodegradability test was conducted following the OPPTS 835.3200 protocol, developed by the Swiss Federal laboratories of Material Science and Technology (EMPA). Activated sludge was acquired from the Lausanne MWTP, stored in a cool place and aerated with an air sparger until used.

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