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SHEAR-INDUCED HYDRODYNAMIC CAVITATION AS A TOOL FOR PHARMACEUTICAL MICROPOLLUTANTS REMOVAL FROM URBAN WASTEWATER

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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.

Highlights

- A novel shear-induced hydrodynamic cavitation is employed to study the removal of pharmaceuticals from wastewaters.
- Shear-induced cavitation resulted in higher removal efficiencies when compared to Venturi design.
- We obtained removal efficiencies of up to 86 % in deionised water and up to 79 % in wastewater effluent.
- Hydrodynamic cavitation as a pre-treatment removed the highest amounts of carbamazepine and diclofenac.

Keywords: Pharmaceutical; Removal; Hydrodynamic cavitation; Wastewater

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

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 characterized by the *in situ* formation of highly oxidative hydroxyl ($^{\bullet}OH$) 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, localised areas of high temperature and pressure ("hotspots") result in the homolytic cleavage of water molecules inside the cavities, generating $^{\bullet}OH$ 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 $^{\bullet}OH$ 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 wastewater 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 (Figure 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 L min^{-1} to 3.5 L min^{-1}.

***** Insert Figure 1 here *****

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, 7: resistance temperature detector).

The HCG (Figure 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.

***** Insert Figure 2 here *****

Fig. 2. Design of the HCG (R1: rotor with 12 grooves, R2: rotor with 11 grooves, A: 0.8 mm gap, EM1: electrical motor, EM2: electrical motor, a: 8° inclination, b: 7 mm depth, c: 10 mm width, B: cavitation zones).

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 is explained in greater detail elsewhere [32].

2.3 Experimental design

The efficiency of the HCG for removing pharmaceutical residues was evaluated in aqueous matrices differing in the amount and diversity of organic substances: deionised water (DW) and WWTP influents and effluents. The DW experiments were performed using a fixed concentration of pharmaceuticals (1 µg L^{-1}) and the efficiency of HC was investigated under both increasing temperature (IT) and constant temperature (CT). During the IT experiments, sample temperature rose due to the dissipation of hydraulic energy as heat. The final temperature was allowed to reach 68 °C before the experiments were halted. In the case of CT, the temperature of the sample was maintained at a desired level (± 1 °C) during the experiments using a heating/cooling system. The optimal operating temperature was then determined and all further experiments involving WW samples were performed under CT. HC was then integrated as a pre- and post-treatment step in a laboratory scale biological WW treatment. As a biological step, an attached-growth biomass process was chosen. A 4 L aerated laboratory scale bioreactor filled with Kaldnes K1 carriers, occupying approx. 30% of the working volume, was used. The design and operation of the bioreactor is described in full in [30]. In experiments involving WW samples besides pharmaceuticals removal efficiency additional parameters, important for WW treatment, were also measured. Mineralisation of organic compounds during experiments was determined in terms of total organic carbon (TOC) removal, and oxidation of nitrogen species was measured by determining concentrations of NH_4-N and NO_3-N before and after experiments. Table 1 gives an overview of the experimental conditions.

Table 1
Experimental conditions.

***** Insert Table 1 here *****

To confirm the hypothesis that removal of pharmaceuticals occurs only when a suitable combination of temperature, cavitation and H_2O_2 exists (Table 2), a series of control experiments were designed to:

- confirm that removal of pharmaceuticals does not occur only because of elevated temperature (Exp 6);

- investigate whether cavitation and elevated temperature are sufficient for pharmaceuticals removal (Exp 7);
- confirm that the formation of $^{\bullet}OH$ from H_2O_2 is due to the catalytic effect of HC and not just H_2O_2 addition and temperature elevation is mainly responsible for removal of pharmaceuticals (Exp 8);
- further investigate the role $^{\bullet}OH$ plays, 1-butanol was added to the cavitating sample to scavenge radicals formed during HC from H_2O_2 (Exp 9).

The results of control experiments were compared to results obtained with a combination of all three investigated operating parameters (Exp 10). In the case of Exp 6 and Exp 8 the longest investigated cavitation time was 30 minutes.

Table 2
Experimental conditions in control experiments.

***** Insert Table 2 here *****

2.4 Sample collection, analytical procedures and method validation

A series of WW samples were obtained from an urban WWTP, servicing a population of 360.000 and treating approx. 80.000 m^3 of WW per day both mechanically and biologically. Grab samples of WW influent and effluent were sampled without taking into account WWTP hydraulic retention time (HRT). After collection, the samples were transported at 4 °C to the laboratory and stored at -18 °C prior to analysis. The concentrations of IB, NP, KP, CBZ, and DF in the WW samples were between 360 to 6330 ng L^{-1} in the influent samples. Clofibric acid was not detected, which was expected, since its parent drugs clofibrate, etofibrate and etofylline clofibrate used as blood lipid regulators are not registered for use in Slovenia. Therefore CLA was spiked (approx. 1 µg L^{-1}) into the WW influent samples. In addition, since the concentrations of pharmaceuticals were below the limit of detection (LOD) in the WW effluent, a mixture of pharmaceuticals was added (approx. 1 µg L^{-1}).

Analysis was performed according to the method described by Zupanc and co-workers [30]. Briefly, samples were filtered (0.45 µm), acidified to pH 2-3 and then spiked with the internal standards. Oasis® HLB cartridges were used for solid phase extraction (SPE). MTBSTFA was used to derivatise the samples prior to analysis by gas chromatography-mass spectrometry (GC-MS).

Both TOC and nitrogen species (NH_4-N, NO_3-N) were determined using LCK 386, LCK 303, LCK 340 and LCK 339 cuvette tests and a DR/2800 spectrophotometer (Hach-Lange, Düsseldorf, Germany). Dissolved oxygen concentrations and temperature were measured simultaneously using a HQ30d probe (Hach, Düsseldorf, Germany) and pH was determined using a pH meter (Thermo Fisher Scientific, Waltham, USA). The amount of attached biomass and suspended solids in the bioreactor was determined according to the method described in Zupanc and co-workers [30].

Method validation parameters such as SPE efficiency, LOD and linearity were determined in DW and in synthetic WW effluent from the lab-scale bioreactor [30]. The SPE efficiency was performed at concentrations of 1 µg L^{-1} and ranged from 81 – 95 %. Limits of detection, calculated as 3-times the standard deviation of the baseline of six blank samples, ranged from 0.4 to 3.7 ng L^{-1}, while linearity was determined by regression analysis ($r^2 \geq 0.98$). Results are presented in Supplementary data Suppl.1.

3 RESULTS AND DISCUSSION

3.1 Removal of pharmaceuticals by HC in deionised water

3.1.1 Increasing temperature (IT) experiments

During these experiments the temperature of the samples during HCG operation increased from 20 to 68 °C within 26 min (Exp 1, Exp 2 and Exp 3) and from 20 to 55 °C within 15 min (Exp 4 and Exp 5). A temperature of 68 °C was chosen as the upper operating temperature limit to secure the durability of materials and seals used in the HCG chamber.

Figure 3 reveals the low removal of all the tested pharmaceuticals during 26 min of cavitation with no additional H_2O_2 (Exp 1), whereas ≥ 94 % removal was observed with the addition of 6.8 g L^{-1} H_2O_2 (Exp 2). No significant reduction in removal was observed in Exp 3 (26 min, 3.4 g L^{-1} of H_2O_2) and Exp 4 (15 min, 6.8 g L^{-1} of H_2O_2). Only when both the cavitation time and the amount of added H_2O_2 were reduced i.e., 15 min, 3.4 g L^{-1} of H_2O_2 (Exp 5), did the removal of the pharmaceuticals reduce significantly. The most significant decrease was observed in the case of CLA (> 50 percentage points). These results show that both cavitation time and H_2O_2 affect the removal of pharmaceuticals and confirm previous findings using the Venturi geometry [30]. In comparison the use of shear-induced cavitation (Exp 2) resulted in significantly higher and more consistent removal efficiencies for all tested pharmaceuticals. The main differences between the Venturi geometry and shear-induced cavitation were observed in the case of CLA, IB and KP, where removal was 42 – 49 percentage points higher. This is especially important in the case of biorecalcitrant CLA. The reasons for the improved removal efficiencies we believe are: (i) the volume where cavitation occurs is greater in the present design than in the Venturi geometry, hence pharmaceuticals are more likely to be exposed to aggressive cavitation conditions, and (ii) a rapid pressure recovery in the present design means that shear cavitation is significantly more aggressive than the cavitation occurring behind an obstruction resulting in higher local temperatures and in the amount of free radicals formed [31].

***** Insert Figure 3 here *****

Fig. 3: Removal of pharmaceuticals with increasing temperature (IT) experiments (n = number of experiments).

3.1.2 Constant temperature (CT) experiments

INFLUENCE OF THE OPERATING TEMPERATURE

The influence of temperature on the elimination of different organic compounds by HC has been investigated in numerous studies [20-22], [29]. Wang and Zang [29] found that an increase from 30 to 40 °C augmented the degradation of alachlor, while increasing the temperature to 60 °C resulted in decreased degradation. Patil and Gogate [22] concluded that increasing the temperature from 32 to 39 °C had no effect on methyl parathion degradation. Joshi and Gogate [20] observed a decrease in the degradation of dichlorvos when increasing the operating temperature from 31 to 39 °C. Contrary to our results, a study by Brautegam and co-workers [21] on CBZ degradation using a combination of hydrodynamic and acoustic cavitation found that the temperature of 25 °C resulted in the highest degradation, which then decreased slightly when the temperature was increased to 35 °C. All these studies suggest that an optimal operating temperature needs to be determined for a specific system in order to achieve the highest HC efficiency and that elimination depends on the investigated compound [12].

Therefore the effect of temperature on removal efficiency was investigated. Experiments were performed with a cavitation time of 15 min and a H_2O_2 dose of 3.4 g L^{-1} (Exp 5). Figure 4 shows how operating temperature affects the removal of the compounds tested. Where depicted with error bars, experiments were performed in triplicate. In all cases the standard deviation was < 8 %.

***** Insert Figure 4 here *****

Fig. 4. Effect of the operating temperature on removal of investigated pharmaceuticals with 3.4 g L^{-1} H_2O_2 dose and 15 min cavitation time (n = number of experiments).

According to literature data [12], lower bulk phase temperatures are generally favourable for the cavitation process to yield higher efficiencies, but this was not the case in this investigation. Experiments at 20 and 30 °C yielded the same results as those at 40 °C (data not shown), while at 40 to 50 °C removal efficiencies were higher (Figure 4). At 60 °C removal was further improved, with the exception of NP and KP, where no statistically significant difference was observed. Further increases in temperature (68 °C) resulted in a decrease in removal efficiency. According to Vassilakis and co-workers [33] and Wang and Zhang [29], increasing the temperature can be beneficial up to a certain point, but as water vapour fills the cavitation bubbles a cushioning effect on cavitation collapse predominates reducing the effectiveness of the HC. This explains why removal efficiency increases up to 60 °C, but then decreases with further temperature increase. This effect was most obvious in case of CLA, CBZ and DF. Even though the highest removal was achieved at 60 °C, we concluded that the difference between removal at 50 and 60 °C is not significant, therefore further testing was performed at 50 °C. At this temperature the removal efficiencies for CLA, IB, NP, KP, CBZ and DF were 48, 60, 83, 66, 72 and 82 %, respectively.

INFLUENCE OF OPERATING TIME

The effect of cavitation time was investigated at 5 min intervals from 5 to 30 min at the optimal operating temperature of 50 °C and 3.4 g L^{-1} of H_2O_2. The results (see Supplementary data Suppl. 2) show that for the majority of investigated pharmaceuticals no significant difference between tested values exists. A cavitation time of 15 min was selected for further experiments.

INFLUENCE OF H_2O_2 DOSE

It is reported that H_2O_2 dissociates into $^{\bullet}OH$ under cavitation conditions [20-21], [29] resulting in additional chemical oxidation, thus intensifying HC efficiency. To investigate this effect different doses of H_2O_2 (0 – 6.8 g L^{-1}) were tested. Figure 5 shows how increasing the H_2O_2 dose positively influences the removal of pharmaceuticals, but only up to a point. For most pharmaceuticals 1.7 g L^{-1} of H_2O_2 was optimal with the exception of DF, which required the addition of 3.4 g L^{-1} of H_2O_2. At the optimal dose removal efficiencies were from 55 – 93 %, but when the amount of added H_2O_2 was increased to 6.8 g L^{-1}, removal efficiency reduced for more than 15 percentage points. This is because H_2O_2, when in excess acts as a scavenger of $^{\bullet}OH$. These observations confirm those of Joshi and Gogate [20] and Zupanc and co-workers [30].

***** Insert Figure 5 here *****

Fig. 5. Effect of H_2O_2 dose on removal efficiency of investigated pharmaceuticals (1 µg L^{-1}) at 50 °C with a 15 min cavitation time (n = number of experiments).

Since the difference between the removal efficiency obtained at 0.34 and 1.7 g L^{-1} of H_2O_2 was not significant for most of the investigated compounds, a concentration of 0.34 g L^{-1} was selected. When compared to results achieved using the Venturi geometry [30], comparable

or higher removals of all pharmaceuticals with much lower H_2O_2 dose and reduced cavitation time (i.e. 0.34 g L^{-1} and 15 min) were obtained.

3.1.3 Control experiments

Figure 6 shows that pharmaceuticals are not removed at elevated temperatures only (Exp 6). Exp 7 shows that cavitation and elevated temperature do not yield the highest removals. Furthermore, Exp 8 and 9 show how $^{\bullet}OH$ radicals formed during cavitation and not just H_2O_2 and elevated temperature are primarily responsible for their removal. As evident from Figure 6, 1-butanol totally inhibited the removal of CBZ and DF. The removal of CLA, IB and KP did not exceed 9 %, whereas NP removal was 29 %. When these results are compared to results obtained in Exp 10, the hypothesis that only a combination of all three parameters i.e. temperature, cavitation and H_2O_2 yields the highest removal of investigated pharmaceuticals, is confirmed.

***** Insert Figure 6 here *****

Fig. 6: Removal of pharmaceuticals during control experiments (Exp 6 – Exp 9) compared to removals achieved under optimal working conditions (Exp 10).

3.2 Removal of pharmaceuticals by HC in real WW influent and effluent

The optimal operating temperature selected during DW experiments (50 °C) was used for these experiments. Heating WW prior to HC requires energy, thus raising costs of the treatment process, this energy can, to large extent, be recovered through heat exchangers. In this way not only the costs of the process are significantly reduced, but also the environmental permissible levels on energy dissipation by introducing the treated water into the watercourses can be reached. With fixed operating temperature different cavitation times and H_2O_2 doses were investigated. This course of experiments was selected due to the presence of different organic and inorganic compounds in WW samples, in higher amounts in WW influents and in lower amounts in WW effluents. The hypothesis is that the removal of investigated pharmaceuticals is influenced by these non-target compounds but can be to some extent diminished or even nullified by varying cavitation time and/or H_2O_2 dose. Based on the amount of non-target compounds, more experiments in WW influents were performed with 30 min cavitation time as opposed to WW effluents (15 min), while the H_2O_2 doses investigated were in both cases 0.34, 1.7, 3.4 and 6.8 g L^{-1}.

The results obtained for WW influents (see Supplementary data Suppl. 3: Exp A – G) showed different preferences of individual pharmaceuticals regarding operational conditions and give no firm conclusions to which one is more important either cavitation time or H_2O_2 addition in their removal. The only exception was CBZ, which was removed almost to the same extent regardless of the operational conditions. During the experiments it was also observed that oxidation of NH_4-N to NO_3-N becomes more pronounced, when H_2O_2 dose was augmented (see Supplementary data Suppl. 4). The WW influents are very complex matrices consisting of numerous organic and inorganic compounds and cavitation and addition of H_2O_2 can affect, beside pharmaceuticals, non-target compounds forming numerous new species. These can act either as sensitizers or radical scavengers and can influence pharmaceutical removal both positively or negatively, respectively.

In the case of WW effluents (Table 3: Exp H – N) removal of pharmaceuticals is increased by increasing both cavitation time and H_2O_2. The highest removal efficiencies (37 to 79 %) were obtained during 30 min cavitation time with 3.4 g L^{-1} of added H_2O_2 (Table 3, Exp N). The same trend is observed for TOC, where the highest removal efficiency was achieved using a cavitation time of 30 min (Table 3, Exp M and N). During these experiments a slight increase

in NO_3-N was observed (see Supplementary data Suppl. 4), which was a result of the oxidation of organic N compounds present in the sample and not NH_4-N which was not present. By comparing the results obtained for WW effluents to those obtained in DW under CT (Table 3, Exp K and N) during 15 min of cavitation, in the case of effluent the removal efficiency is lower, which means that non-target constituents still hinder the removal of pharmaceuticals which becomes negligible for most pharmaceuticals within 30 min cavitation time. When compared to the results obtained with Venturi geometry [30] and synthetic wastewater effluents, the removals of all pharmaceuticals are much higher (from 19 – 48 percentage points) with the same cavitation time and lower H_2O_2 dose.

Table 3

Removal of selected pharmaceuticals by HC in WW effluents under different operational conditions.

***** Insert Table 3 here *****

A comparison between removals (%) achieved in WW influents and WW effluents (Exp F and N) can be made in the case of CLA, IB, CBZ and DF. We see that CLA and CBZ were removed to the same extent regardless of the matrix, while a matrix effect was more pronounced in the case of IB and DF. It can be assumed that species that compete for free radicals and are in higher concentrations present in WW influent inhibit removal of these two compounds. For NP and KP the removal efficiencies (%) achieved in WW influents and WW effluents (Exp F and N) cannot be compared in the same way since their concentrations were much higher in WW influents. Higher initial concentrations of NP and KP result in lower removal efficiencies (%), but in total a higher amount in nmol is removed after 30 min. This agrees with the results of other studies [21], [29]. The reasoning behind this is that by augmenting the amount of the compound in the sample, the probability that it encounters reactive radicals, responsible for its removal is increased [21], [29]. Based on the physico-chemical properties of pharmaceuticals (see Supplementary data Suppl. 5), it can be assumed that the investigated pharmaceuticals are mostly found in the liquid bulk phase and are not in close proximity of the radicals that mostly appear at the gas-liquid interface. When the concentration of NP and KP is increased, more molecules can encounter radicals. Thus the removal efficiency tends to zero, when the concentration of investigated compound falls below a certain value, since the probability to encounter radicals diminishes. In this case removal efficiency could be increased by extending the cavitation time.

3.3 Estimation of energy efficiency in WW samples

Economical feasibility i.e., the energy efficiency of investigated HC process was estimated for WW influents and effluents (see Supplementary data Suppl. 3: Exp. A, C, F; and Table 3: Exp. H, J, N). It was calculated as the ratio between the amount of the removed pharmaceuticals and the electrical energy consumed during HC, similar to the method proposed by Braeutigam and co-workers [21], using Eq.1.

$$EE = \frac{\sum Nr}{EC} \quad (1)$$

where, EE is the energy efficiency, ∑Nr the amount of pharmaceuticals (nmol) removed from 2.5 L of WW sample during HC experiments and EC is energy consumption (kJ). For calculation of the EC the sum of power needed to drive the electrical motors (2 x 500 W) and the circulation pump (80 W) was multiplied by the cavitation time (s). The sum of power needed to drive the electrical motors was 1.08 kJ s^{-1}.

Table 4
Estimation of energy efficiency of the HC process in 2.5 L of WW samples.

***** Insert Table 4 here *****

Table 4 shows higher amounts of removed pharmaceuticals (∑Nr) in WW influents compared to WW effluents under the same operational conditions. This difference can be attributed to the removal of higher amounts of NP and KP present in considerably higher concentrations (see Supplementary data Suppl. 3) in the WW influents. The highest EE was achieved within 5 min cavitation in influent and effluent samples but with the lowest overall removal of pharmaceuticals and/or TOC. For WW influents the highest removal of pharmaceuticals was achieved with 15 min cavitation time and 1.7 g L^{-1} H_2O_2. In the case of WW effluents it can be observed that pharmaceutical and TOC removal increases with prolonged cavitation (from 15 to 30 min) at the expense of EE. The highest removal of pharmaceuticals was achieved with a 30 min cavitation time and 3.4 g L^{-1}, which is in accordance with the highest removals presented above (Table 3). Almost the same amounts of pharmaceuticals in WW influents and effluents were obtained during 30 min of cavitation and 3.4 g L^{-1} of H_2O_2 mostly because of higher removals of IB, CBZ and DF in the WW effluents.

3.4 Removal of pharmaceuticals by HC integrated as a pre- or post-treatment step to biological treatment

Nowadays, numerous photochemical and chemical advanced treatment techniques (i.e. photolysis, ozonation and AOPs) that could be used to upgrade conventional WW treatment are being investigated. Advanced oxidation processes integrated as a pre-treatment step to biological treatment are generally used for enhancing biodegradability and/or to reduce the toxicity of WW influent, while when integrated as a post-treatment step they serve as a means of removing of bio-recalcitrant compounds [34]. For example, De la Cruz and co-workers [16] investigated the efficiency of direct photolysis (10 min) as a post-treatment step to biological treatment and observed removals of IB, NP, KP, CBZ and DF ranging from 23 – 100 % and also reported on their complete removal when they combined UV with the addition of H_2O_2 (50 mg L^{-1}, 30 min). Ternes and co-workers [35] investigated the efficiency of ozonation as a post-treatment step and observed removal efficiencies of >50 % for CLA, IB, NP, CBZ and DF (10 mg L^{-1} O_3, 18 min). Also, high removal efficiencies of the investigated pharmaceuticals were reported for other AOPs (i.e. photo-Fenton process and O_3/H_2O_2) when they were used as a post-treatment to biological process [16], [36]. All these techniques have shown great potential to remove pharmaceuticals when used in the post-treatment step. However, in order to fully evaluate their potential and the possibility to incorporate them into WW treatment, more studies are needed and scaled-up experiments are warranted.

In this study, the aim of was to test the efficiency of HC as a pre- and post-treatment step to biological treatment to improve the overall removal of pharmaceuticals. Attached-growth (biofilm) process was used for biological treatment step. Based on the highest EE determined for WW influents (Table 4), 1.7 g L^{-1} of H_2O_2 and a 15 min cavitation time were used.

Figure 7 gives a summary of the two experimental setups, i.e. the first is when HC is used as a pre-treatment (PRE) and as post-treatment step (POST) to a biofilm treatment process. Having the results of both setups depicted together, revealed several interesting relationships. First, with the exception of CLA and IB, the PRE setup gives higher removal than the POST setup. Second, when HC was integrated as a pre-treatment, biological removal of pharmaceuticals was smaller than during the POST setup. In the case of CLA and CBZ, no removal was observed during the biological treatment. It was expected that HC will begin to decompose the pharmaceutical residues making them more amenable to biological

degradation. The explanation for this surprising outcome may be that the HC actually created degradation products more resistant to biological degradation. Finally, the POST setup, is more efficient at removing CLA and IB, where for IB it seems that the bio step is extremely efficient (90 %). When these results are compared to those achieved using only cavitation (see Supplementary data Suppl. 3) overall removal of IB was increased. Clearly, this study show evidence, for the investigated pharmaceuticals, of distinctive degradation pathways and we thus cannot unanimously give advantage to any of the tested setups.

During PRE and POST sequence experiments, nitrogen species, TOC, DO and biomass concentration were also measured (see Supplementary data Suppl. 6). In the PRE sequence, chemical oxidation of NH_4-N to NO_3-N occurred while during the POST sequence, oxidation of NH_4-N occurred only during the biological treatment step. The amount of total TOC removed during both sequences was comparable (80 %; see Supplementary data Suppl. 6). When SHC was used as a post-treatment, residual H_2O_2 could affect the consecutive biofilm process. Based on the parameters measured during the biofilm process (see Supplementary data Suppl. 6), H_2O_2 did not affect the biofilm process.

***** Insert Figure 7 here *****

Fig. 7. Removal of pharmaceuticals with HC integrated as a pre-treatment (PRE) and post-treatment step (POST) to biological step.

Overall, the results were not as expected. Initially, it was hypothesised that AOP used as a pre-treatment should (without exemption) enhance both removal of recalcitrant target compounds during the HC step and their biodegradability. The results (Figure 7) did not confirm this hypothesis as low removal efficiencies were observed for most test compounds in the second, biological treatment step (exception is IB). Still, significant combined (overall) removals of pharmaceuticals during PRE hydrodynamic cavitation were confirmed (20 – 65 %). The overall treatment efficiency of hydrodynamic cavitation and biological treatment show that for NP, KP, CBZ, and DF this combination is better than the POST sequence. The second hypothesis that AOP used as a post-treatment should further enhance removal of bio-recalcitrant compounds was confirmed for all pharmaceuticals. When HC was used as pre-treatment (Figure 7) it yielded higher overall removal efficiencies in case of NP, KP, CBZ and DF and thus for these compounds the pre-treatment sequence is more efficient. Furthermore, based on the TOC results (see Supplementary data Suppl. 6) HC reduces TOC for >45 % in 15 min with addition of 1700 mg L^{-1} of H_2O_2, whereas, it takes 48 hours to reach >65 % TOC reduction with biological treatment. This information is very important if HC is to be considered as an industrial technology. The results show that HC with the addition of H_2O_2 is worthy of further investigation as a technology applicable for advanced WW treatment.

CONCLUSIONS

This study reveals that the removal of target organic compounds i.e. pharmaceuticals with hydrodynamic cavitation in different aqueous matrices depends on several parameters. The design of the hydrodynamic cavitation device, operating temperature, cavitation time, H_2O_2 dose, matrix composition and chemical properties of the compounds under investigation all play an important role in the removal efficiency. The aggressiveness of hydrodynamic cavitation, which is related to the design of the cavitating device, influences the amount of free radicals formed and consequently the removal efficiency. Shear-induced cavitation, investigated in this study, proved to be more aggressive and led to higher removals of pharmaceuticals in deionised water and real wastewater samples than the cavitation formed using a Venturi constriction. Increasing the operating temperature also proved advantageous for removal but only up to a certain point. A temperature of 50 °C was selected as optimal.

Cavitation time proved an important operating parameter only in the case of real wastewater samples (30 min) while H_2O_2 addition enhanced the efficiency of cavitation in both deionised water and wastewater effluents (0.34 g L^{-1} and 3.4 g L^{-1}, respectively). Matrix composition effect on removal efficiency was confirmed for wastewater influents and effluents. Different removal efficiencies under identical operating parameters proved that the individual chemical properties of the compounds also play an important role. Hydrodynamic cavitation is more effective as a pre-treatment step to biological treatment for most investigated pharmaceuticals and was the most pronounced in the case of carbamazepine and diclofenac.

The continued redesign of the hydrodynamic cavitation device and a better understanding of how different parameters affect the removal of pharmaceuticals will lead to even more efficient treatment process thus making hydrodynamic cavitation worthy of further investigation. Since monitoring of diclofenac, a WFD priority pollutant candidate, in surface waters will likely become obligatory in the near future, one can anticipate that studies investigating improved removal of bio-recalcitrant pharmaceuticals will become very important. Hydrodynamic cavitation and subsequent biological treatment (or vice-versa) may be a good option.

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[2] Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2000:327:0001:0001:EN:PDF
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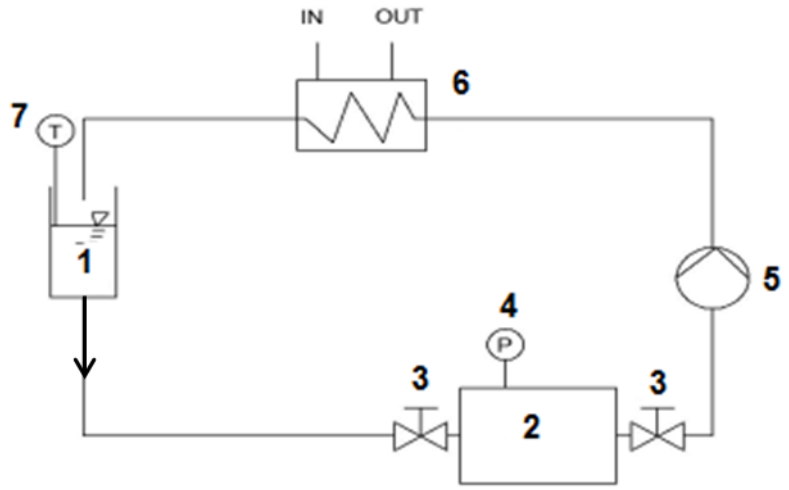

Fig. 1. Schematic presentation of the open loop HC set-up (1: feeding reservoir, 2: HCG chamber, 3: control valves, 4: pressure transmitter, 5: centrifugal pump, 6: cooling system, 7: resistance temperature detector).

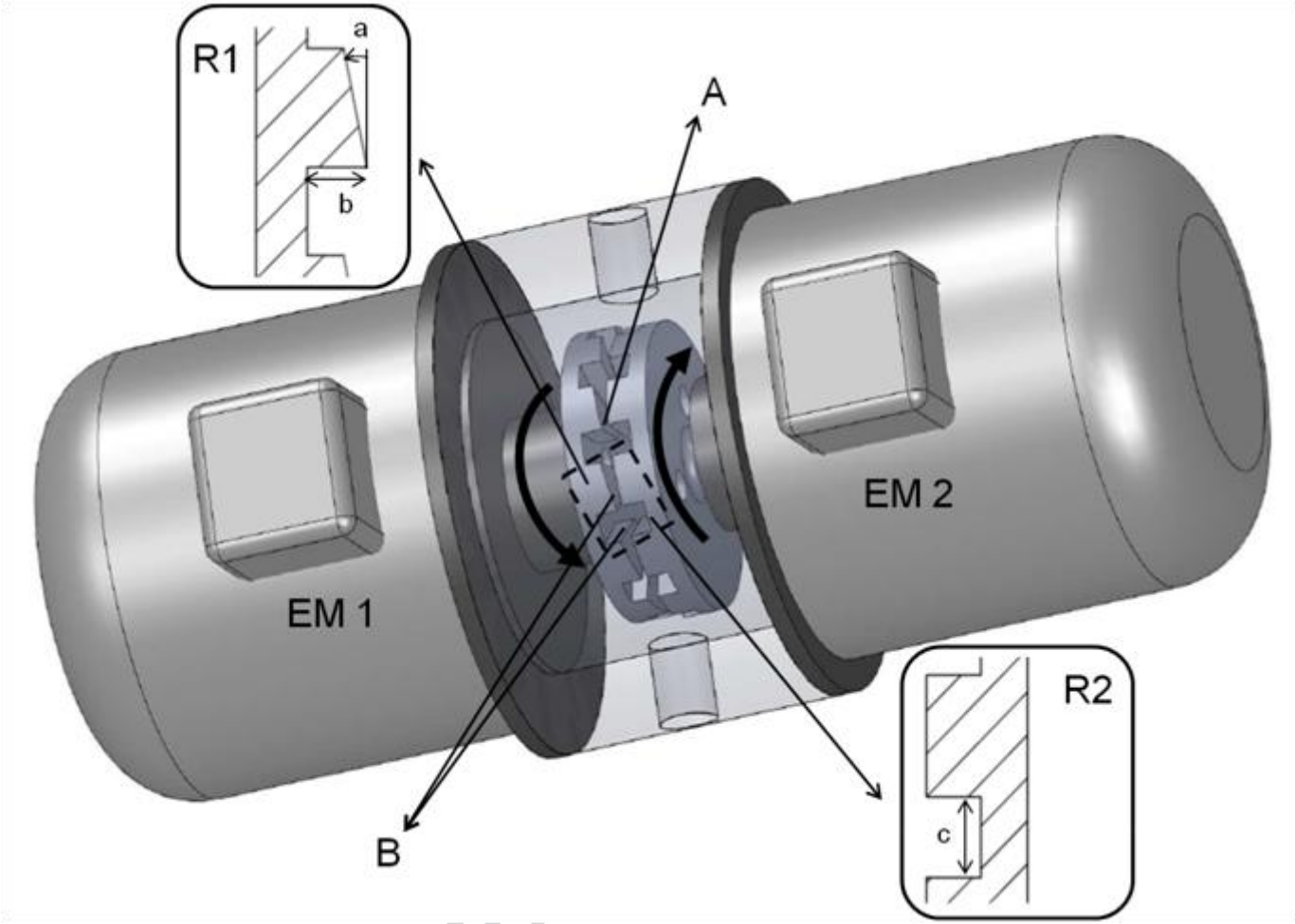

Fig. 2. Design of the HCG (R1: rotor with 12 grooves, R2: rotor with 11 grooves, A: 0.8 mm gap, EM1: electrical motor, EM2: electrical motor, a: 8° inclination, b: 7 mm depth, c: 10 mm width, B: cavitation zones).

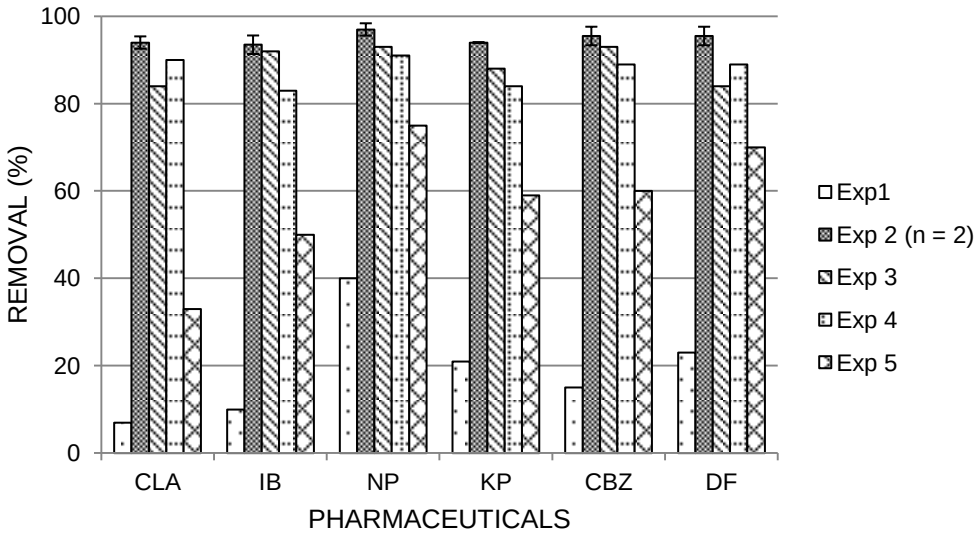

Fig. 3: Removal of pharmaceuticals with increasing temperature (IT) experiments (n = number of experiments).

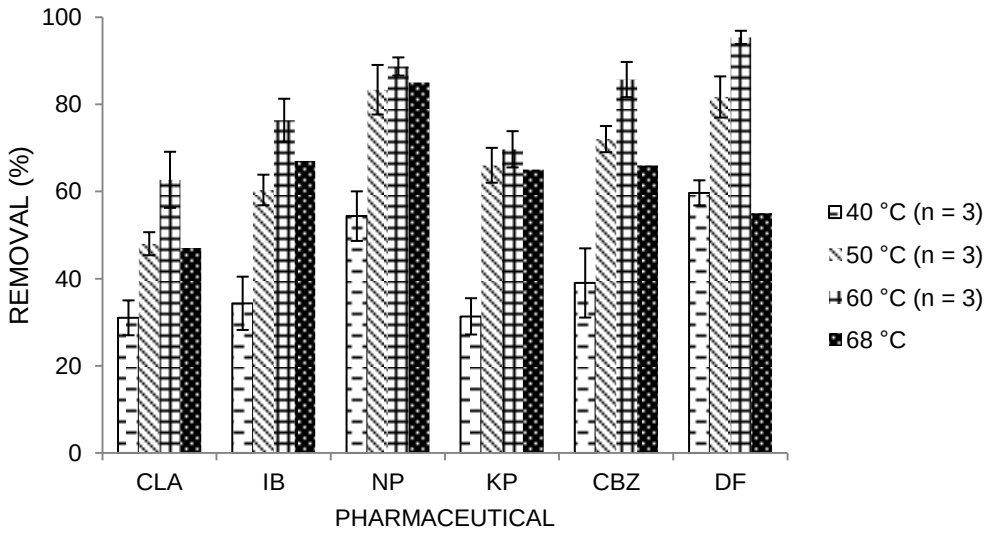

Fig. 4. Effect of the operating temperature on removal of investigated pharmaceuticals with 3.4 g L^{-1} H_2O_2 dose and 15 min cavitation time (n = number of experiments).

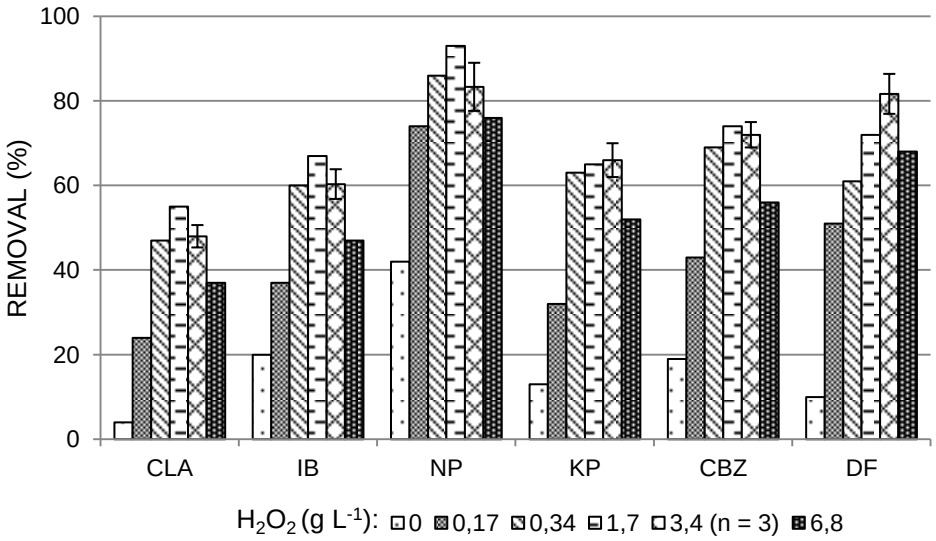

Fig. 5. Effect of H_2O_2 dose on removal efficiency of investigated pharmaceuticals (1 µg L^{-1}) with 15 min cavitation time and 50 °C (n = number of experiments).

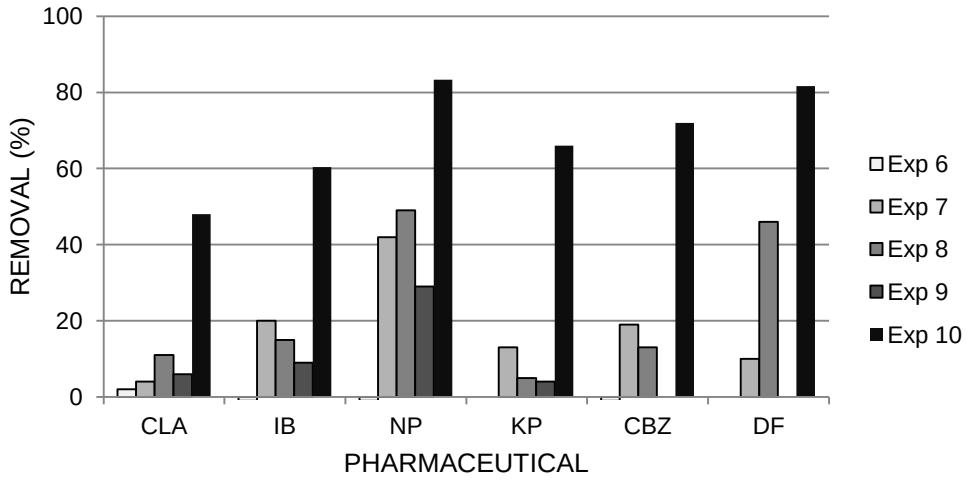

Fig. 6: Removal of pharmaceuticals during control experiments (Exp 6 – Exp 9) compared to removals achieved under optimal working conditions (Exp 10).

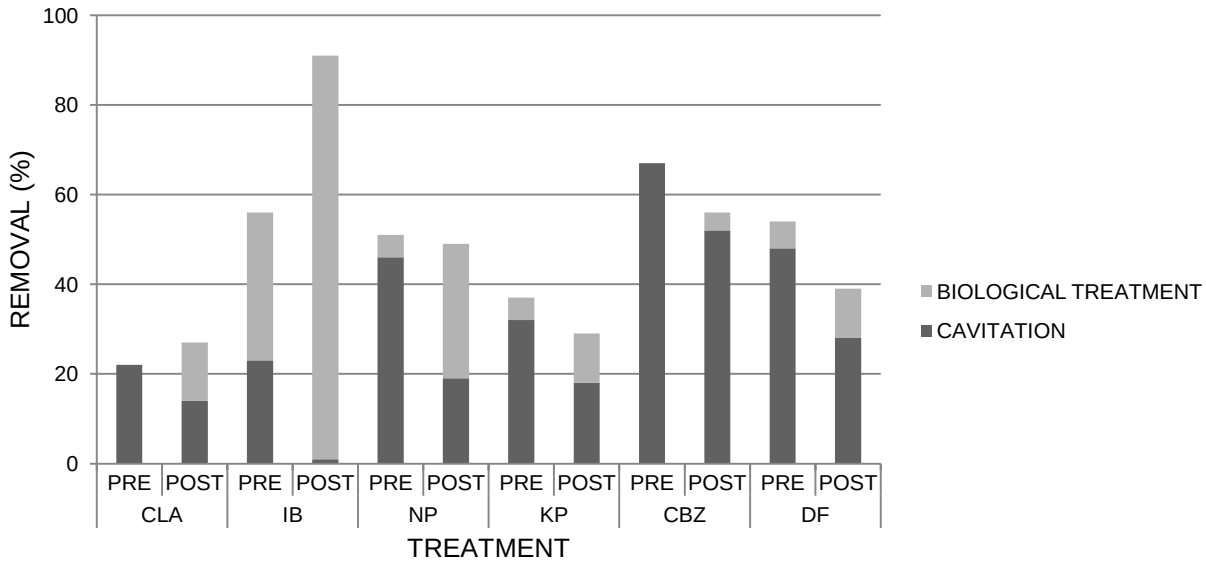

Fig. 7. Removal of pharmaceuticals with HC integrated as a pre-treatment (PRE) and post-treatment step (POST) to biological step.

Table 1
Experimental conditions.

	HC		
variable / matrix	TEMPERATURE (°C)	CAVITATION TIME (min)	$c(H_2O_2)$ (g L^{-1}) Exp. No/letter (in brackets)
DW	**IT:** 20-68	26	0 (1); 3.4 (3); 6.8 (2)
	IT: 20-55	15	3.4 (5); 6.8 (4)
	CT: 40, 50, 60, 68	15	3.4
	CT: 50	5 - 30 (5 min interval)	3.4
	CT: 50	15	0; 0.17; 0.34; 1.7; 3.4; 6.8
WW infl	**CT**: 50	5	3.4 (A)
		15	1.7 (B); 3.4(C)
		30	0.34 (D); 1.7 (E); 3.4 (F); 6.8 (G)
WW effl		5	3.4 (H)
		15	0.34 (I); 1.7 (J); 3.4 (K); 6.8 (L)
		30	1.7 (M); 3.4 (N)
WW infl	HC → BIOLOGICAL TREATMENT (48 h)		
	CT: 50	15	1.7
WW infl	BIOLOGICAL TREATMENT (48 h) → HC		
	CT: 50	15	1.7

Table 2
Experimental conditions in control experiments.

Exp No.	cavitation	temperature (°C)	H_2O_2 (g L^{-1})	time (min)	1-butanol (g L^{-1})
Exp 6[a]	-	50	-	30	-
Exp 7	yes	50	-	15	-
Exp 8[a]	-	50	6.8	30	-
Exp 9	yes	20	3.4	15	3.3
Exp 10	yes	50	3.4	15	-

[a] performed in a 5 L beaker on a magnetic stirrer

Table 3
Removal of selected pharmaceuticals by HC in WW effluents under different operational conditions.

				concentrations before HC						
				ng L^{-1}						mg L^{-1}
				CLA	IB	NP	KP	CBZ	DF	TOC
				1192	1186	981	933	1371	1190	100
	Exp	time (min)	H_2O_2 (g L^{-1})	REMOVAL (%)						
effluent	H	5	3.4	13	7	45	12	9	36	19
	I	15	0.34	4	0	40	2	1	26	17
	J	15	1.7	10	3	40	9	6	31	37
	K	15	3.4	15/48[a]	28/60[a]	44/83[a]	24/66[a]	24/72[a]	45/82[a]	28
	L	15	6.8	5	11	51	24	12	43	33
	M	30	1.7	18	24	58	30	26	55	53
	N	30	3.4	37/35[a]	54/60[a]	74/93[a]	55/58[a]	62/70[a]	79/79[a]	40

[a] removal determined in DW under identical experimental conditions

Table 4
Estimation of energy efficiency of the HC process in 2.5 L of WW samples.

operational conditions			WW influent				WW effluent			
time (min)	H_2O_2 (g L^{-1})	EC (kJ)	$\sum N_i$ (nmol)	$\sum N_r$ (nmol)	TOC_r (%)	EE (nmol kJ^{-1})	$\sum N_i$ (nmol)	$\sum N_r$ (nmol)	TOC_r (%)	EE (nmol kJ^{-1})
15	1.7	927	147	**52**	**59**	**0.053**	73	11	37	0.011
30				43	54	0.022		24	53	0.012
5	3.4	324		35	50	0.110		14	19	0.042
15		927		46	64	0.047		21	28	0.022
30		1944		47	67	0.024		**42**	**40**	**0.022**

where $\sum N_i$ = sum of amounts (nmol) of all investigated pharmaceuticals in 2.5 L sample before HC; $\sum N_r$ = sum of amounts (nmol) of all investigated pharmaceuticals removed; TOC_r = TOC removal; EE = energy efficiency

Highlights

- A novel shear-induced hydrodynamic cavitation is employed to study the removal of pharmaceuticals from wastewaters.
- Removal efficiency when using shear-induced cavitation increases up to 49 percentage points when compared to a cavitating Venturi.
- Removal efficiencies of the investigated pharmaceuticals are up to 86 % in deionised water and up to 79 % in wastewater effluent.
- Hydrodynamic cavitation as a pre-treatment yields higher removal of carbamazepine and diclofenac than when applied as a post-treatment.