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Ultrasound assisted destruction of estrogen hormones in aqueous solution: Effect of power density, power intensity and reactor configuration

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Abstract

There are many reports documenting the adverse effects, such as feminization of fish, of estrogen hormones in the environment. One of the major sources of these compounds is from municipal wastewater effluents. The biological processes at municipal wastewater treatment plants cannot completely remove these compounds. This paper discusses the use of ultrasound to destroy estrogen compounds in water. The study examines the effect of ultrasound power density and power intensity on the destruction of various estrogen compounds which include: 17α-estradiol, 17β-estradiol, estrone, estriol, equilin, 17α-dihydroequilin, 17α-ethinyl estradiol and norgestrel. These tests were conducted in single component batch and flow through reactors using 0.6, 2 and 4 kW ultrasound sources. The sonolysis process produced 80–90% destruction of individual estrogens at initial concentration of 10 μg/L within 40–60 min of contact time. First order rate constants for the individual compounds under different conditions are presented. The estrogen degradation rates increase with increase in power intensity. However, the energy efficiency of the reactor was higher at lower power density. The 4 kW ultrasound reactor was more energy efficient compared to the 0.6 and 2 kW sonicators.

Keywords: Ultrasound; Sonication; Sonolysis; Estrogens; Hormones

1. Introduction

The occurrence of estrogen hormones in natural systems like surface water, soil and sediment has become a subject of significant concern. There are many sources of estrogenic pollution which include effluent from municipal and industrial wastewater treatment plants, livestock wastes, biosolids, septic tanks and landfills. The complete removal of estrogens does not occur in municipal wastewater treatment plants, and which then end up in the natural system [1,2]. The presence of estrogens in the effluent of sewage treatment plants has been reported in many countries [3–6]. The most reported problem from the presence of estrogens in natural waters is the feminization of male fish. Vitellogenin induction in fish has been used as a biomarker for endocrine disruptors [7–10]. Estrogenic hormones have also been linked to lower sperm counts in adult males and an increase of cancer [11,12]. The accumulation of estrogens in the environment could pose risk to human health in the long run. It is therefore important to investigate and develop effective treatment technologies to destroy estrogens in wastewater. There are papers that investigate estrogen removal using techniques such as ozonation [13,14], chlorine application [15], activated carbon adsorption [16] and membrane bioreactors.

The sonolysis process could be used for the effective destruction of estrogen compounds present in aqueous solutions. Sonication is a process wherein ultrasound waves are irradiated into a liquid medium to destroy the contaminants. The high acoustic energy generates physical and chemical reactions that can degrade organic chemicals present in the liquid. These reactions result from the creation and violent collapse of cavitation bubbles. These cavitation bubbles, produced acoustically in a matter of microseconds upon implosion result in extreme conditions (5000 K and 500 bar in the gaseous phase [17]) at microscopic points in the solution. Cavitation produces high mechanical shear stresses that are exerted on the substances in the liquid. Thermal breakdown of volatile substances occurs in the gaseous phase and in the interfacial region [18]. Sonochemical reactions are also caused by the generation of highly

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reactive radicals, such as hydroxyl radical, which cause chemical transformation in the bulk solution [19].

In this paper, we investigate the destruction of certain natural and synthetic estrogen hormones with ultrasound. The sonication process can be influenced by several parameters such as ultrasound power density, power intensity and reactor configuration, amongst others. It is reported that reaction kinetics increases with increase in power, power density and intensity [20–23]. The type of reactor used can influence the imparted energy to the solution and, hence, the power density (kW/L). The reactor geometry can influence the effective zone of reaction and the resulting reaction kinetics. We selected three different power sources: 0.6, 2 and 4 kW to examine the impact of different power intensities and power densities on estrogen degradation. Sonication of single-component estrogen compounds in aqueous solution was carried out in batch and flow through reactors. The degradation rates of the individual estrogens were compared for the different reactors.

2. Experimental methods

2.1. Materials

Estrogen hormones were obtained from Sigma–Aldrich. The hormones used were: 17α-estradiol (98%), 17β-estradiol (97.1%), estrone (100%), estriol (100%), equilin (99.9%), 17α-dihydroequilin (99.4%), 17α-ethinyl estradiol (99.1%), norgestrel (100%) and 3-*O*-methyl estrone (internal standard, 98%). The solvent (HPLC grade), i.e. methanol was obtained from Fisher Scientific. Varian Bond 3 mL/500 mg solid phase extraction (SPE) cartridge used was from Varian Inc.

2.2. Ultrasound power sources

The ultrasonic irradiation of the aqueous solutions was performed using three different ultrasound systems at 100% amplitude setting. These power sources were of 0.6, 2 and 4 kW. Table 1 shows the power characteristics associated with the three sonicators. The power output from the sonicators was displayed on the control unit of the sonicator. The 0.6 kW sonication unit had a probe diameter of 4.5 cm (Sonics and materials, USA) that was operated at 20 kHz. The 0.6 kW reactor was setup for batch sonication experiments with a 200 mL reactor volume. The 2 kW (UIP2000) sonication unit had a probe diameter of 5.5 cm which operated at 20 kHz and was setup for batch sonication experiments with a 600 mL reactor volume. The 4 kW (UIP4000) sonication unit had an ultrasound probe diameter of 8 cm which operated at 20 kHz. The 4 kW system was setup as a continuous flow reactor and had reactor volume of 3 L. During the sonication process, the ultrasound probes were completely immersed in the solution.

Table 1
Select operational parameters of 0.6, 2 and 4 kW ultrasound reactors

Parameter	0.6 kW reactor	2 kW reactor	4 kW reactor
Power output (kW)	0.25	0.32	1.3
Reactor volume (L)	0.2	0.6	3
Power density (kW/L)	1.25	0.53	0.43
Power intensity (kW/m^2)	157	135	259
Reactor type	Batch	Batch	Continuous flow

2.3. Experimental procedure

All the glassware for the experiments was silanized prior to use [25]. Aqueous solutions of single component (individual) estrogens of 10 μg/L were prepared in milli-Q water. 200 and 600 mL sample volumes were taken for batch sonication experiments for the 0.6 and 2 kW sonicators in Pyrex glass vessels, respectively. The 4 kW ultrasound reactor had a variable flow-rate positive displacement pump (having a maximum flow-rate of 225 mL/min). The volumetric flow-rate of the pump was changed to obtain different retention times of the solution inside the 4 kW sonication unit. Prior to collecting effluent samples for analysis, the 4 kW reactor was operated for at least two retention times to achieve steady state. Two hundred millilitre of the sonicated solution was collected in silanized amber glass bottles for analysis. The analysis was performed in duplicate and the data reported in this paper was an average of these analyses.

2.4. Analysis of samples

The samples were analyzed as follows:

Solid phase extraction—200 mL of the sonicated sample was passed through the Bond Elute C-18 SPE column at a flow rate of 5 mL/min. A fixed amount of internal standard (3-*O*-methyl estrone) was added to the samples prior to extraction. Before loading, the SPE cartridges were activated with 3 mL methanol and then rinsed with 3 mL of milli-Q water. After the sample was passed through the SPE column, the column was rinsed with milli-Q water and then eluted with 3 mL of methanol. The methanol eluent was collected in a silanized test tube and was dried in a Genevac centrifugal evaporator at 45 °C and 12 mbar.
Derivatization—Once the samples were dried, they were derivatized [4]. Fifteen microlitre of pyridine and 65 μL of bis(trimethylsilyl)trifluoroacetamide containing 1% trimethylchlorosilane were added to the dried sample. The sample was allowed to react in a capped test tube for 15 min at 26 °C. 0.5 mL of toluene was added to the derivatized sample vortexed and placed in amber GC vials containing 0.25 ml silanized glass inserts. The headspace free GC vials were then placed on the GC-MS for analysis.
Gas chromatograph–mass spectrometry analysis—GC/MS analysis was performed using an Agilent 6890N GC and 5973N MS. Splitless injections were made onto a Pursuit DB-225 capillary column (60 m × 0.25 mm × 0.25 μm; J&W Scientific) with an initial temperature of 50 °C/min with a flow of 4.5 mL/min and held for 95 min. Finally, the oven temperature was ramped to 220 °C at 10 °C/min and held for 27 min. The post run was held at 240 °C for 10 min, with a flow of 4.8 mL/min. Helium was used as the carrier gas. The inlet and source temperature was 240 °C with a relative source voltage of 1447 V. The quad was set to 150 °C. Analyte data from the

GC/MS was normalized with the internal standard as shown in Eq. (1).

$$D_N = \frac{A_p}{IS_p} \quad (1)$$

where, D_N is normalized data, A_p the peak area of estrogen compound and IS_p is peak area of the internal standard from the GC/MS. Estrogen standards were prepared and analyzed in a similar method to that described earlier. Using the standards calibration, the estrogen concentration of the samples was determined. Table 2 shows the relative standard deviation (% R.S.D.) and detection limits for the individual estrogens that were tested. The data on the estrogen retention times, quantitation ions and confirming ions is published elsewhere [4].

3. Results and discussion

Seven estrogens were sonicated in single component in the 0.6 and 2 kW batch reactors; and they were: 17α-estradiol, 17β-estradiol, estrone, 17α-dihydroequilin, 17α-ethinyl estradiol, norgestrel and estriol. In the 4 kW flow through reactor, the following three estrogens were sonicated in single component: estrone, 17α-dihydroequilin and equilin. Figs. 1–3 show the sonolytic destruction of individual estrogens in the 0.6, 2 and 4 kW sonicator systems, respectively. Destruction of the individual estrogens varied from 87 to 99% for batch sonication time of 60 min in the 0.6 kW reactor. 17α-Dihydroequilin was observed to have the highest degradation in 60 min, and it was about 99% removed. Estriol had the least removal of 87% in 60 min of sonication time. 17α-Estradiol, 17β-estradiol, estrone, norgestrel and 17α-ethinyl estradiol showed high percentage destruction of 98, 97, 98, 95 and 91%, respectively. Approximately 66–98% destruction of the individual estrogens was observed in 40 min of sonication in the 2 kW batch system. 17α-Estradiol showed the most destruction of 98% in the 40 min of sonication time. Estriol and norgestrel had lower destruction percentages of 66 and 67%, respectively. 17β-Estradiol, estrone, 17α-dihydroequilin and 17α-ethinyl estradiol showed percentage destruction of 95, 85, 97 and 91%, respectively. In the 4 kW continuous flow-through system, 64–90% removal of the estrogens was observed in 35 min of residence time. 17α-Dihydroequilin had the most destruction of 90%, while equilin had the least destruction of 64% during 35 min of residence time. Estrone destruction was 86%.

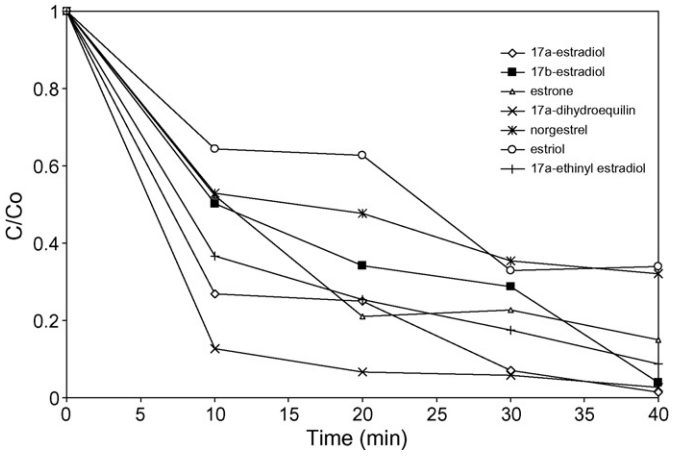


Fig. 2. Estrogen degradation profiles. Sonication reactor: 2 kW; batch system; initial estrogen concentration (C_o): 10 μg/L.

The mass balance on a batch reactor for first order kinetics can be written, as shown in Eq. (2):

$$\ln\left(\frac{C}{C_o}\right) = -kt \quad (2)$$

where k is the first order degradation rate constant, t the sonication time, C the concentration of the estrogen compound at time t, and C_o is the initial concentration of the estrogen compound. The degradation model shown in Eq. (2) was fitted to the analyte degradation data. It was observed that the degradation kinetics followed a first order model. For example, Fig. 4 shows the degradation of estrone in 0.6 and 2 kW ultrasound batch reactors. The kinetic rate constants of estrogens for 0.6 and 2 kW ultrasound reaction systems are listed in Table 3.

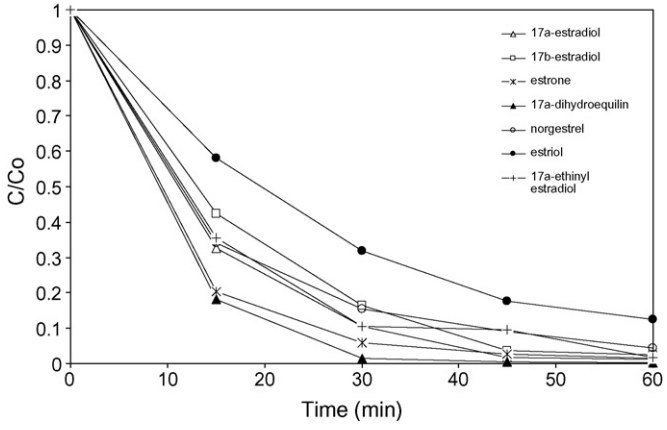


Fig. 1. Estrogen degradation profile. Sonication reactor: 0.6 kW; batch system; initial estrogen concentration (C_o): 10 μg/L.

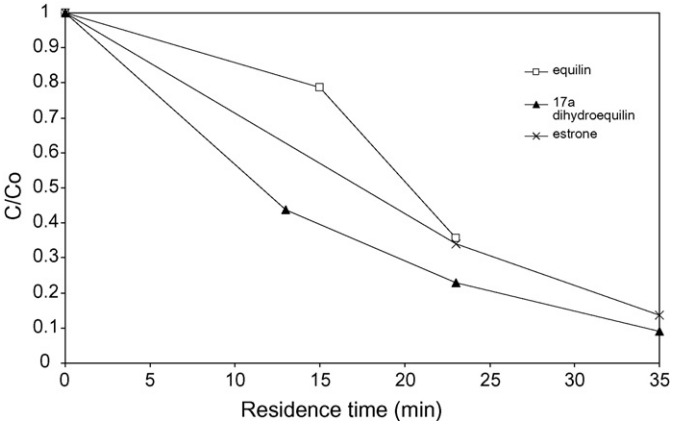
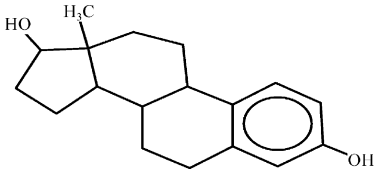
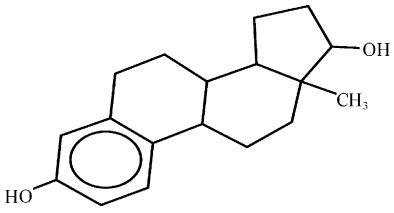
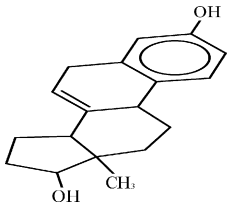
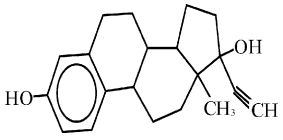
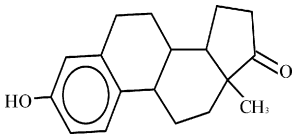
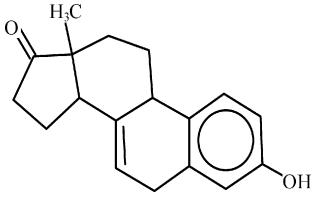
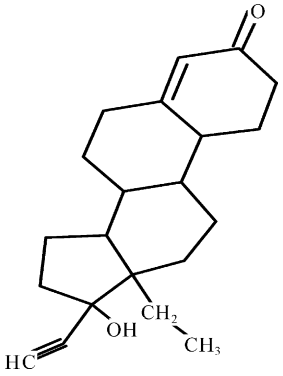


Fig. 3. Estrogen degradation profiles. Sonication reactor: 4 kW; continuous flow system; initial estrogen concentration (C_o): 10 μg/L.

Table 2
GC-MS detection limits and %R.S.D. for estrogens

Estrogen compound	CAS #	Chemical structure	% R.S.D.	Detection limit (μg/L)
17α-Estradiol	57-91-0		1.1	0.03
17β-Estradiol	50-28-2		0.4	0.03
17α-Dihydroequilin	16680-48-1		0.4	0.03
Ethinyl estradiol	57-63-6		2.2	0.03
Estrone	53-16-7		1.4	0.03
Equilin	474-86-2		0.6	3.99
Norgestrel	6533-00-2		2.5	0.87

Sample volume 200 mL.

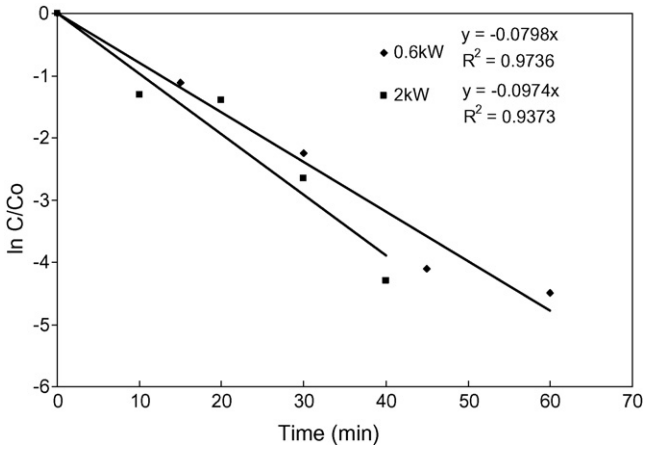


Fig. 4. Comparison of estrone degradation in 0.6 and 2 kW ultrasound batch reactors. Initial estrone concentration: 10 μg/L.

The mass balance on a mixed, continuous flow reactor for a first order reaction can be written as shown in Eq. (3):

$$QC_o - QC + r_a V = V\left(\frac{dc}{dt}\right) \quad (3)$$

where Q is the volumetric flow-rate, V the volume of the reactor, r_a is the first order rate of reaction. At steady state, Eq. (3) may be written as Eq. (4):

$$\frac{C_o - C}{C} = k\tau \quad (4)$$

where C_o is the influent concentration, C the steady state effluent concentration, k the first order degradation rate constant, and τ is the residence time in the reactor. The 4 kW reactor system was operated at steady state and the degradation of the three estrogens is shown in Fig. 3. Eq. (4) model was fitted to the degradation data shown in Fig. 3 to obtain the rate constant values, which are listed in Table 4. It was observed that the degradation of the estrogens followed a first order kinetics. The degradation of 17α-dihydroequilin was observed to be the highest.

It may be observed from Table 3 that the estrogen rate constants for the 0.6 and 2 kW batch reactors were very similar. The rate constants were significantly higher (by a factor of about 2) for the 4 kW sonication reactor, as shown in Tables 3 and 4. The power output by the 0.6, 2 and 4 kW ultrasound units were

Table 3
First-order degradation rate constants (min^{-1}) and regression coefficients (r^2) of estrogens for 0.6 and 2 kW sonication reactors

Estrogen compound	0.6 kW [r^2]	2 kW [r^2]
17α-estradiol	0.0798 [0.9736]	0.0974 [0.9373]
17β-estradiol	0.0649 [0.9787]	0.0648 [0.8405]
Estrone	0.0772 [0.9366]	0.0527 [0.8671]
17α-dihydroequilin	0.1078 [0.923]	0.1009 [0.7521]
17α-ethinyl estradiol	0.0647 [0.9505]	0.0622 [0.9453]
Norgestrel	0.0546 [0.9761]	0.0326 [0.8321]
Estriol	0.0364 [0.9921]	0.0301 [0.893]

Reactor type: batch.

Table 4
First-order degradation rate constants (min^{-1}) and regression coefficients (r^2) of estrogens for 4 kW unit sonication reactor

Estrogen compound	4 kW [r^2]
Estrone	0.1513 [0.8382]
17α-dihydroequilin	0.2313 [0.8251]
Equilin	0.0605 [0.6951]

Reactor type: continuous flow.

0.25, 0.32 and 1.3 kW, respectively, as shown in Table 1. The power output by the 0.6 and 2 kW units were very similar whereas the power output by the 4 kW unit was significantly higher. Some of the factors which influence the power output from the ultrasound unit include solution viscosity, surface tension, vapor pressure, suspended solids, pressure, temperature, ultrasound frequency, power of the sonicator, and size and type of the reactor vessel [24]. In this study, different power sonicators and reactor vessels were used. Other factors such as solution viscosity, surface tension, vapor pressure, suspended solids, pressure and sound frequency were similar. The temperature inside the batch reactors during sonication was 25 °C. Since there was no temperature control system applied for the 4 kW sonicator, the solution temperature would reach up to 60 °C for 23 min of residence time. The power intensity was calculated from the power output and the sonication probe surface area, and the values are listed in Table 1 for the three reactors. The power intensity in the 0.6, 2 and 4 kW sonicator reactors was 157, 135 and 259 kW/m^2, respectively. The power intensity in the 0.6 and 2 kW reactors was similar whereas it was significantly higher in the 4 kW reactor. In sonication process, the production and implosion of cavities is dependent upon the ultrasound intensity. Previous studies [22,23] have examined the effects of power intensity on sonochemical degradation of *p*-nitrophenol and chlorinated compounds. It was reported that first order degradation rate constant increases with power intensity of sonication systems until a maximum value is reached. Higher power intensity is thought to result in higher pressure which causes a more complete implosion of the cavities [22]. This would lead to higher reactivity during cavity implosion. Higher intensity of the ultrasound is also likely to produce more cavities in the solution. The ultrasound intensity was similar in both the 0.6 and 2 kW reactors, and hence, the degradation rate constants were observed to be similar (Table 3). The degradation rate constants were higher in the 4 kW reactor because the power intensity was significantly higher than the other two reactors.

The power density for the three reactors is listed in Table 1. It was calculated from the power output and the reactor solution volume. The power density for the 0.6, 2 and 4 kW reactors was 1.4, 0.53 and 0.43 kW/L, respectively. The 4 kW reactor provided higher degradation kinetics (Tables 3 and 4) and had the lowest power density. This is in contrast to previous reports that the reaction kinetics increases with power density [22,23]. This maybe due to the type of reactor used and the effective reaction zone. The concentration profile of estrone as a function of product of energy density and time (kW-h/l) is shown

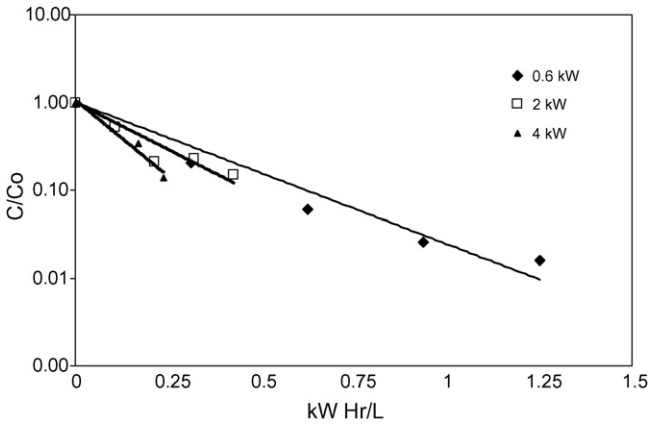


Fig. 5. Concentration vs. energy graph for estrone for 0.6, 2 and 4 kW ultrasound reactors.

in Fig. 5. The 4 kW reactor was observed to be more energy efficient. For example, at an energy input of 0.25 kW-h/L, the percentage removal of estrone was 55, 75 and 85% in the 0.6, 2W and 4 kW reactors, respectively. Hence, the 4 kW reactor was more energy efficient than the 0.6 and 2 kW reactors for degradation of estrone. The results of this study show that power intensity, power density and reactor configuration are important criteria for efficient sonochemical degradation of estrogen hormones. From the perspective of process economics, reactors with high intensities and low power densities would be favorable.

4. Conclusions

Ultrasound was observed to be efficient for destruction of estrogen hormones in aqueous solutions. The sonolysis process produced 80–90% destruction of individual estrogens at initial concentration of 10 μg/L within 40–60 min of contact time. 17α-Dihydroequilin was observed to have the highest degradation kinetics. The estrogen degradation followed first order kinetics. The degradation kinetics and energy efficiency are dependent on the reactor configuration and power characteristics such as power intensity and power density. The estrogen degradation rates increase with increase in power intensity. The reactor that provided higher degradation kinetics and had the lowest power density was observed to be most energy efficient. The study shows that the choice of reactor and ultrasound power are important to achieve optimized kinetics and energy efficiency. Reactors with high ultrasound intensity and low power density would be favorable for cost effective destruction of pharmaceutical compounds in water.

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