Ultrasonics Sonochemistry 21 (2014) 1213–1221

Contents lists available at ScienceDirect

Ultrasonics Sonochemistry

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

Shear-induced hydrodynamic cavitation as a tool for pharmaceutical micropollutants removal from urban wastewater

Mojca Zupanc [a,b,c], Tina Kosjek [a], Martin Petkovšek [d], Matevž Dular [d], Boris Kompare [e], Brane Širok [d], Marjeta Stražar [f], Ester Heath [a,b,*]

[a] Jožef Stefan Institute, Department of Environmental Sciences, Ljubljana, Slovenia
[b] Jožef Stefan International Postgraduate School, Ljubljana, Slovenia
[c] Ecological Engineering Institute Ltd, Maribor, Slovenia
[d] Faculty of Mechanical Engineering, University of Ljubljana, Ljubljana, Slovenia
[e] Faculty of Civil and Geodetic Engineering, University of Ljubljana, Ljubljana, Slovenia
[f] JP CCN Domzale-Kamnik d.o.o., Domzale-Kamnik WWTP, Domzale, Slovenia

ARTICLE INFO

Article history:
Received 20 June 2013
Received in revised form 23 October 2013
Accepted 27 October 2013
Available online 9 November 2013

Keywords:
Pharmaceutical
Removal
Hydrodynamic cavitation
Wastewater

ABSTRACT

In this study, the removal of clofibric acid, ibuprofen, naproxen, ketoprofen, carbamazepine and diclofenac residues from wastewater, using a novel shear-induced cavitation generator has been systematically studied. The effects of temperature, cavitation time and H_2O_2 dose on removal efficiency were investigated. Optimisation (50 °C; 15 min; 340 mg L^{-1} of added H_2O_2) resulted in removal efficiencies of 47–86% in spiked deionised water samples. Treatment of actual wastewater effluents revealed that although matrix composition reduces removal efficiency, this effect can be compensated for by increasing H_2O_2 dose (3.4 g L^{-1}) and prolonging cavitation time (30 min). Hydrodynamic cavitation has also been investigated as either a pre- or a post-treatment step to biological treatment. The results revealed a higher overall removal efficiency of recalcitrant diclofenac and carbamazepine, when hydrodynamic cavitation was used prior to as compared to post biological treatment i.e., 54% and 67% as compared to 39% and 56%, respectively. This is an important finding since diclofenac is considered as a priority substance to be included in the EU Water Framework Directive.

1. Introduction

Pharmaceuticals are an important and indispensable element of modern life but parallel to the continuous rise in their consumption, is the increasing burden on the environment posed by pharmaceutical residues. The main sources of these residues are wastewaters that even after conventional (biological) treatment still contain pharmacologically active compounds. The European Commission recently issued a Proposal for a Directive (COM(2011)876) [1] amending the European Union Water Framework Directives 2000/60/EC [2] and 2008/105/EC [3], where amongst the proposed 15 additional priority substances, for the first time are pharmaceutical compounds, one of which is diclofenac.

Biological wastewater treatment has in many cases proven unsatisfactory for eliminating recalcitrant pharmaceuticals like carbamazepine [4,5], diclofenac [6] and clofibric acid [7]. To prevent these compounds entering the aquatic environment, where they can potentially induce toxic effects [8–10], alternative non-biological treatments are being investigated. For example various oxidation methods, collectively referred to as advanced oxidation processes (AOPs), have been proposed [11–16]. They are characterised by the *in situ* formation of highly oxidative hydroxyl (·OH) radicals, which with an oxidation potential of 2.80 V are capable of non-selectively attacking structurally diverse organic micropollutants with rate constants of 10^6–10^9 M^{-1} s^{-1} [11,17].

One such promising AOP is cavitation. The phenomenon of hydrodynamic cavitation (HC) occurs when a drop in pressure, due to velocity variations created by the geometry of a flowing system, results in the formation of bubbles (cavities) [12,18–19]. When these cavities implode, extreme energies that can drive chemical and mechanical effects are released. For instance,

Abbreviations: AOP, advanced oxidation process; HC, hydrodynamic cavitation; WW, wastewater; CLA, clofibric acid; IB, ibuprofen; NP, naproxen; KP, ketoprofen; DF, diclofenac; CBZ, carbamazepine; MTBSTFA, N-(t-butyldimetylsilyl)-N-methyltrifluoroacetamid; WWTP, wastewater treatment plant; HCG, hydrodynamic cavitation generator; DW, deionised water; IT, increasing temperature; CT, constant temperature; TOC, total organic carbon; HRT, hydraulic retention time; LOD, limit of detection; SPE, solid phase extraction; GC–MS, gas chromatography–mass spectrometry; EE, energy efficiency; EC, energy consumption; WFD, Water Framework Directive.

* Corresponding author at: Jožef Stefan Institute, Department of Environmental Sciences, Ljubljana, Slovenia. Tel.: +386 1 477 3584.
E-mail address: ester.heath@ijs.si (E. Heath).

1350-4177/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.ultsonch.2013.10.025

localised areas of high temperature and pressure ("hotspots") result in the homolytic cleavage of water molecules inside the cavities, generating ·OH radicals [18,20–21]. For these reasons the cavitation phenomenon has been the focus of scientific attention as a possible process for removing various organic compounds [20–22]. Breakdown during cavitation can occur at three locations: (i) in the gas phase i.e., inside the bubble, where thermolytic decomposition of volatile compounds and ·OH formation take place; (ii) at the gas–liquid interface, where degradation of non-volatile and hydrophobic compounds can occur, and (iii) in the liquid bulk phase, where degradation of non-volatile and hydrophilic compounds can take place [19,23]. Since only a small amount of radicals reach the liquid bulk phase, since they either react between themselves or with any oxidizable compound in the vicinity, removal of organic compounds depends on their chemical nature [19]. To intensify this process, the addition of external oxidants e.g. H_2O_2 as a source of radicals is also an option [22].

Published studies investigating HC as a tool for disinfection [24], cell disruption [25], preparation of stable nano-suspensions [26] and the removal of various organic compounds from wastewater (WW) [20,22,27–29] are available, but data about the efficiency of HC for the removal of pharmaceutical residues from WW are scarce. To our knowledge only two studies have been published on this topic; Brauetigam and co-workers [21] investigated the removal of carbamazepine by hydrodynamic and acoustic cavitation, while Zupanc and co-workers [30] studied the removal of clofibric acid, ibuprofen, naproxen, ketoprofen, carbamazepine and diclofenac by hydrodynamic cavitation alone.

Hydrodynamic cavitation is usually generated either by high-velocity passage of the liquid through a constriction such as an orifice plate or Venturi pipe, the use of high-speed homogenizers, devices based on the rotor–stator principle or by a rotating propeller blade [27,28]. This study is a continuation of this group's previous research where a Venturi constriction was used as a means of cavitation. In this study a novel design approach is taken that uses two facing counter-rotating discs to generate shear-induced HC. When compared to the Venturi geometry [30], cavitation in the present design extends over a larger volume and pressure recovers more rapidly, which leads to more aggressive cavitation resulting in the formation of more radicals [31].

In Zupanc and co-worker's study [30] the authors focused on the removal of clofibric acid (CLA), ibuprofen (IB), naproxen (NP), ketoprofen (KP), carbamazepine (CBZ) and diclofenac (DF) in deionised water and synthetic WW effluent using Venturi geometry to generate HC. In this study the removal of pharmaceuticals by shear-induced HC is investigated with the aim of improving the removal of pharmaceuticals from wastewaters, testing the efficiency of the system using real WW samples, and determining whether or not HC would be more efficient as a pre- or post-treatment to biological removal.

2. Materials and methods

2.1. Standards and chemicals

All six investigated compounds were provided either by Sigma–Aldrich (Steinheim, Germany) or Acros Organics (New Jersey, USA) and were of high purity (⩾97%). CDN Isotopes (Quebec, Canada) supplied isotopically labelled internal standards (±)-ibuprofen-d_3 (α-methyl-d_3), carbamazepine-d_{10} (rings-d_{10}) and (±)-ketoprofen (α-methyl-d_3). N-(t-butyldimetylsilyl)-N-methyltrifluoroacetamid (MTBSTFA), used for derivatisation, was supplied by Acros Organics (New Jersey, USA). Analytical grade solvents acetonitrile (preparation of standard solutions), methanol and ethyl acetate, were supplied by J.T. Baker (Deventer, the Netherlands). Analytical grade chemicals used were 37% hydrochloric acid (AppliChem, Darmstadt, Germany) and 30% hydrogen peroxide (Merck, Darmstadt, Germany). Potassium dichromate was purchased from Riedel-de-Haën, Hannover, Germany.

2.2. Hydrodynamic cavitation set-up

In this study an open-loop experimental set-up for shear-induced HC generation was designed (Fig. 1). An open-loop design was chosen in order to establish conditions comparable to an actual wastewater treatment plant (WWTP). Before each experiment, 2.5 L of sample was introduced into the feeding reservoir (1) and allowed to fill the hydrodynamic cavitation generator (HCG) chamber (2). Flow and pressure adjustments inside the HCG, were made possible by adjusting the valves (3) situated prior to and aft of the chamber. The static pressure inside the HCG was set to 100 kPa and monitored using a pressure transmitter (4). During the experiments the sample was circulated through the device using a small centrifugal pump (5). A cooling system was used to maintain a constant temperature (6) and monitored using a resistance temperature detector (Fluke Corporation, Washington, USA) (7). Installation of the cooling system reduced the flow rate in the system from approx. 10 to 3.5 L min^{-1}.

The HCG (Fig. 2) consists of two facing rotors (Fig. 2: R1 and R2) made of stainless steel with a 0.8 mm gap between them (Fig. 2: A). The housing of the HCG chamber is made of plexi-glass. The rotors have a diameter of 90 mm and are spun at 2800 rpm (reaching local velocities of up to 26 m s^{-1}) by two electrical motors (Fig. 2: EM1 and EM2). To avoid resonance, the rotors differ slightly in their design; rotor R1 has 12 grooves and teeth with an 8° inclination (Fig. 2: a), while R2 has 11 grooves and level angled teeth. The grooves on both rotors are 7 mm deep (Fig. 2: b) and 10 mm wide (Fig. 2: c). When a tooth and a groove of R1 are aligned with a tooth and a groove of R2 (Fig. 2: dashed rectangle in the centre of the figure), the gap between the opposing teeth resembles the Venturi geometry. By spinning the rotors in opposite directions, zones of low static pressure form, sufficient to induce the cavitation phenomenon (Fig. 2: B). Shear-induced cavitation is, therefore, a consequence of the opposite movement of the two shear layers that form between the two rotors.

Cavitation was visually observed using a high speed camera. In addition, high frequency pressure oscillations, measured with a hydrophone, enabled evaluation of the true extent and aggressiveness of cavitation. Design and operation of the HC chamber set-up are explained in greater detail elsewhere [32].

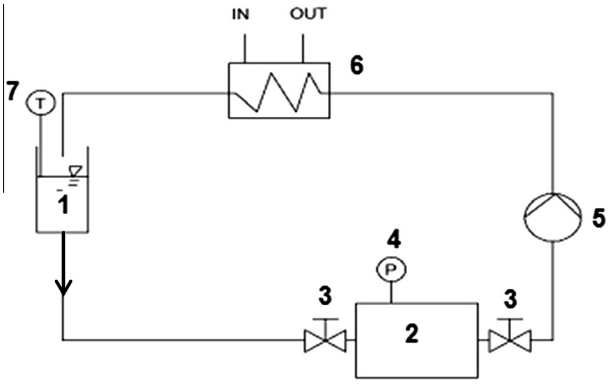

Fig. 1. Schematic presentation of the open-loop HC set-up (1: feeding reservoir, 2: HCG chamber, 3: control valves, 4: pressure transmitter, 5: centrifugal pump, 6: cooling system, and 7: resistance temperature detector).