

## Ultrasonication for removal of organic micropollutants from water

MIHAI STEFANESCU

<sup>1</sup>National Research and Development Institute for Industrial Ecology – ECOIND, 57-73 Drumul Podu Dambovitei, 060652, Bucharest, Romania

\* Correspondence: [mihai.stefanescu@incdecoind.ro](mailto:mihai.stefanescu@incdecoind.ro)

Received:  
18.10.2022

Accepted:  
19.12.2022

Published:  
28.12.2022

### Abstract

*This review collects the most theoretical and experimental data about the fundamentals of ultrasonic cavitation and its application in the domain of water and drinking water treatment. It is describing the most important mechanism of acoustic cavitation based on "Hot spot theory" which is based on free radicals, especially hydroxyl radicals. The experimental examples are focused on organic micropollutants removal from wastewater and drinking water. There are many organic pollutants resistant to classical treatment flows in wastewater and drinking water treatment plants which means there must be updated with new technologies like Advanced Oxidation Processes (AOPs). Ultrasonication and advanced ultrasonication is one of these new approaches. Ultrasonication was the base of a new chemistry domain - sonochemistry and its development led to new and modern degradation methods of natural and industrial organic pollutants: natural organic matter, phenols, organochlorinated compounds, surfactants, etc. with high mineralization degree. Some examples are described below.*

**Keywords:** *ultrasonication, sonolysis, cavitation, water, micropollutants*

### INTRODUCTION

Ultrasonic field is generated by acoustic waves having frequencies over 16 kHz. The existence of an ultrasonic field is possible in water, soil, and atmosphere but not in vacuum space because of the absence of matter. The existence of ultrasonics was discovered with the development of measuring devices but the ultrasonic field is used for orientation (echolocation) and hunting by different species (bats, fish, dolphins, birds).

The first scientific application of ultrasonic waves was the sonar which was used with success in the first World War, nowadays having more applications in different domains including water and wastewater treatment.

The present review aims to put into light the science of the ultrasonic field starting with theoretical aspects of the specific application of organic micropollutants removal from drinking and wastewater.

There are emphasized the most important applications of the last years in the field of potabilization and wastewater treatment from pharmaceutical, petroleum, ammunition, textile, metallurgical industries, and so on. All ultrasonic application is based on acoustic cavitation phenomena which are presented below.

### *Theoretical fundamentals of cavitation effect*

The cavitation phenomena are generally defined as the process of generating, growing, and collapse of microbubbles or cavitations which appear and disappear in microseconds because of compression and expansion of the aqueous liquid under the action of ultrasonic pulse [1]. The main result is the hotspots/microbubbles generation which releases high levels of energy that can be used for the

removal of organic pollutants from water. The degradation of organic pollutants and microorganisms in water is the consequence of the mechanical, thermal, and chemical effects of the acoustic cavitation phenomenon [2].

Four types of cavitation depending on generation way are as follows:

- Acoustic cavitation: pressure variations in the liquid are due to the acoustic waves (ultrasonic, 16 kHz-100 MHz); study of chemical transformations during the cavitation phenomenon led to a new branch of chemistry - sonochemistry;
- Hydrodynamic cavitation: is generated by the pressure variations because of system configuration changes (e.g., pipe diameter diminishing, Venturi effect);
- Optical cavitation: is generated by the photons of high-intensity light (laser beam);
- Cavitation of elemental particles (e.g., protons).

Acoustic cavitation was the most studied because of its applications in chemistry and environmental chemistry and the beginning of research was in 1880 with the discovery of the piezoelectric effect by the Curie brothers [3].

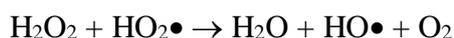
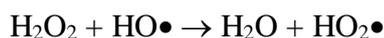
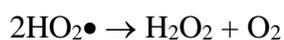
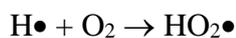
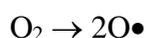
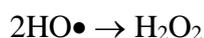
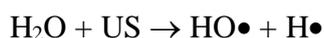
In the seventies were studied the effects of ultrasonication on cellular degradation and in the nineties, it started the experiments of advanced removal of xenobiotics from water with a high degree of mineralization.

Four theories of ultrasonic cavitation effect in water are known these days: the theory of hot points; the electric theory; the theory of plasma discharges; supercritical theory.

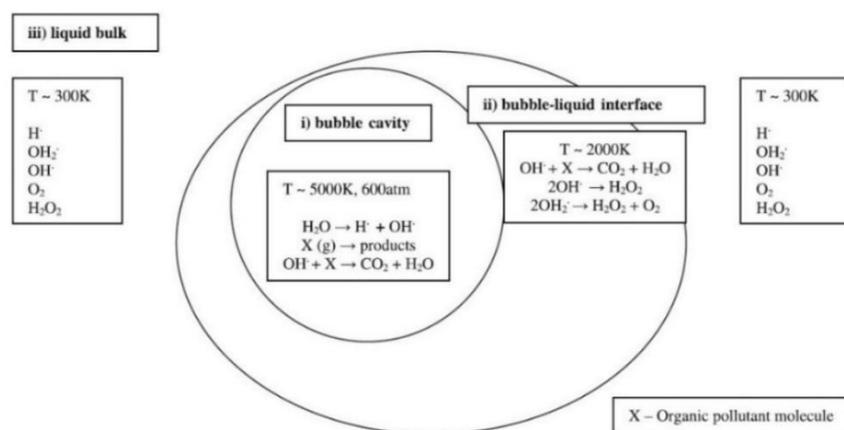
The hot spots theory is generally accepted to explain the mechanism of sonochemical reactions [1, 4, 5]. According to this theory, the main consequences of the cavitation effect are high temperatures (thousands of degrees) and pressures (hundreds of atmospheres) which generate very reactive free radicals and the appearance of turbulences leading to the increase of transport velocities. The organic pollutants bear these effects/actions being degraded because of physical and chemical interactions.

The main free reactive radicals in aqueous liquid after ultrasonication are  $H\bullet$  (hydroxyl radical is a very strong reactive reagent having the potential  $\epsilon_0 = 2.79$  V),  $HO\bullet$ ,  $HOO\bullet$  and  $O\bullet$ .

The mechanism of generation, combination, and recombination of these radicals is as follows:



In these critical conditions generated during acoustic cavitation three reaction zone were defined (fig.1) [1]: cavitation (inside the bubble); supercritical interface (bubble/liquid); the volume of liquid.



**Fig. 1.** The reaction mechanism of the bubble cavity

The applications of ultrasonication in the domain of water treatment belong to the category of advanced oxidation processes (AOPs) having six main classes [1]: photolysis: UV irradiation (A, B or C) without catalyst add; the process doesn't lead to complete mineralization of the pollutant but to the formation of byproducts one of them being more dangerous than initial product; photocatalysis: UV irradiation (usually A 315-400 nm) with catalyst ( $\text{TiO}_2$ ,  $\text{ZnO}$ , etc); sonolysis: direct ultrasonication without a catalyst; sonocatalysis: ultrasonication with catalyst ( $\text{TiO}_2$ ), without UV irradiation; sonophotolysis: simultaneous ultrasonication and UV irradiation without catalyst add; sonophotocatalysis: simultaneous ultrasonication and UV irradiation with catalyst add.

The intensity of radiation, ultrasonic frequency, and initial radius of the bubble are determined factors of the acoustic cavitation effect.

**The intensity** of the ultrasonic generator is represented by the ratio of input power and the area of power dissipation [2].

The pressures generated by a single cavity (bubble) are decreasing with increasing ultrasonication intensity, thus lower intensities must be used for the efficient operation of ultrasonic reactors. However, the irradiation intensity does not be lowered than specific limits because the consequence will be the diminishing of cavity number and the formation of free radicals. If the intensity will be raised by increasing the system input power, the number of bubbles will be higher, the pressure will be higher because of the cumulative effect of all collapsed bubbles. In these conditions, the pollutants removal efficiency will be better.

Still, at a certain time, saturation level will be reached because of the phenomenon of the joining of more microbubbles into large bubbles having a lower pressure in the moment of collapse. More efficient use of ultrasonic energy can be done using a larger dissipation surface.

The best micropollutants removal efficiencies will be in case of small intensities dissipated to large contact areas between ultrasonic probe and liquid.

**The ultrasonic frequency** is another important parameter for sonolysis efficiency. The increase in ultrasonic frequency leads to a higher bubble collapse pressure and better pollutant removal yields.

In the case of higher frequencies, the resonance and collapse of cavities will be reached faster. The generation speed of hydrogen peroxide is 12 times higher at 514 kHz compared to 20 kHz. In general, high frequencies are more efficient for the degradation of organic compounds even in cases of them over 200 kHz when the operation could be more complicated.

For maximization of ultrasonic removal efficiencies, it is advisable to use ultrasonic reactors with more sonotrodes mounted in parallel with a small distance between them (the formation of stationary waves and bubble merging are avoided), especially in the case of a single ultrasonic frequency application. *In the case of reactors with more ultrasonic frequencies, the mineralization degree of organic pollutants is better.*

Small bubbles are preferred instead of large bubbles because of their higher collapse energy [2]. The organic and inorganic compounds of reaction volume have an important role in the pollutant degradation yield because of the influence on the bubbles' collapse energy. The ultrasonic

degradation efficiency can be higher in the presence of  $\text{TiO}_2$ ,  $\text{NiSO}_4$ ,  $\text{CCl}_4$ ,  $\text{CuSO}_4$ , or  $\text{NaCl}$  and other gases (the air is already in the aqueous system) in the reaction volume ( $\text{Ar}$ ,  $\text{O}_3$ ), or gases mixtures could improve the ultrasonication efficiency.

The theoretical base of cavitation has been proven by experimental tests, one of them being the study of the temperature of the ultrasonication process.

The ultrasonic degradation efficiency is inversely proportional to operating temperature; a lower temperature (10-15 °C) will favor the development of cavitation effects still if the pyrolyze is the main process of pollutant degradation the temperature will increase the removal efficiency (e.g., trichloroethylene).

The rate of chemical reactions depending on temperature was studied (comparative chemical thermometry) in normal conditions and during the presence of an ultrasonic field [4]. The results emphasized the existence of two main reaction zones, with different temperatures: inside the bubble (higher temperature) and outside the contact bubble/volume of solution.

Sonoluminescence is also proof of the cavitation phenomenon. It was observed for the first time in the water in 1934 by Frenzel and Schultes and it is of two types [4]:

- sonoluminescence with multiple bubbles;
- sonoluminescence with individual bubbles.

Cavitation is a nuclear process and ultrasonicated liquids usually have a lot of particles that can become cores for acoustical cavitation.

Thus, the "cavitation field" contains many bubbles which interact with each other in a large area in the solution volume. If the cavitation is intensive enough to produce sonoluminescence, will be the first type, multi-bubble sonoluminescence.

In specific conditions, the acoustic pressure can balance the bubble's floatability and keep it inside the solution volume by acoustic levitation. That allows the study of the dynamic characteristics of the bubbles from both theoretical and experimental points of view. Usually, bubble dimensions are below the acoustic length wave (e.g., at 20 kHz frequency the resonance dimension is  $\sim 150 \mu\text{m}$ ).

The phenomenon of individual bubble sonoluminescence is characterized by the production of sonoluminescence to each acoustic cycle by a single stable bubble which will become oscillate for a specific amplitude of the acoustic pulse.

Light emission allows the study of emitted specters and the generation and reaction mechanisms of various radicals and reaction byproducts of sonochemical reactions. Solutions with metals and carbon were mainly studied because there are specter libraries available for vaporized metals at different temperatures (frequently used in star surfaces spectrometry). This makes it possible to study the influence of cavity phenomenon by comparison considering that compounds with carbon modify the spectrum of the metals which are used to study sonolysis.

Ultrasonic probes (sonotrodes) are the most used for the construction of ultrasonic reactors [5] the effects of acoustic cavitation being observed near the vibrating surface. The intensity of cavitation decreases exponentially with distance such that disappears at 2-5 cm depending on the energy and the frequency of the equipment.

Thus, the reactor with multiple sonotrodes will be more efficient but it must be considering the geometry of the probes and their corrosion in time (especially in case of high amplitude).

The ultrasonic field has many industrial applications. The mechanical effect of acoustic cavitation leads to cellular membrane rupture having applications in microbiology (proteins and enzymes formation, genetic engineering) or in wastewater treatment (increases biodegradability and the efficiency of secondary treatment stage in wastewater treatment plants) or in disinfection, both of wastewater and drinking water.

Classical disinfection of drinking water is based on reagents with chlorine or ozone; in the case of chlorine the main disadvantage is the generation of byproducts (THMs, and HAAs) and in the case of ozone the absence of remanence in the network pipes because of ozone depletion. Ultrasonic disinfection has four main effects: mechanical effect (involving turbulence, currents, and shear stresses), chemical effect (free radicals formation), thermal effect (formation of hot spots with high pressure and temperatures levels), the combined effect due to the association with other oxidation

methods ( $\text{Cl}_2$ ,  $\text{H}_2\text{O}_2$ ,  $\text{O}_3$ ). Generally, in the case of disinfection, the mechanical effect of the ultrasonic field is more important than the chemical and thermal effects. The combination of ultrasonic disinfection with conventional technics ( $\text{Cl}_2$ ,  $\text{H}_2\text{O}_2$ ,  $\text{O}_3$ ,  $\text{NaClO}$ ) could lead to a decrease in costs and reagent stock and an increase in the disinfection rate.

Often, sonolysis applications in the field of water and wastewater treatment are hybrid technologies, ultrasonication being associated with other classic methods from the category of Advanced Oxidation Processes (AOPs) or adsorption or membrane processes [6, 7].

#### ➤ **US + $\text{H}_2\text{O}_2$ system**

Hydrogen peroxide is a well-known hydroxyl radical source being widely used for organic pollutants oxidation. It is no toxic reagent so, no secondary pollution adding during the treatment. It is cheaper and easy to handle. The most disadvantages are instability, and sensitivity to operation conditions like pH, temperature, and metallic impurities.

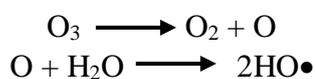
The bond O-O from peroxide is relatively weak (~210 kJ/mol) and can be homolytic broken by some methods: thermal, photolytic, radiolytic, redox, and ultrasonic. The  $\text{HO}\bullet$  radicals are not selective oxidants; they can attack both micropollutants and hydrogen peroxide. This is a "scavenging" effect and is unfavorable to chemical pollutants mineralization.

The recombination of hydroxy radicals to recreate hydrogen peroxide depends on ultrasonication parameters (frequency, power, amplitude, etc.) and must be taken into consideration when the  $\text{H}_2\text{O}_2$  doses are selected.

The most important parameters which must be considered for the ultrasonication treatment option are pH, which will influence the state of the micropollutant (molecular or ionic), the type of pollutant (hydrophobic or hydrophile), the composition of the water to be treated, sonication optimal frequency, the power dissipated and ultrasonic reactor configuration.

#### ➤ **US + $\text{O}_3$ system**

The ozone is a strong oxidant reagent, very efficient for the degradation of refractory organic pollutants with no secondary pollution. Its efficiency is based on multiple own oxidative actions and its derivative products as hydroxyl radicals.



This mechanism involves the thermal decomposing of ozone inside the vapor phase of cavities with atomic oxygen generation which will react later with water vapor and form gaseous hydroxyl radicals in the gaseous state.

The decomposing rate of ozone is higher under ultrasonic field action. The ozone can react with an oxygen atom or could be consumed by other reactive species inside the bubble or by the bubble interface like  $\text{HO}\bullet$  (generated during the sonolysis). This will reduce both the efficiency of hydroxyl radical generation and the available ozone amount for reaction with substrate.

On the other hand, the turbulences due to the ultrasonic waves favor the absorption of ozone and decrease the resistance to mass transfer in solution volume.

Despite the performance of this hybrid system, its reaction rate is below the sum of the separated reaction rates of each method. A possible explanation is the intensification of free radicals (generated by sonolysis) recombination which leads to a decrease in the number of those that can attack pollutants and a decrease in reaction rates.

The increase of ultrasonic frequency could be unfavorable for the oxidation process because of bubble dynamics change. Bubble collapse is faster and the available time for ozone molecules diffusion inside the bubble is much shorter and the hydroxyl radical amount will be smaller.

The ozonation mode (continuous bubbling or initial saturation of solution with ozone) is important too. The efficiency of this hybrid treatment is limited both by molecular ozone reactivity with pollutant species and their secondary products and decomposing of ozone in the gaseous phase into more reactive radical species.

### ➤ US +UV system

This advanced oxidation system is a hybrid of ultrasonic cavitation effects and photolysis effects. The negative interferences between the ultrasonic field and electromagnetic waves of UV are unlikely because of their nature. The light absorption is very fast while the cavitation phenomena is too slow to interfere. In fact, the hybrid system US/UV mainly means the generation of hydrogen peroxide during ultrasonication and its utilization in the photolysis process. The addition of H<sub>2</sub>O<sub>2</sub> will significantly increase the degradation efficiency of the micropollutants.

### ➤ US + adsorption

Adsorption is an old process used especially for the treatment of industrial water and drinking water. The principle is to retain the micropollutants on the surface/micropore surface of different, specific carriers: activated carbon, volcanic tuff (zeolites), and different natural or synthetic new materials. The main disadvantage is that the carrier/support material will become the new pollution source if the retained pollutant will be not recovered and reused after concentration.

The ultrasonic field could be a regeneration method for these carriers. The energy of the sonolysis process is over the affinity of micropollutants for the carrier and they will pass into the solution keeping intact the carrier.

### ➤ US + electrochemical oxidation

The electrochemical processes can be used for water and wastewater treatment especially because there are compact systems and very efficient in the case of specific micropollutants but with higher cost because of electricity consumption.

In the case of ultrasonic coupling, the ultrasonic field improves the mass transfer of electrochemical processes avoiding at the same time the polymerization of the byproducts on the electrode surfaces. The name of this hybrid technology is Sono-electro-Fenton [8].

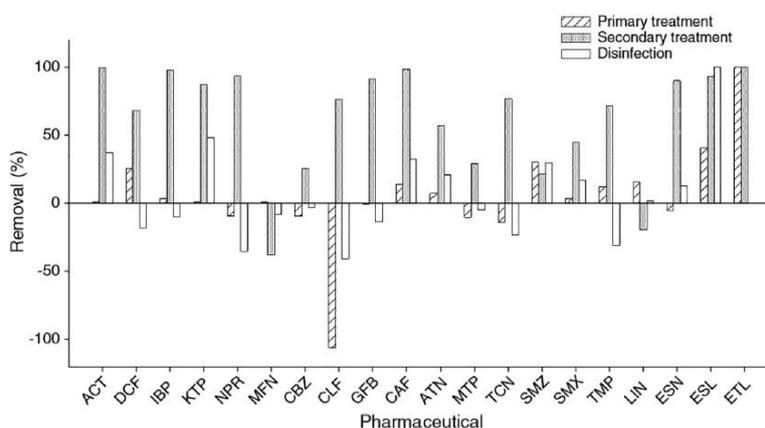
## *Applications of ultrasonics in the field of wastewater and water treatment*

The available data in the field of ultrasonic application revealed that many industries use it in their production processes but in the domain of wastewater treatment [9-11]. Referring to this last application ultrasonication has proved to be useful for the treatment of wastewater with pharmaceuticals [12-26], pesticides [27-33], hormones [34], explosive derivatives [35], petroleum products [36-38], polyfluorinated compounds [39, 40], surfactants [41], dyes [42-45]. Likewise, ultrasonication can be used in the field of drinking water treatment for hardness control [46-47], turbidity control [48], ammonia removal [49], bromates removal [50], trihalomethanes [51, 52] and haloacetic acids removal [53] and for disinfection [54-57].

### *The treatment of wastewater with pharmaceuticals content - anti-inflammatory (diclofenac)*

Municipal wastewater can contain pharmaceuticals having sources in pharmaceutical industry wastewater and household wastewater (drugs are not completely metabolized inside the human body and are evacuated unmodified or as byproducts of biochemical degradation).

*P. Alfonso-Muniozgueren et al.*



**Fig. 2.** The removal efficiency of 20 pharmaceuticals during the classic treatment flow of municipal wastewater

A recent study [13] shows (fig. 2) the high removal efficiencies of 20 representative pharmaceuticals: acetaminophen (ACT), diclofenac (DCF), ibuprofen (IBP), ketoprofen (KTP), naproxen (NPR), mefenamic acid (MFN), carbamazepine (CBZ), clofibric acid (CLF), gemfibrozil (GFB), caffeine (CAF), atenolol (ATN), metoprolol (MTP), triclosan (TCN), sulfamethazine (SMZ), sulfamethoxazole (SMX), trimethoprim (TMP), lincomycin (LIN), estrone (ESN), estriol (ESL), estradiol (ETL).

Must be noted that in the case of some compounds (DCF, IBP, NPR, MFN, CBZ, CLF, TCN, TMP) the removal efficiency is negative because they are concentrated in the primary treatment step (slow release in the water of some drugs) and after disinfection phase. The majority are totally (mineralization) or partially degraded in the secondary treatment stage (biological treatment).

The pharmaceutical compounds are removed in the secondary treatment stage by autotrophic biodegradation (bacteria populations from the nitrification process which use inorganic carbon as substrate) or heterotrophic biodegradation (bacteria that use organic carbon as substrate). Both processes are simultaneous during the active sludge treatment, the main degradation path depending on the pharmaceutical's specific characteristics, some of them being resistant to biological treatment as antibiotics which can unselectively destroy aerobic and anaerobic bacteria involved in nitrification and denitrification processes. Ultrasonication could be the solution for the advanced removal of these refractory organic compounds [22, 23, 39].

The experimental tests of many research teams in the field emphasized that pharmaceuticals can be efficiently degraded if the sonolysis operating parameters are optimal. The main parameters which are determinants for the ultrasonic degradation of pharmaceuticals from water are [24-26]:

- pH: pH variation can modify micropollutant structure and the way of free radical action; most studies show the link between pH and  $pK_a$  ( $K_a$  - acidity constant) and with the hydrophobicity level of the organic compound. For the most part, the advanced degradation of pharmaceutical compounds is more efficient at low pH values  $pH = 3-5$  because of the high oxidation potential of hydroxyl radicals and hydrogen peroxide (both are generated during the sonolysis). The association of sonolysis with other AOPs like ozonation leads to a significant change of removal efficiencies in the sense of its growth together with pH increasing;
- temperature: the rise of temperature favors pharmaceuticals degradation because of the threshold diminishing for cavitation beginning and hydroxyl radicals generation. Still, the rise of temperature over the limit ( $50^{\circ}C$  in the case of diclofenac) could lead to a sudden drop in degradation efficiency (20% in the case of diclofenac). This is because of vapor pressure inside the microbubbles and the decrease in cavitations collapse intensity;
- type and initial concentration of pharmaceutical: the type of organic compounds has an important influence on the reaction with hydroxyl radicals and peroxide and in consequence degradation efficiency; in the case of diclofenac and other compounds is rising to a specific level (must be established for each micropollutant) and after that is decreasing;
- ultrasonication frequency: is a very important parameter for organic compound degradation; experimental studies emphasized different frequencies (low, medium, and high) and different behavior of ultrasonicated pharmaceuticals (table 1).

**Table 1.** Direct sonolysis of pharmaceuticals - removal yields

Pharmaceutical	Frequency (kHz)				
	<300	300-500	500-700	700-900	>900
	Removal efficiency (%)				
Losartan	-	70	60	15	-
Diclofenac	-	92	95	25	-
Atenolol	65	95	90	-	90
Levodopa	-	-	91	90	66
Paracetamol	-	-	95	92	67
Ibuprofen	50	-	-	-	85
Sulfamethoxazole	40	-	-	-	75

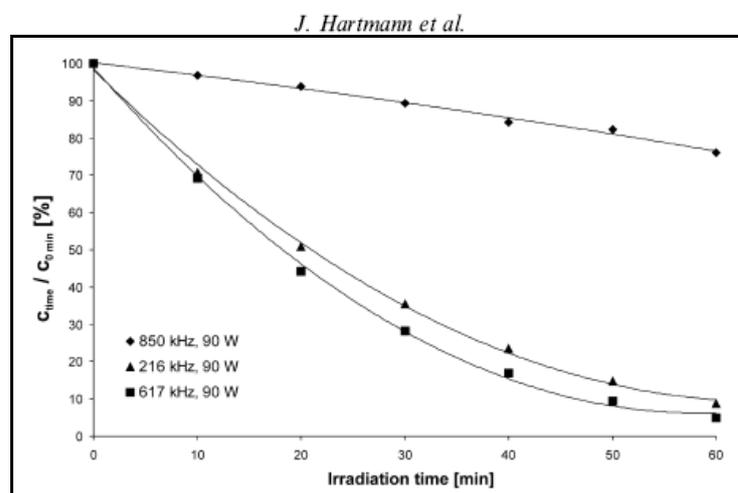
The removal percent is an average value of specific efficiencies which were established based on experimental sets on a laboratory scale. Most of the selected pharmaceuticals are highly removed at medium frequencies (500-700 kHz): diclofenac 95%, atenolol 90%, and paracetamol 95% but also at high frequencies. The differences between removal efficiencies can be because of free radicals generation combined with mechanical and thermal effects.

- ultrasonication mode: ultrasonic field can be applied in a continuous or discontinuous (ultrasonic pulse) way; removal efficiency increases in the case of pulsatory ultrasonication for some pharmaceuticals (DCF, CBZ, PCT, and IBU).

**Diclofenac** is one of the most worldwide anti-inflammatories used being a presence in municipal wastewater for many years because of its resistance to natural biodegradation and reduced degradation in the secondary treatment step of wastewater treatment plants (WWTPs). WWTPs can remove only 40% of diclofenac (ibuprofen removal is ~90%).

Some studies have studied ultrasonic degradation of diclofenac by direct sonolysis or sonolysis with hydrogen peroxide and catalysts ( $\text{TiO}_2$ ,  $\text{SiO}_2$ , etc).

Figure 3 shows the evolution of DCF removal during the time at three different ultrasonic frequencies: 216 kHz, 617 kHz, and 850 kHz (power of 90 W constant,  $C_0$  - DCF = 50 mg/L).



**Fig. 3.** Diclofenac ultrasonic degradation (ultrasonic frequency influence)

The best removal efficiency was ~90% (removal efficiency as  $c/c_0$  below 10%) after 60 minutes of reaction time.

Ten reaction intermediaries of DCF sonolysis were determined after 30 minutes and 60 minutes of direct sonolysis (initial concentration of 157,73  $\mu\text{M}$ , 50 mg DCF/L). The residual concentration was shown in table 2. Based on the analytical determination (concentrations of different derivatives) it was proposed a degradation mechanism (figure 4).

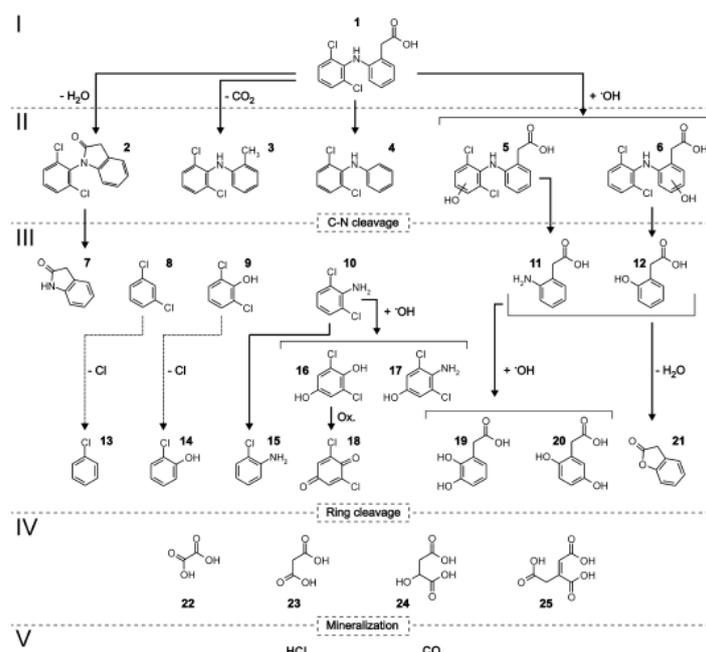
There are four levels of diclofenac ultrasonic degradation based on table 2 data analysis:

- level I: generation of chlorinated derivatives of N-phenylanilines, indolinone, and hydroxylated derivatives;
- level II: cleavage of C-N bond and generation of dichloroanilines, dichlorophenol, and indolinone;
- level III: generation of phenylacetic derivatives;
- level IV: generation of hydroxycarboxylic acid derivatives;
- level V: mineralization to HCl and  $\text{CO}_2$ .

**Table 2.** Degradation intermediaries of DCF

Micropollutant	Concentration ( $\mu\text{M}$ )	
	after 30 min of sonolysis	after 60 min of sonolysis
Diclofenac	31.44	2.65
(2,6-Dichlorophenyl)-indolin-2-one	3.12	0.25
N-Phenyl-2,6-dichloroaniline	0.04	0.03
2-Indolinone	-	2.8
1,3-Dichlorobenzene	1.34	1.15
2,6-Dichlorophenol	1.30	2.09
2,6-Dichloroaniline	15.24	11.44
Chlorobenzene	0.05	0.03
2-Chlorophenol	0.05	0.07
2-Chloroaniline	0.05	0.08

Figure 4 shows the resulted possible degradation mechanism of diclofenac by ultrasonication.

**Fig. 4.** The mechanism of diclofenac ultrasonic degradation (617 kHz, 90W)

#### The treatment of wastewater with pharmaceuticals content - antibiotics (penicillin)

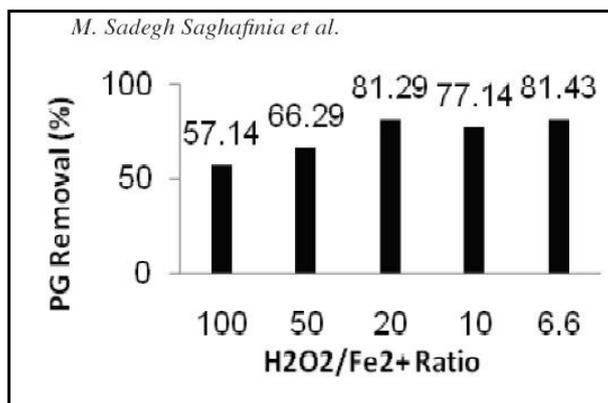
Antibiotics are often present in the influents of WWTPs together with anti-inflammatories and Penicillin and its derivatives are among them [14-17].

**Penicillin** is the first antibiotic still being efficient for the treatment of infections and still present in the influents of WWTPs. The concentration levels of penicillin in wastewater are in the range of 50-200 mg/L.

Some studies emphasized the efficiency of **direct sonolysis** and **Fenton photolysis** to penicillin degradation as will be present below [19]:

- Fenton photolysis: UV lamp (254 nm), penicillin concentration 200 mg/L,  $\text{Fe}^{2+}$  doses 0.2-4 mM  $\text{Fe}^{2+}/\text{L}$ ,  $\text{H}_2\text{O}_2$  dose 20 mM/L, pH correction with  $\text{H}_2\text{SO}_4$  and  $\text{NaOH}$  (pH = 3.5), molar ratio  $\text{H}_2\text{O}_2:\text{Fe}^{2+} = 5-100$ ;
- direct sonolysis: frequency 35 kHz, 860 W.

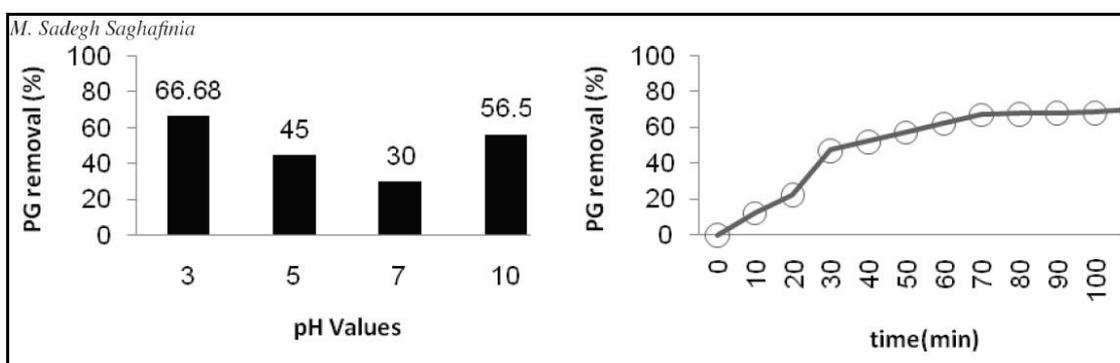
In the case of **Fenton sonolysis**, for 50 minutes of irradiation time, the removal efficiency of penicillin increases with the diminishing of the molar ratio  $\text{H}_2\text{O}_2:\text{Fe}^{2+}$  from 100 to 20 (Figure 5).



**Fig. 5.** Fenton photolysis of Penicillin G - the influence of H<sub>2</sub>O<sub>2</sub>:Fe<sup>2+</sup> ratio

In the case of pH influence tests, pH = 2-4 the best efficiency was at pH = 3.5 and 30 minutes of UV irradiation (Figure 6).

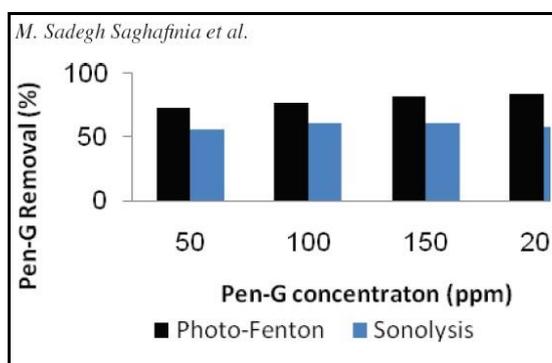
**Ultrasonic degradation of Penicillin G** (200 mg/L) is strongly influenced by two main parameters: reaction pH and sonolysis time (figure 6).



**Fig. 6.** Direct sonolysis of Penicillin G - the influence of pH and reaction time

The analysis of these results shows that optimal conditions of penicillin removal at low frequency are pH = 3 and 70 min. reaction time. The removal yield was 66.7%.

Comparative analysis of both treatment methods in the same graphic (figure 7) emphasized the better removal efficiency of Fenton photolysis.



**Fig. 7.** Comparing efficiencies of Fenton photolysis and sonolysis

For all concentrations of penicillin, the removal yield by Fenton photolysis was above the ultrasonication efficiencies but we can consider that both are efficient methods for antibiotics removal and it is possible to put in the same treatment flow both AOPs to get better results [24-26].

### *The treatment of wastewater with hormones*

Estrogens are one of the most present micropollutants both in wastewater and surface waters. There are five main categories: progestin (progesterone), glucocorticosteroids (cortisol), mineral corticosteroids (aldosterone), androgen (testosterone) and estrogen. Estrone (E1) and 17 beta-estradiol (E2) are estrogen hormones very often identified in wastewater and will find below the efficiency of ultrasonic degradation in their case [34].

The hormones are usually partially removed from wastewater in the biological treatment step of WWTPs but it was necessary to develop advanced better methods such as nanofiltration, reverse osmosis, adsorption, and advanced oxidation processes. Ultrasonication is one of them and was proven to be efficient in the range of 480-540 ng/L which is the domain of hormones mixture in wastewater. They have endocrine disruptors and stimulate the development of tumors so, they are very dangerous at a very low level of concentrations.

In the case of E1 and E2 hormones (485 ng E1/L, 511 ng E2/L) the ultrasonication (simple sonolysis) tests were focused on the main operating parameters: ultrasonic frequency 30 kHz, 45 kHz, 60 kHz, pH: 3; 7; 10, sonolysis time: 30 min, 45 min, 60 min, 120 min. The main results are in Table 3 [34].

The main observations referring to the ultrasonic degradation of estrone and 17 beta-estradiol are as follows:

- the rise of pH reaction from 3 to 10, for the same frequency and reaction time, leads to the increase of E1 and E2 removal efficiencies from 12.4% to 67.1% and 12.2% to 66.5% respectively;
- the increase of ultrasonic frequency leads to a small increase in removal efficiency for both hormones the maxim values being 75.6% and 75.3% respectively;
- the increase in ultrasonication time doesn't have a significant effect on the degradation of E1 and E2 so, it can be considered that shorter reaction times are enough to assure removal efficiencies of ~80%.

**Table 3.** Ultrasonic degradation of estrone (E1) and 17 beta-estradiol (E2)

Hormone	pH, units	Frequency, kHz	Ultrasonication time, min.	Removal efficiency, %	Test goal
E1	3	30	30	12.4	pH influence
E1	7	30	30	26.3	
E1	10	30	30	67.1	
E2	3	30	30	12.2	
E2	7	30	30	25.8	
E2	10	30	30	66.5	
E1	10	30	30	67.1	frequency influence
E1	10	45	30	70.8	
E1	10	60	30	75.6	
E2	10	30	30	66.5	
E2	10	45	30	70.9	
E2	10	60	30	75.3	
E1	10	60	30	75.6	time influence
E1	10	60	60	75.9	
E1	10	60	90	77.5	
E1	10	60	120	79.6	
E2	10	60	30	75.3	
E2	10	60	60	75.9	
E2	10	60	90	76.8	
E2	10	60	120	78.5	

### The treatment of drinking water with trihalomethanes and haloacetic acids content

Disinfection of drinking water with chlorine was an important step for the improvement of human life because of its high efficiency in removing large categories of bacteria and parasites reducing the spread of many diseases and extending the average life span. It is estimated that over 80% of drinking water treatment plants in medium and big cities have chlorination as the main disinfection method.

Despite the many advantages, including the remanence of the drinking water pipe system, there are two main disadvantages: the presence of chlorine in the air with additional health and security problems and the generation of disinfection byproducts (DBPs). Trihalomethanes (THMs) and haloacetic acids (HAAs) are the main representatives. They are not considered pollutants in the conventional sense but have a cumulative toxic effect and considering some studies, even carcinogen potential [51, 52].

Taking into consideration the new European legislation in the field of drinking water with the obligation of monitoring THMs and HAAs starting with 2026 more and more research teams try to find efficient and cost-effective removal methods.

Ultrasonication can become a good option because of its oxidation potential and the no reagent add to already treated drinking water.

In the case of four representative THMs ( $\text{CHCl}_3$ ,  $\text{CHBrCl}_2$ ,  $\text{CHBr}_2\text{Cl}$ ,  $\text{CHBr}_3$ ) there were performed oxidation tests in three configurations [51]:

- direct sonolysis (simple ultrasonication, 90 minutes);
- Fenton oxidation (with hydrogen peroxide and iron);
- sonolysis + Fenton oxidation

The hydrogen peroxide dose was 250 mg  $\text{H}_2\text{O}_2/\text{L}$  and iron doses were 20 mg  $\text{Fe}^{2+}/\text{L}$  and 40 mg  $\text{Fe}^{2+}/\text{L}$ .

Figure 8 the evolution of  $C/C_0$  as an expression of removal efficiencies ( $C_0 = 10 \text{ mg/L}$  for each compound).

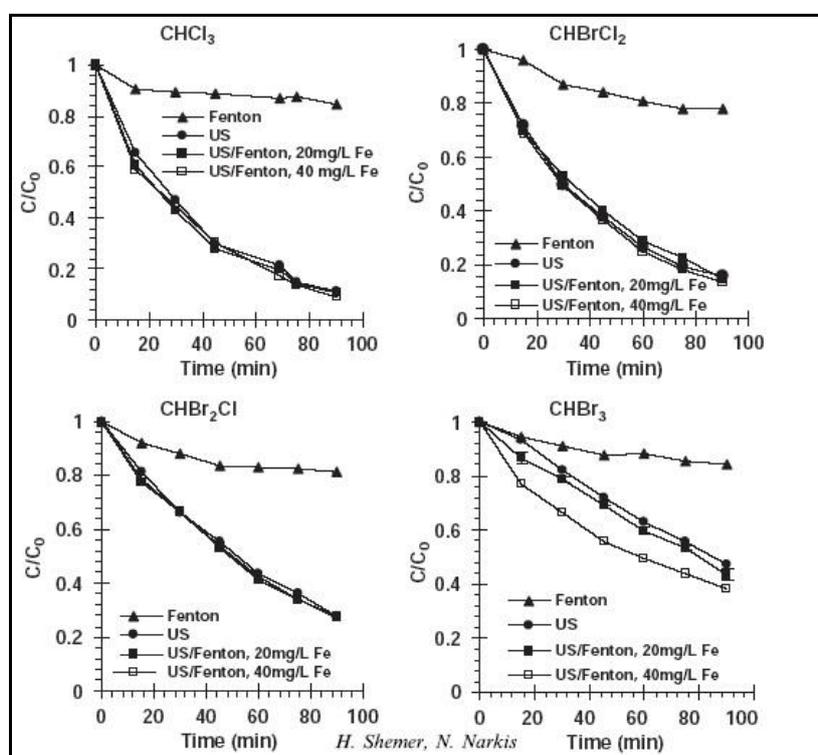


Fig. 8. Sonolysis and Fenton sonolysis of THMs

The main observations based on these tests on selected THMs compounds and other additional experiments are as follows:

- hydrogen peroxide alone does not oxidize selected THMs;
- peroxide added in case of simple sonolysis tests does not improve sonolysis efficiency;
- the maxim THMs removal efficiency was ~40% for the combined treatment of ultrasonication and Fenton oxidation with 20 mg Fe<sup>2+</sup>/L

Haloacetic acids are the second DBPs' important category. They are generated together with THMs and must be removed. Laboratory tests have proved the efficiency of ultrasonication for haloacetic acid removal from drinking water. In the case of trichloroacetic acid (TCA), sonolysis (20 kHz), photocatalytic oxidation (TiO<sub>2</sub> catalyst, 62.5 mg/L), and combined ultrasonication with photolysis were performed (60 minutes reaction time).

Figure 9 shows the dechlorination efficiencies of TCA (C<sub>0</sub> = 100 mg/L) [53].

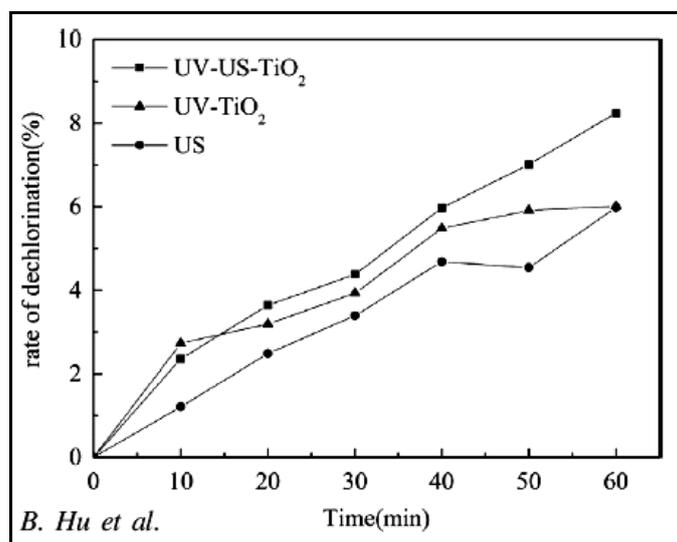


Fig. 9. Sonolysis, photolysis, and sono-photolysis of TCA

The maximal dechlorination efficiency was 8% in the case of ultrasonication + photocatalytic oxidation after 60 minutes and 25% after two weeks. The dechlorination yield is not big but became important if the treatment system is set to work continuously and the TCA concentrations are lower. Even so, the mineralization degree was higher than the dechlorination degree (total organic carbon removal was 35-40% after 60 minutes).

## CONCLUSIONS

The above-selected application of ultrasonic field in the realm of wastewater and water treatment proved that can be used with optimal results for the removal of different classes of micropollutants (anti-inflammatory, antibiotics, endocrine disruptors, trihalomethanes, and haloacetic acids).

The removal efficiencies can be raised in many cases by combining sonolysis with other advanced oxidation processes (Fenton oxidation, photolysis, catalytic photolysis, Fenton photolysis, etc.).

All these ultrasonic applications can be integrated into the classic wastewater treatment flows as additional treatment phases to assure the advanced removal of some organic pollutants which are toxic for humans and aquatic ecosystems even at very low concentration levels.

The perspective of ultrasonic in the field of water and wastewater treatment is very optimistic considering a few advantages: no additional pollution because of reagents, flexibility for integration in wastewater treatment plants or drinking water treatment plants, possibility to use it together with other treatment methods.

## ACKNOWLEDGEMENTS

The work was funded by the Ministry of Research and Innovation of Romania through Program Nucleu, Project code PN 19 04 03 01.

## REFERENCES

- [1] COLLIN, G.J., GIANLUCA, L.P., AWANG, B., DUDUKU, K., *Ultrason. Sonochem.*, **16**, 2009, p. 583.
- [2] GOGATE P.R., *Adv. Environ. Res.*, **6**, 2002, p. 335.
- [3] MAHVI, A.H., *Iranian J Publ Health*, **38**, no. 2, 2009, p.1.
- [4] SUSLICK, K.S., McNAMARA, W.B., DIDENKO, Y., *Sonochemistry and Sonoluminescence*, Kluwer Publishers, Dordrecht, Netherlands, 1999, p. 191.
- [5] PARAG, R.G., ABHIJEET, M.K., *Biochem. Eng. J.*, **44**, 2009, p. 60.
- [6] YEAN, L.P., AHMAD, Z.A., SUBHASH, B., *Desalination*, **277**, 2011, p. 1.
- [7] GOGATE P.R., *Ultrason. Sonochem.*, **15**, 2008, p. 1.
- [8] HASANI, K., PEYGHAMI, A., MOHARRAMI, A., VOSOUGHI, M., *Arabian J. Chem.*, **13**, 2020, p. 6122.
- [9] SVENDSEN, E., DAHLE, S.W., HAGEMANN, A., BIRKEVOLD, J., DELACROIX, S., ANDERSEN, B.A., *Aquacult. Res.*, 2018, **49**, p. 1166.
- [10] ROSSI, G., MAINARDIS, M., ANEGGI, E., WEAVERS, L.K., GOI, D., *Environ. Sci. Pollut. Res.*, **28**, 2021, p. 700.
- [11] NASSERI, S., VAEZI, F., MAHVI, A.H., NABIZADEH, R., HADDADI, S., *Iran.J.Health.Sci.Eng.*, **3**, no. 2, 2006, p. 109.
- [12] ANANDANA, S., PONNUSAMYB, V.K., ASHOKKUMAR, M., *Ultrasonics - Sonochemistry*, **67**, no. 105130, 2020, <https://www.sciencedirect.com/science/article/pii/S135041772030211X>.
- [13] MUNIOZGURENA, P.A., SERNA-GALVIS, E.A., BUSSEMAKERA, M., TORRES-PALMA, R.A., LEEA, J., *Ultrason. Sonochem.*, **76**, no. 105656, 2021, <https://www.sciencedirect.com/science/article/pii/S135041772100198X>.
- [14] GUYER, G.T., INCE, N.H., *Ultrason. Sonochem.*, **18**, 2011, p. 114.
- [15] HARTMANN, J., BARTELS, P., MAU, U., WITTER, M., TUMPLING, W., HOFMANN, J., NIETZSCHMANN, E., *Chemosphere*, **70**, 2008, p. 453.
- [16] CHAKMA, S., MOHOLKAR, V.S., *Ultrason. Sonochem.*, **29**, 2016, p. 485.
- [17] ZIYLAN-YAVASA, A., MIZUKOSHIB, Y., MAEDAC, Y., INCEA, N.H., *Applied Catalysis B: Environmental*, **172-173**, 2015, p. 7, <https://www.sciencedirect.com/science/article/abs/pii/S0926337315000636>.
- [18] ZIYLAN, A., KOLTYPIN, Y., GEDANKEN, A., INCE, N.H., **20**, 2013, p. 580.
- [19] SAGHAFINIA, M.S., EMADIAN, S.M., VOSSOUGHIA, M., *Procedia Environ. Sci.*, **8**, 2011, p. 202.
- [20] KALININA, I., NAUMENKO1, N., FATKULLIN, R., *IOP Conf. Series: Earth and Environmental Science*, **272**, 2019, [https://www.researchgate.net/publication/333932957\\_Perspectives\\_of\\_Using\\_of\\_Ultrasonic\\_Cavitation\\_in\\_Water\\_Treatment\\_Technology\\_for\\_the\\_Food\\_Productions](https://www.researchgate.net/publication/333932957_Perspectives_of_Using_of_Ultrasonic_Cavitation_in_Water_Treatment_Technology_for_the_Food_Productions).
- [21] KRISHNAN, R.Y., MANIKANDAN, S., SUBBAIYA, R., BIRUNTHA, M., GOVARTHANAN, M., KARMEGAM, N., *Environ. Technol. Innovation*, **23**, no. 101757, 2021, <https://www.sciencedirect.com/science/article/abs/pii/S2352186421004053>.
- [22] AL-HAMADANIA, Y.A.J., PARKA, C.M., ASSIA, L.N., CHUA, K.H., HOQUE, S., JANGB, M., YOONA, Y., ZIEHL, P., *Ultrasonics - Sonochemistry*, **39**, 2017, p. 354.
- [23] LIU, P., WU, Z., ABRAMOVA, A.V., CRAVOTTO, G., *Ultrason. Sonochem.*, **74**, no. 105566, 2021, <https://www.sciencedirect.com/science/article/pii/S1350417721001085>.
- [24] Adityosulindroa, S., Barthea, B., González-Labrada, K., Hazab, U.J.J., Delmasa, H., Julcour, C., *Ultrason. Sonochem.*, **39**, 2017, p. 889.

- [25] MERONIA, D., JIMÉNEZ-SALCEDO, M., FALLETTA, E., BRESOLIN, B.M., KAITD, C.F., BOFFITTO, D.C., BIANCHIA, C.L., PIROLA, C., *Ultrason. Sonochem.*, **67**, no. 105123, 2020, <https://www.sciencedirect.com/science/article/abs/pii/S1350417720301073>.
- [26] PANDYA, K., SINGH, A., KODGIRE, P., 2021, <https://www.researchsquare.com/article/rs-297267/v1>.
- [27] DESHMUKH, N.S., DEOSARKAR, M.P., *Mater. Today. Proc.*, **57**, 2022, p. 1575.
- [28] SCHIEPPATIA, D., GALLIA, F., PEYOTC, M.L., YARGEAUC, V., BIANCHIA, C.L., BOFFITO, D.C., *Ultrason. Sonochem.*, **54**, 2019, p. 302.
- [29] WEN, D., CHENG, B., LIUC, B., *Water Sci. Technol.*, **85**, 2022, no.1, p. 230.
- [30] THANGAVADIVEL, K., MEGHARAJ, M., SMART, R., LESNIEWSKI, P.J., NAIDU, R., *J. Hazard. Mater.*, **168**, 2009, p. 1380.
- [31] WANG, C.K., SHIH, Y.H., *Sustainable Environ. Res.*, **26**, 2016, p. 110.
- [32] AYAREA, S.D., GOGATE, P.R., *Chemical Engineering & Processing: Process Intensification*, **154**, no. 108040, 2020, <https://www.sciencedirect.com/journal/chemical-engineering-and-processing-process-intensification>.
- [33] KASK, M., KRICHEVSKAYA, M., BOLOBAJEV, J., *J. Environ. Chem. Eng.*, **7**, no. 103095, 2019, <https://www.sciencedirect.com/science/article/pii/S2213343719302180>.
- [34] ROUDBARI, A., REZAKAZEMI, M., ROUDBARI and REZAKAZEMI, *AMB Expr*, **8:91**, 2018, [https://www.researchgate.net/publication/325510619\\_Hormones\\_removal\\_from\\_municipal\\_wastewater\\_using\\_ultrasound](https://www.researchgate.net/publication/325510619_Hormones_removal_from_municipal_wastewater_using_ultrasound).
- [35] CHEN, W.S., HUANG, Y.L., *Ultrason. Sonochem.*, **18**, 2011, p. 1232.
- [36] SPONZA, D.T., OZTEKIN, R., *Chem. Eng. J.*, **162**, 2010, p. 142.
- [37] RASHEED, Q.J., PANDIAN, K., MUTHUKUMAR, K., *Ultrason. Sonochem.*, **18**, 2011, 1138;
- [38] WOODA, R.J., SIDNELLA, T., ROSSB, I., MCDONOUGH, J., LEEA, J., BUSSEMAKERA, M.J., *Ultrason. Sonochem.*, **68**, no. 105196, 2020, <https://www.sciencedirect.com/science/article/pii/S1350417719312878>.
- [39] SIDNELLA, T., WOODB, R.J., HURST, J., LEEA, J., BUSSEMAKER, M.J., *Ultrason. Sonochem.*, **87**, no. 105944, 2022, <https://www.sciencedirect.com/science/article/pii/S1350417722000372>.
- [40] GOLEA, V.L., FISHGOLDA, A., SIERRA-ALVAREZB, R., DEYMIERA, P., KESWANIA, M., *Sep. Purif. Technol.*, **194**, 2018, p. 104.
- [41] SINGLA, R., GRIESER, F., ASHOKKUMAR, M., *Ultrason. Sonochem.*, **18**, 2018, p. 484.
- [42] CHAKMA, S., DAS, L., MOHOLKAR, V.S., *Separation and Purification Technology*, **156**, 2015, p. 596.
- [43] ERTUGAY, N., ACAR, F.N., *Appl. Surf. Sci.*, **318**, 2014, p. 121.
- [44] SUKHATSKIY, Y., ZNAK, Z., ZIN, O., CHUPINSKY, D., *Chem. Chem. Technol.*, **15**, no. 2, 2021, p. 284.
- [45] MADHAVANA, J., KUMARA, P.S.S., ANANDANB, S., GRIESERA, F., ASHOKKUMARA, M., *Sep. Purif. Technol.*, **74**, 2010, p. 336.
- [46] HIRATSUKA, A., PATHAK, R.D., *J. Water Resour. Prot.*, **5**, 2013, p. 604.
- [47] DOOSTI, M.R. KARGAR, R., SAYADI, M.H., *Proceedings of the International Academy of Ecology and Environmental Sciences*, **2**, no. 2, 2012, p. 96.
- [48] STEPNIAK, L., STANCZYK-MAZANEK, E., *Energies*, **15**, no. 5186, 2022, [https://www.researchgate.net/publication/362081620\\_Ultrasonic\\_Energy\\_as\\_an\\_Agent\\_to\\_Aid\\_Water\\_Treatment\\_in\\_the\\_Coagulation\\_Process](https://www.researchgate.net/publication/362081620_Ultrasonic_Energy_as_an_Agent_to_Aid_Water_Treatment_in_the_Coagulation_Process).
- [49] TAN, W.K., CHEAH, S.C., PARTHASARATHY, S., RAJESH, R.P., PANG, C.H., MANICKAM, S., *Chemosphere*, **274**, no. 129702, 2021, <https://www.sciencedirect.com/science/article/pii/S0045653521001715>.
- [50] CUI, M., CHOI, J., LEE, Y., MAB, J., KIM, D., CHOI, J., JANG, M., KHIM, J., *Chem. Eng. J.*, **317**, 2017, p. 404.
- [51] SHEMER, H., NARKIS, N., *Water Res.*, **39**, 2005, p. 2704.

- [52] HUA, B., WU, C., ZHANG, Z., WANG, L., *Ceram. Int.*, **40**, 2014, p. 7015.
- [53] ZHOU, X., ZHAO, J., LI, Z., LAN, J., LI, Y., YANG, X., WANG, D., *Ultrason. Sonochem.*, **28**, 2016, p. 376.
- [54] CHEN, W., SONG, X., QIN, F., *International Forum on Energy, Environment Science and Materials*, 2015, <https://www.atlantis-press.com/proceedings/ifeesm-15/25841163>.
- [55] VRONSKA, N., MALOVANYYY, M., KOVAL, I., STARCHEVSKYY, V., *Environmental Problems*, **1**, no. 1, 2016, p. 65.
- [56] BROEKMAN, S., POHLMANN, O., BEARDWOOD, E.S., CORDEMANS DE MEULENAER, E., *Ultrason. Sonochem.*, **17**, 2010, p. 1041.
- [57] YADAV, M., GOLE, J.V.L., *IJEST*, **13**, no. 1, p. 69.

Citation: Stefanescu, M, Ultrasonication for removal of organic micropollutants from water, *Rom. J. Ecol. Environ. Chem.*, **2022**, 4, no. 2, pp. 32-47.



© 2022 by the authors. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.Org/licenses/by/4.0/>).