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Reduction of sonificated pharmaceutical residues determined using gas chromatography, in terms of water resource management

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ABSTRACT

Pharmaceuticals can interact negatively in an uncontrolled and unpredictable manner with microorganisms and aquatic animals, and additionally pose a threat of contamination of drinking water sources. The purpose of the study was to determine the effectiveness of the decomposition of pharmaceutical residues contained in municipal wastewater, using an active ultrasonic field, in terms of water resource management. The novelty of this work is to demonstrate that there is a potential possibility of implementing technology based on the use of an ultrasonic field in the wastewater treatment process and, as a result, increasing the susceptibility to decomposition of diclofenac and ketoprofen present in municipal wastewater using the active action of an ultrasonic field with a high nominal power of 750 W and a low frequency of approximately 20 Hz at an ultrasonic field intensity of 1.72 Wcm^{-2}. Pharmaceuticals belonging to the group of non-steroidal anti-inflammatory drugs, i.e.: diclofenac and ketoprofen, were selected for the study. The degree of concentration reduction of selected pharmaceuticals was determined by quantitative analysis of pharmaceuticals present in municipal wastewater. It was observed that subjecting pharmaceuticals to exposure to ultrasounds influenced the decrease in their concentration. With the increase in the applied sonification time, a decrease in the toxicity of the tested pharmaceuticals was observed, i.e. for diclofenac, from 83 to 91% for 120 s and for ketoprofen from 94 to 99% for 240 s. It should be noted that the sonication of sewage sludge by initiating the phenomenon of ultrasonic cavitation and generating highly reactive hydroxyl radicals affects the reduction of selected pharmaceuticals, which determines the implementation of the tested technology on a larger scale.

Keywords: disintegration, sonification, non-steroidal anti-inflammatory drugs (NSAIDs), municipal wastewater, water resource management.

INTRODUCTION

Traditional technological systems of wastewater treatment plants do not guarantee sufficient removal of pharmaceuticals from the stream of wastewater flowing into the facility, so there is a potential risk of their release into the environment. Migration pathways of pharmaceuticals in the environment are shown in Figure 1.

Pharmaceuticals entering the water and wastewater environment undergo biotic, or abiotic, hydrolysis and photolysis processes. The main method of degradation of pharmaceuticals in the aqueous environment is photolysis (although some pharmaceuticals are resistant to its action, e.g. diclofenac) [3]. The intensity of the photodegradation process varies depending on the amount of UV radiation reaching the Earth's surface. Therefore, the intensity of photolysis depends on the season, length of day, latitude, cloud cover, amount of snow cover. Photodegradation of pharmaceuticals can occur, as a direct or indirect process. Direct photolysis involves an oxidation process, resulting in the formation of new chemical compounds or the breaking of existing chemical bonds. Indirect photolysis takes place

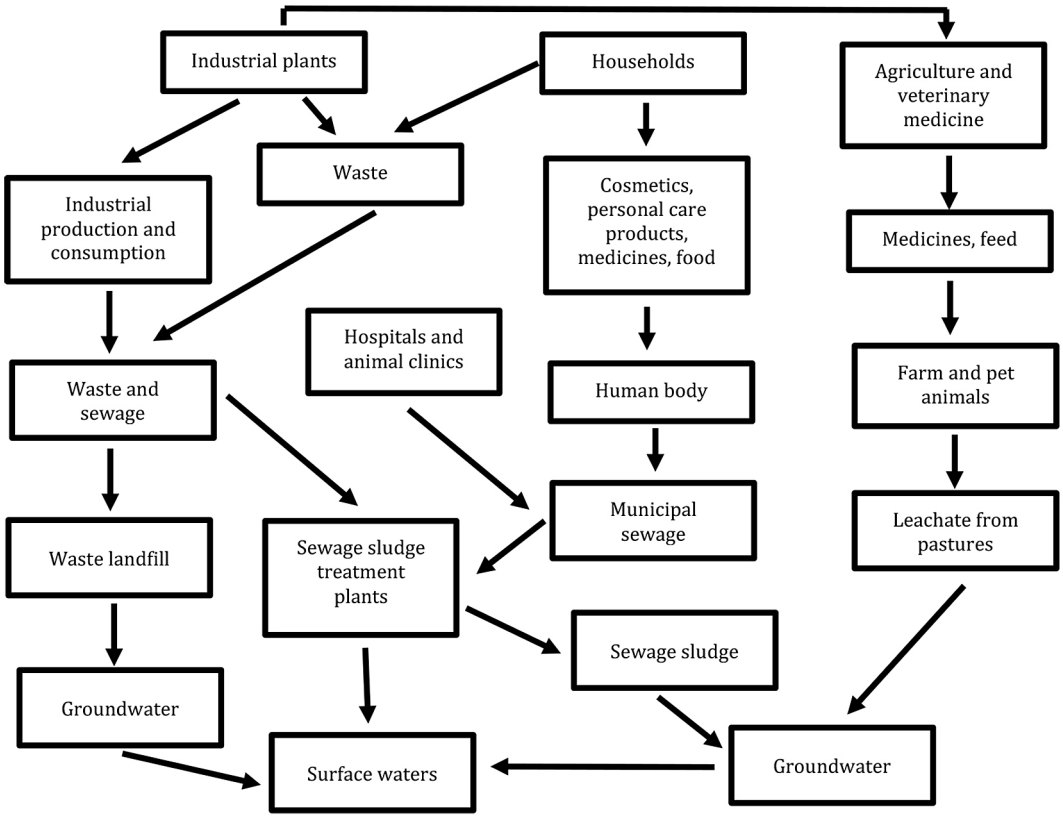


Figure. 1. Migration pathways of pharmaceuticals in the environment [1, 2]

under the influence of reactions with OH- radicals. In water and wastewater environments, both of these processes occur simultaneously. Other factors influencing the speed and intensity of degradation of pharmaceuticals in the environment are microorganisms, aquatic plants and humic substances [4]. Moreover, it is possible to use advanced oxidation methods to decompose hazardous and flame-retardant organic compounds [5].

At present, most water treatment plants work in a set pattern that includes sedimentation, coagulation and mechanical filtration. This technological sequence does not take into account the possibility of removing the newest contaminants, or so-called "emerging contaminants," which, due to the development of industry, agriculture, cosmetology and pharmaceuticals, end up in municipal wastewater [6–9].

The volume of pharmaceuticals is impressive, amounting to about 200,000 preparations worldwide. In domestic markets, it is estimated that the number of available preparations varies between 5.000 and 10.000 and depends on the size of the country, population, economic situation and market specifics [10]. The effect of excessive consumption of pharmaceuticals, especially refractory antibiotics, can have a significant impact on changes in the qualitative and quantitative composition of wastewater, as well as on the quality of surface water and drinking water [11–14]. Pharmaceuticals are assimilated by the body to some extent, and their residues and metabolites enter wastewater in urine and feces [15]. The main sources of water pollution by pharmaceuticals are households, pharmaceutical companies and hospitals [16, 17].

The most popular non-steroidal analgesic and anti-inflammatory drugs (NSAIDs) include salicylic acid derivatives, propionic acid derivatives and phenylacetic acid derivatives. NSAIDs are used for the relief of pain of various causes. They are administered during trauma, joint and muscle pain, as well as during and after surgical procedures. Due to their action, they are used as antipyretics. An important advantage of these pharmaceuticals is that they have a much weaker effect than narcotic painkillers such as opioids, and do not cause such frequent addiction. A major problem is consuming them in large quantities, which is not indifferent to the body. Like all synthetic pharmaceuticals, NSAIDs have numerous side effects. Since non-steroidal

anti-inflammatory drugs are a very broad group, the individual pharmaceuticals vary greatly in their structure [18, 19].

The presence of NSAIDs and their metabolites has been the subject of many studies both in European Union countries and around the world. In Finland, the most commonly used NSAID is ibuprofen. It is also the most abundant pharmaceutical-derived contaminant in wastewater.

A study of the Finnish area showed that the pharmaceuticals found in wastewater are mainly: ibuprofen 2.0–4.0 μgL^{-1}, naproxen 0.4–2.0 μgL^{-1}, ketoprofen 0.2–0.8 μgL^{-1}, diclofenac 0.2–1.3 μgL^{-1} [19, 20]. As already written, due to differences in structure within NSAIDs, these substances are not removed equally in wastewater treatment or water treatment. In water treatment, the highest purification efficiency was observed for ibuprofen and ranged from 84 to 99%, while the lowest for diclofenac, from 9% to 43% [21].

An attempt to study the phenomenon of pharmaceutical residues in the water and wastewater environment has also been made in South America. The removal rate of individual pharmaceuticals in treated wastewater from 10 wastewater treatment plants located in Brazil ranged from 12 to 90%. As a result of the incomplete elimination of pharmaceutical residues from wastewater during the treatment process, they are present in the treated wastewater and enter the environment. This has resulted in the contamination of the country's main 18 rivers. In the waters around Rio de Janeiro, the average concentration of NSAIDs ranged from 0.02 µgL to 0.04 $\mu g/L^{-1}$ in river waters, with maximum values observed up to 0.5 μgL^{-1}. The most common substances were ibuprofen 0.1 μgL^{-1} naproxen 0.2 μgL^{-1}, ketoprofen 0.2 μgL^{-1}, and diclofenac 0.2 μgL^{-1} [22].

The first published study of the state of water in Germany in 1998 confirmed that more than 32 pharmaceuticals from various groups were present in rivers and surface waters. Due to incomplete treatment of wastewater flowing through treatment plants, more than 80% of these substances are found in German rivers [23, 24]. The most commonly labeled NSAIDs are: ibuprofen 0.5–0.2 μgL^{-1}, naproxen 0.05–0.22 μgL^{-1}, ketoprofen 0.1–0.2 μgL^{-1}, diclofenac 0.2–0.7 μgL^{-1} [25].

Also in Switzerland, attention has been drawn to the danger of inadequate treatment of pharmacutical wastewater. A detection trial of five analgesic pharmaceuticals was conducted in Lausanne: mefenamic acid, ibuprofen, ketoprofen, diclofenac and clofibric acid. The study was conducted at three wastewater treatment plants, and the concentrations of the pharmaceuticals tested ranged from 0.5 μgL^{-1} to 2.0 μgL^{-1}. The average treatment efficiency ranged from 50% for mefenamic acid to 80% for ibuprofen [26].

In the UK, studies were conducted on 12 pharmaceutical compounds and their metabolites [27]. The pharmaceuticals selected for the monitoring program were ranked and selected using a previously developed ranking procedure that determined which substances had the greatest potential risk to the aquatic environment. NSAIDs detected included mefenamic acid 0.133 μgL^{-1}, dextropropoxyphene 0.195 μgL^{-1}, ibuprofen 3.086 μgL^{-1}, diclofenac 0.424 μgL^{-1}, and paracetamol 3.0 μgL^{-1} [28, 29].

A study conducted in Romania detected 15 pharmaceutical compounds, including parent pharmaceuticals, intermediate compounds, metabolites, fragrances and musk. The listed substances were detected in concentrations ranging from 0.03 μgL^{-1} to 10μgL^{-1}. The detected pharmaceuticals can be arranged according to their purpose into the following groups: analgesic pharmaceuticals, antiepileptic pharmaceuticals, psychiatric pharmaceuticals, stimulants, anticoagulants, anticancer pharmaceuticals and disinfectants. In general, it should be stated that in most European countries, the most abundant group of pharmaceutical substances in wastewater are non-steroidal anti-inflammatory drugs [29]. In order to highlight the problem of the significant impact of pharmaceuticals on the environment and the functioning of living organisms, Table 1 lists commonly used pharmaceuticals and their intended use, which clearly indicates the need to take actions to reduce this negative impact.

Advances in laboratory methodology have made it possible to detect the presence of micropollutants in the aquatic environment even at very low concentrations, on the order of a few nanograms per liter. Many of these substances are potentially dangerous because micropollutants can have direct or indirect effects on ecosystems and their negative impacts can be both immediate and chronic, such as the intersex of fish. Micropollutants accumulate in the trophic chain as a result of which they reach the human body, posing a potential threat to its functioning. Progressive contamination of waters with the aforementioned substances can therefore have an increasing negative impact on human health and life.

Table 1. Selected groups of pharmaceuticals and their use [30]

A group/class of compounds	Compound
Antibiotics used in animals and humans	trimethoprim, erythromycin, lincomycin, sulfametaxol, chloramphenicol, amoxicillin
Anti-inflammatory medicines and painkillers	ibuprofen, diclofenac, fenoprofen, acetaminophen, naproxen, acetylsalicylic acid, fluoxetine, ketoprofen, indomethacin, paracetamol
Psychotropic drugs	diazepam, carbamazepine, primidone, salbutamol
Anticancer drugs	cyclophosphamide, ifosfamide
Sympathomimetic drugs	albuterol
Regulators of fat metabolism	clofibrotic acid, bezafibrate, fenofibrate, etofibrate, gemfibrozil
β-blockers	metoprolol, propranolol, timolol, sotalol, atenolol
Contrast agents used in X-rays	Iohexol iopromide, iopamidol, diatrizan
Steroids and hormones	dihydrotestosterone, progesterone, estradiol, estrone, cholesterol, coprostanol, estriol, diethylstilbestrol, ethinylestradiol

It should be noted that there are no documents in Polish and European, or even global, legislation that standardize the permissible concentrations of specific pharmaceuticals delivered to wastewater treatment plants.

Due to the limited effectiveness of conventionally used technologies in the aspect of removing the so-called "emerging contaminants", it is necessary to look for new ways of wastewater treatment and water treatment. Highly efficient methods of purification and treatment of municipal wastewater such as membranes, nanofiltration, activated carbons, osmotic processes, sonification and UV radiation can be a solution [7, 8].

Exposure of organic micropollutants (NOCs) in the ultrasonic field lead to the decomposition of these substances and reduce their harmful toxic effects. In view of this, ultrasonic decomposition of pharmaceutical contaminants may be the optimal method for removing pharmaceuticals from wastewater.

An important phenomenon affecting the occurrence of sonolysis and, consequently, the decomposition of pharmaceutical residues is ultrasonic cavitation. Cavitation is a physical phenomenon, occurring only in liquids, involving a sudden phase transformation from the liquid phase to the gas phase under the influence of a decrease in pressure. If the liquid suddenly accelerates according to the principle of conservation of energy, the static pressure of the liquid decreases. This phenomenon can be observed, for example, on the surface of a ship's propeller, or during ultrasound [31]. Ultrasonic cavitation involves the creation of pulsating bubbles in a liquid by an ultrasonic wave. Cavitation bubbles appear due to local ruptures of the continuous medium under the influence of large tensile forces, occurring during the dilution phase of the wave. The spherical bubbles formed at the sites of ruptures in the medium are filled, by inward diffusion, with molecules of vapor of saturated liquid or gas dissolved in it. The formation and collapse of bubbles is the source of local shock waves propagating in the liquid, and at a constant intensity of the ultrasonic wave, a state of dynamic equilibrium is reached, between the bubbles that are formed and those that collapse. The cavitation phenomenon occurs only when the intensity of the ultrasonic wave reaches and exceeds a certain threshold value, the so-called cavitation threshold. The threshold value of the intensity depends on the type of liquid, the frequency of the wave and the presence of microscopic impurities and gas molecules in the liquid, which act as a foothold for the formation of cavitation bubbles [31, 32]. Figure 2 shows the mechanism of cavitation bubble growth.

In the course of solution supersaturation, three areas are formed in which cavitation-initiated reactions can occur, these are the cavitation bubble, the interfacial boundary (gas-liquid interface) and the solution proper [34]. The degradation processes taking place differ among these three zones. In some studies, hydrophilic and nonvolatile compounds were found to degrade mainly in solution, while hydrophobic, non-polar and volatile compounds reacted in all three zones. Diclofenac is a hydrophilic and non-volatile compound, so the interaction of the OH-radical on the diclofenac molecule in solution proper is considered the main reaction occurring in the ultrasound field [35]. The first area is the interior of the collapsing cavitation bubble,

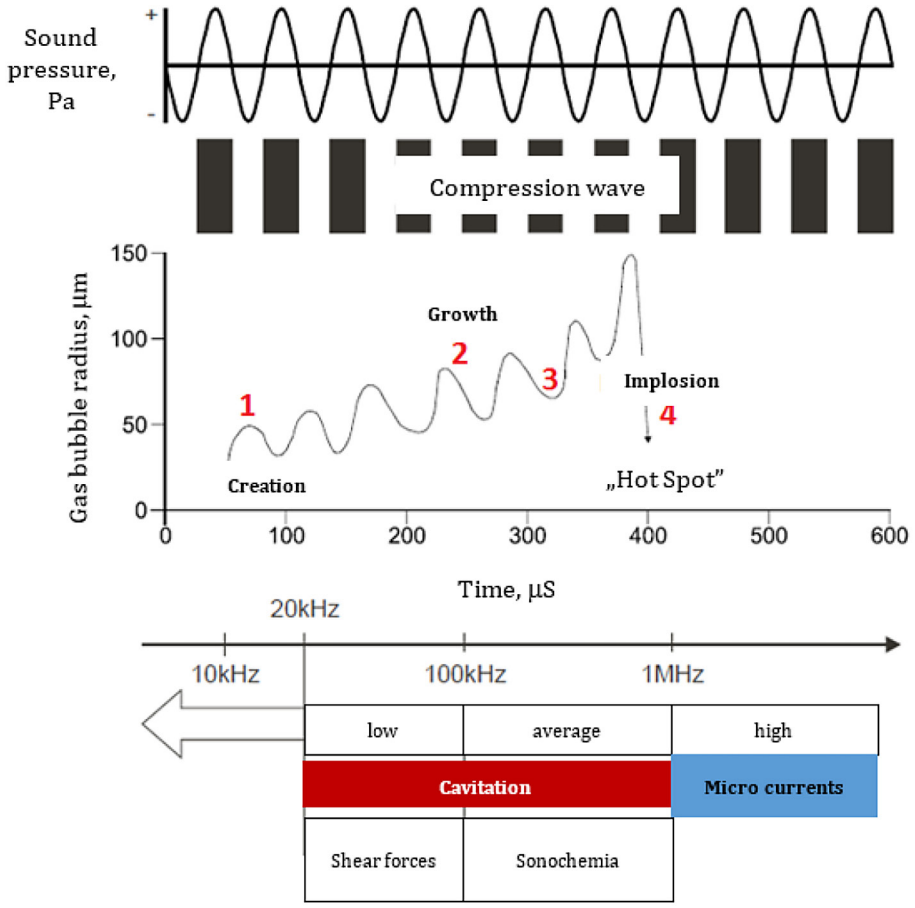


Figure 2. Mechanism of cavitation bubble formation: 1 – cavitation cave formation, 2,3 – gradual growth, 4 – cavitation cavitation cave implosion [33]

where the temperature is several thousand K and the pressure reaches several hundred atmospheres. Thermal dissociation of water results in the formation of hydroxyl radicals and hydrogen atoms, which react with substances present in the gas phase [31]. The second area is the gas-liquid interface, the area between the collapsing cavitation bubble and the solvent, where temperature and pressure are high. An important factor affecting this process is hydrophobicity, which determines the ability to accumulate at the gas-liquid interface. The greater the hydrophobicity of the solution, the more thermal decomposition products are formed [31, 36].

In the third area, in solution with unchanged ambient temperature, free radicals formed in cavitation bubbles that have not reacted in the boundary zone react with the solute in solution to give products similar to those present in water radiolysis [37]. In solution, mechanochemical degradation of macrostructures can occur as a result of shear forces generated around collapsing cavitation bubbles. Hydrodynamic shear does not significantly affect small molecules, but is capable of damaging macromolecules, such as breaking polymer chains [38, 39].

According to Li et al. [40] sonochemical reactions take place mainly inside the cavitation bubbles and at the interfaces. Studies indicate that sonochemical phenomena occur not only at low frequencies, but also between 100–1000 kHz, the optimal frequency is substrate-specific.

Under these conditions, sonochemical reactions take place leading to chemical transformations of organic compounds by generating radicals, hydrogen peroxide and ozone, according to the following reactions (1÷5):

$$H_2O \rightarrow H^{\circ} + HO^{\circ} \quad (1)$$

$$O_2 \rightarrow 2\,O \quad (2)$$

$$HO^{\circ} + O \rightarrow HOO^{\circ} \quad (3)$$

$$O_2 + O \rightarrow O_3 \quad (4)$$

$$2\,HO^{\circ} \rightarrow H_2O_2 \quad (5)$$

The purpose of the study was to determine the decomposition efficiency of pharmaceutical residues contained in municipal wastewater, subjected to an active ultrasonic field, an important environmental problem in terms of water resources management. Gas chromatography coupled with mass detection was used for the study. Pharmaceuticals belonging to the group of non-steroidal anti-inflammatory drugs (NLPs), i.e.: diclofenac and ketoprofen, whose residues are commonly found in municipal wastewater, were selected for the study. The reduction rate of the selected pharmaceuticals was determined by quantitative analysis of pharmaceuticals found in municipal wastewater.

High frequency and low-power ultrasounds show a lower degree of compounds degradation compared to lower-frequency and high-power ultrasounds [41].

The sonication of sewage sludge by initiating the phenomenon of ultrasonic cavitation and generating highly reactive hydroxyl radicals affects the reduction of selected pharmaceuticals, which determines the implementation of the tested technology on a larger scale.

The novelty of this study is the demonstration of the enhanced susceptibility to the decomposition of diclofenac and ketoprofen present in municipal sewage in using the active action of an ultrasonic field with a high nominal power of 750 W and a low frequency of approximately 20 Hz with an ultrasonic field intensity of 1.72 Wcm^{-2}, which is a potential premise for the implementation of the tested technology in the wastewater treatment process.

THE EXPERIMENTAL PART

Research materials

The study involved wastewater from a mechanical-biological wastewater treatment plant that used advanced methods to remove nutrients. Selected physical and chemical parameters were analyzed on the day of collection and repeated three times, with standard deviations determined. Table 2 presents the concentration values of selected pollutants present in municipal sewage.

For the study, 2 pharmaceuticals were selected from the NSAID group: diclofenac and ketoprofen, which exhibit toxic effects on aquatic organisms and the environment. Diclofenac has a water solubility of 2.4 mgL^{-1}, while ketoprofen has a water solubility of 51 mgL^{-1}. The biological half-life, of the tested pharmaceuticals is for diclofenac 2 h, while for ketoprofen it is in the time range of 1.5÷2.5 h. For the conducted tests, the initial concentration of diclofenac and ketoprofen in the samples of municipal sewage was in the range of 9.2 to 21 mgL^{-1}. Table 3 shows the general characteristics of the pharmaceuticals selected for testing [42].

Table 2. Concentrations of pollutants in the tested sewage

Types of pollution	Pollutant concentrations, mg m^{-3}
BOD_5	257
SCOD	619
Suspension	354
Total nitrogen	94
Total phosphorus	7

Sonification conditions

Samples of constant volume and pharmaceutical concentration were subjected to an active ultrasonic field using a SONIC generator named Vibra- cell VC750. The SONIC generator's operating parameters were chosen in this way: power of 750 W, a frequency of 20 kHz and an ultrasonic field intensity of 1.72 Wcm^{-2}. Sonication times of 120 and 240 seconds were used. The ultrasonic disintegration process was conducted under static conditions with the vessel filled once. The volume of the modified sediment sample was 0.5 L. The intensity of the ultrasonic wave was calculated from the following relationship [43]:

$$I_a = \frac{E_a}{S \cdot t_s} \tag{6}$$

where: I_a – ultrasonic wave intensity, Wcm^{-2},
E_a – amount of energy delivered, J,
S – cross–sectional area of the vessel inside which the sonicated sample was placed, cm^{-2}, t_s – sonication time, s.

Gas chromatography conditions

Gas chromatography coupled with mass detection (Agilent 7890A Gas Chromatograph) was used for the study. Quantitative analysis of pharmaceuticals dissolved in aqueous solutions was

Table 3. The characteristics of the pharmaceuticals selected for testing

Name	Synonyms	CAS	Formula	Molecular mass, $gmol^{-1}$
Diclofenac	Diclofenac acid, dichlofenac	15307-86-5	$C_{14}H_{11}Cl_2NO_2$	296.10
Ketoprofen	Orudis	22071-15-4	$C_{16}H_{14}O_3$	254.28

carried out. The changes in the concentration of pharmaceuticals in the samples before and after the sonification process were compared. Pharmaceuticals were examined using chromatography after prior sample preparation: centrifugation, filtration, and solid phase extraction (SPE) [44].

The electrospray ionization (ESI) source was operated in positive ion mode for ibuprofen (IBU), and ketoprofen (KET). Table 4 shows the optimized mass spectrometer parameters for the analysis of selected pharmaceuticals.

The conditions of the chromatographic study are shown in Table 5. A "split" mode was used in which only a portion of the sample introduced into the gas chromatograph (GC) hits the chromatographic column, while the remaining sample is removed through a side outlet, which allows the analysis of high-concentration samples. The study used a gas chromatograph equipped with a split-splitless injector, a 30 m-long Agilent capillary column with an inner diameter of 0.32 mm with a film thickness of 1 μm.

RESULTS AND DISCUSSION

During tests on the effectiveness of conditioning using an active ultrasonic field as an agent for degrading the structure of pharmaceuticals, gas chromatography studies were performed to determine the degree of reduction in the concentration of selected pharmaceuticals. Seven test runs were conducted for each pharmaceutical. Both pharmaceuticals were sonificated for 120s and 240s, and the results were compared with non-sonificated samples.

In the first test series, the concentration of diclofenac in the unsonificated samples was 14.2 mgL^{-1}, and in the sample sonificated for 120s, the concentration dropped to a value of 1.29mgL^{-1}. For the 240s sonification, there was a more than 99% reduction in concentration, which fell below the 0.1 mgL^{-1} value. In the second series, there was a decrease in concentration from 12.1 mgL^{-1} to 1.12 mgL^{-1} (120s) and 0.15 mgL^{-1} (240 s). In the next study series, a reduction in diclofenac concentration was observed from 15.1 mg/L to 1.6 mgL^{-1} (120 s) and 0.23 mgL^{-1} (240 s). In the 4th test series, the diclofenac concentration decreased from 21mgL^{-1} to a value of 0.88mg/L as a result of 240 s over-sounding. In the 5th and 6th series, there was a reduction in diclofenac concentration from 17 mgL^{-1} to 1.12 mgL^{-1} and from 13 mgL^{-1} to 0.45 mgL^{-1}, respectively. The smallest decrease in diclofenac concentration was observed in the last study series, in which the concentration dropped from 9.2 mgL^{-1} to 1.58 mgL^{-1} for 120s sonification and to 0.69 mgL^{-1} for 240s sonification. The average reduction in diclofenac concentration for 120s sonification time was 87.46% and 96.4% for 240s sonification time of the sample.

Assuming a 95% confidence interval, the percentage of concentration reduction can be determined to be 94.05–98.75% for the longest sonification time.

The results obtained by Meriem Sandaoui et al. [46] showed that 78.93% degradation rate of pharmaceutical solution containing both gentamicin sulfate and parabens was obtained for optimized parameter values, i.e. ultrasound power 90 W, exposure time 120 min, temperature 25 C ± 2, natural pH 4.7, probe immersion depth 40 mm.

So far, there is not much information on the ultrasonic degradation of ketoprofen. Successful degradation of ketoprofen has been observed in AOP (advanced oxidation processes), combining

Table 4. Optimized mass spectrometer parameters for the analysis of selected pharmaceuticals

Analyte	Precursor ion Q1 (m/z)	Fragment ion Q3 (m/z)	Declustering potential DP (V)	Entrance potential EP (V)	Collision energy CE (V)	Collision cell exit potential CXP (V)
ESI+						
DIK	294.1	249.9	-45	-12	-16	-13
KET	252.9	208.7	-30	-5	-10	-15

Table 5. Chromatographic conditions [45]

Conditions GC	
Column	Agilent DB5-MS325 °C (30 m/0.32 mm id/1 μm d_f)
The column temperature:	35 °C
Injection program:	Split (distribution wsp. 2:1)
Injection volume:	2 μL
The constant flow rate of the mobile phase:	1.5 mLmin^{-1}
Pressure:	4.3174 psi
Oven temperature program: Helium injection program:	from 100 °C (0 min) to 260 °C 15 °C/min in total 15.667 min Split
Conditions MS (full scan mode)	
Program:	Scan/SIM
Measurement range:	100–350 amu
Sampling frequency:	2 (scanning speed about 4 scans/s)
Solvent delay time:	3.50 min
MS Temperature:	230 °C (Source) 150 °C (Quadrupol)

UV irradiation, chemical additives such as H_2O_2, Fenton reaction and ultrasonic field. It has been observed that the use of ultrasound increases the formation of radicals, including hydroxyl radicals [47]. Since sonification is also among the processes of advanced oxidation, it is possible, based on the known mechanisms of ketoprofen degradation in other processes (AOP), to assume a similar mechanism of ultrasonic degradation of ketoprofen. In addition, it is known that there are two main mechanisms for the removal of organic impurities during sonolysis: radical reactions of $H^{\bullet}$, $OH^{\bullet}$ radicals formed during water sonolysis.

The wet oxidation is a promising method for the highly efficient degradation of pharmaceutical sludge, the highest removal efficiencies of VSS 86.8% and COD 62.5% were achieved at 260 °C for 60 min with an initial oxygen pressure of 1.0 MPa and initial COD 15,000 mg·L^{-1} [48].

According to Xiaohui Lu et al. [49] the combination of ultrasound with other oxidation methods has a synergistic effect on degradation. The combination of AOP and ultrasound requires large energy inputs, especially with respect to the stand-alone AOP methods. Therefore, the implementation of ultrasound with a specific effect that is economically acceptable is still a serious scientific and technological problem.

The concentration values of diclofenac in the samples are shown in Table 6.

In the first test series, the concentration of ketoprofen in the unsonificated samples was 12 mgL^{-1} and in the sample sonificated for 120s, the concentration dropped to a value of 1.01 mgL^{-1}. For the 240 s sonification, there was a more than 99% reduction in concentration. which fell below the value of 0.1 mgL^{-1}. In the second series, there was a decrease in concentration from 10.5mgL^{-1} to 0.94 mgL^{-1} (120 s) and 0.1 mgL^{-1} (240 s). In the 3rd study series, a reduction in ketoprofen concentration was observed from 12.3 mgL^{-1} to 1.47 mgL^{-1} (120 s) and 0.15 mgL^{-1} (240 s). In the 4th test series, ketoprofen concentration decreased from 15 mgL^{-1} to a value of 0.51 mgL^{-1} as a result of 240 s over-sounding. In the 5th and 6th series, there was a reduction in ketoprofen concentration from 13 mgL^{-1} to 0.84 mgL^{-1} and from 8.8 mgL^{-1} to 0.25 mgL^{-1}, respectively. The smallest decrease in ketoprofen concentration was observed. as in earlier studies on diclofenacim, in the last study series, in which the concentration dropped from 4.9 mgL^{-1} to 0.44 mgL^{-1} for 120 s sonification and to 0.33 mgL^{-1} for 240 s sonification. The average reduction in ketoprofen concentration for 120 s sonification time was 89.59% and 96.79% for 240 s sonification time of the sample. Assuming a 95% confidence interval, the percentage of concentration reduction can be determined to be 94.58–99.00% for the longest over-sounding time.

As reported Meriem Sandaoui et al. [46] the results revealed a considerable increase in the rate of degradation of pharmaceutical solution during the first 120 min of sonolysis (74.92%), then degradation progressed slowly between 120 min and 240 min, achieving (88.1%) at the end.

Table 6. Diclofenac concentration values in unmodified and sonificated samples for 120 and 240 s

Series	Diclofenac				
	Unmodified wastewater samples	Sonification 120 s		Sonification 240 s	
	Concentration, mgL^{-1}	Concentration, mgL^{-1}	Concentration reduction, %	Concentration, mgL^{-1}	Concentration reduction, %
1	14.2	1.29	90.91	<0.1	99.29
2	12.1	1.12	90.74	0.15	98.76
3	15.1	1.6	89.40	0.23	98.48
4	21	2.13	89.85	0.88	95.81
5	17	3.46	79.65	1.12	93.41
6	13	1.45	88.85	0.45	96.54
7	9.2	1.58	82.83	0.69	92.5
$\bar{x}$	-	-	87.46	-	96.4
σ	-	-	4.08	-	2.47
P	-	-	83.58–91.34	-	94.05–98.75

Note: $\bar{x}$ average value, σ standard deviation, P confidence interval.

Over sonification of diclofenac solution causes the release of Cl^- ions. The concentration of released Cl^- ions formed by sonification corresponds to the first-order growth curve. Since there are two chlorine atoms in each diclofenac molecule, this indicates, that during the ultrasonic degradation of diclofenac, the first and main reaction is dechlorination [50]. The concentration values of ketoprofen in the samples are shown in Table 7.

On the basis of the obtained test results, it was observed. that the exposure of pharmaceuticals to the ultrasonic field contributed to changes in the concentration of the tested substances (for each tested supersonic time). It was noted, that the longer the sample exposure time in the ultrasonic field was used, the decrease in toxicity was more significant: from 83–91% for 120 s sonification. up to 94–99% for 240 s exposure.

Chemical methods may provide an alternative to sonochemical degradation of pharmaceuticals in wastewater. In this regard, it is possible to use one of the strongest oxidants, peroxymonosulfate (PMS), in combination with cobalt ferrite materials to degrade sulfamethoxazole. As a result of this process, an approximately 81% reduction

Table 7. Ketoprofen concentration values in samples unmodified and sonificated for 120 and 240 s

Series	Ketoprofen				
	Unmodified wastewater samples	Sonification 120 s		Sonification 240 s	
	Concentration, mgL^{-1}	Concentration, mgL^{-1}	Concentration reduction, %	Concentration, mgL^{-1}	Concentration, mgL^{-1}
1	12	1.01	91.58	0.1	99.16
2	10.5	0.94	91.05	0.1	99.04
3	12.3	1.47	88.05	0.15	98.78
4	15	1.56	89.6	0.51	96.6
5	13	1.99	84.69	0.84	93.54
6	8.8	0.78	91.14	0.25	97.16
7	4.9	0.44	91.02	0.33	93.26
$\bar{x}$	-	-	89.59	-	96.79
σ	-	-	2.29	-	2.32
P	-	-	87.41–91.77	-	94.58–99.00

Note: $\bar{x}$ – average value, σ – standard deviation, P – confidence interval.

in the concentration of this pharmaceutical was achieved after 60 seconds of exposure [51].

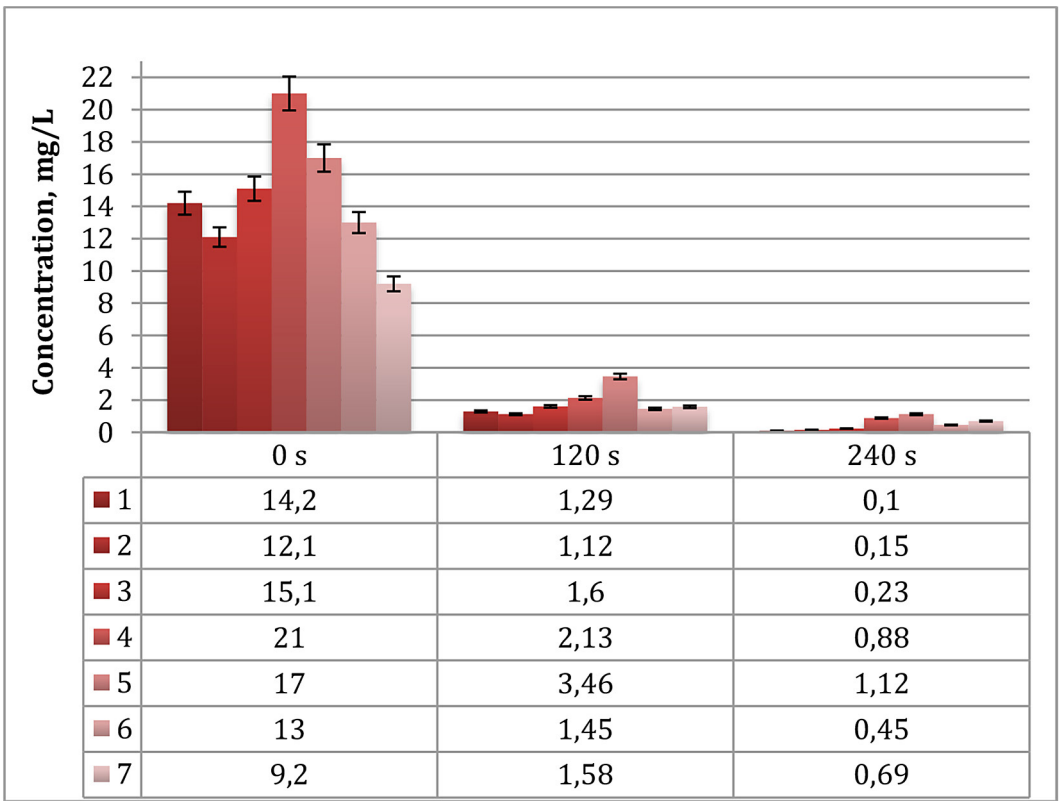
Er Nie et al. [52] found that ultrasonic waves are an effective method for diclofenac degradation. At different H_2O_2 concentrations in air, oxygen, argon and nitrogen saturated conditions, first-order degradation constants of diclofenac were determined in three zones: bulk solution, cavitation bubble and supercritical interface. Complete mineralization of nitrogen occurred in air, oxygen and argon saturated conditions, but no mineralization of nitrogen occurred in nitrogen saturated conditions. However, partial mineralization of carbon was noted in four gas saturated conditions. It was proven that in the case of diclofenac degradation, the cavitation bubble and supercritical interface are important elements determining the degradation, which is as effective as the degradation with OH in bulk solution.

Active interaction of the ultrasonic field, causing a local increase in pressure and temperature, and especially the phenomenon of ultrasonic cavitation, directly responsible for the decomposition of pharmaceutical residues [53, 54].

A comparison of the changes in the concentration values of non-steroidal anti-inflammatory pharmaceuticals for the tested sonification times in successive test series is shown in Figures 3 and 4.

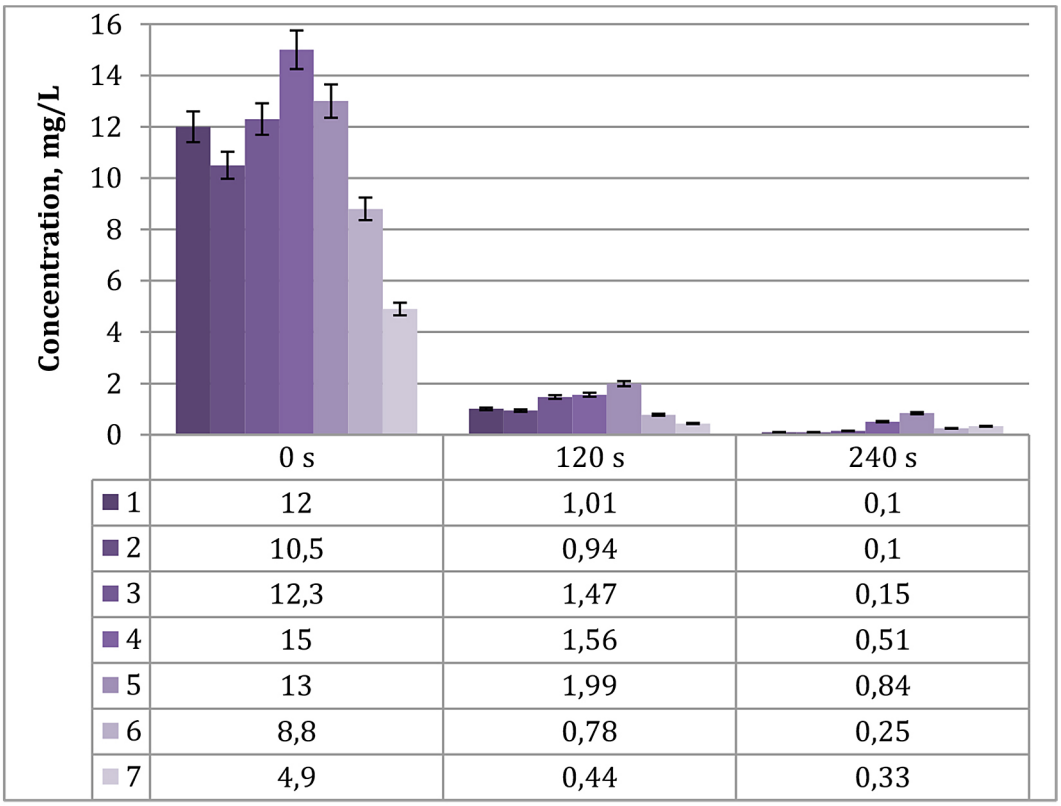
Heberer et al. [55] obtained a diclofenac elimination rate of 17%. While Quintana et al. [56] presented a diclofenac reduction of 23–30% in the municipal wastewater treated by a membrane bioreactor. Andreozzi et al. [57] presented results indicating large changes in diclofenac removal rates. On the order of 75%. Ternes [1] indicated, that diclofenac can be removed with up to 75% efficiency, a similar result was obtained by Sternn et al. [58] 53–74% and Roberts and Thomas [59] 71%. Strumpf et al. [22] determined a reduction in ketoprofen of 48–69%. In 2005, Strumpf's results were confirmed by a study by Quintana et al. [56], which obtained a reduction rate in the rather wide range of 62±21%. Thomas and Foster [60] put the elimination rate of ketoprofen at 98%.

The collected data indicate the need for more efficient removal of pharmaceuticals and other micropollutants from wastewater. Significant discrepancies. contained in the literature reports on this important from the aspect of water resources management. research problem. justify conducting research using an ultrasonic field. as a factor to ensure a moderate, but steady and reproducible



	0 s	120 s	240 s
1	14,2	1,29	0,1
2	12,1	1,12	0,15
3	15,1	1,6	0,23
4	21	2,13	0,88
5	17	3,46	1,12
6	13	1,45	0,45
7	9,2	1,58	0,69

Figure 3. Changes in concentration values (average of 7 series) of diclofenac in successive test series. For unmodified sludge and those treated with UD field for 120 and 240 s



	0 s	120 s	240 s
1	12	1,01	0,1
2	10,5	0,94	0,1
3	12,3	1,47	0,15
4	15	1,56	0,51
5	13	1,99	0,84
6	8,8	0,78	0,25
7	4,9	0,44	0,33

Figure 4. Changes in concentration values (average of 7 series) of ketoprofen in successive test series. For unmodified sludge and those treated with UD field for 120 and 240 s

decrease in the concentration of selected pharmaceuticals in municipal wastewater.

The costs of construction and operation of sewage treatment plants are very high, therefore economic conditions force facility operators to search for technologically and economically effective solutions. It should be noted that ultrasonic disintegration is an energy-intensive technology, therefore it is necessary to conduct a technical and economic analysis before its implementation, taking into account the desired effect of disintegration, the efficiency of the installation, the operating costs of the disintegration installation, the balance of costs related to effective modification of sewage in terms of the decomposition of the pharmaceuticals tested. It should be emphasized that the use of sonification to support the removal of selected pharmaceuticals from wastewater is a promising solution, especially due to the lack of harmful by-products of disintegration with the ultrasonic field. To sum up, according to Li Zhu et al. [61] due to its simplicity, ease of use and environmental friendliness resulting from the lack of secondary environmental pollution. The disadvantages of the proposed solution include high energy losses and purification efficiency requiring process optimization, which hinders wider industrial application.

CONCLUSIONS

The need to eliminate pharmaceutical residues from wastewater takes on a new, crucial importance in terms of water resources management. Preventing the spread of micropollutants in the aquatic environment, such as pharmaceutical residues, among others, requires the implementation of rapid measures to upgrade conventionally operating wastewater treatment plants, or the implementation of innovative solutions in their technological cycle, ensuring a high degree of elimination.

During tests on the effectiveness of conditioning using an active ultrasonic field, as an agent for degrading the structure of pharmaceuticals. tests were performed using gas chromatography to determine the degree of reduction of selected pharmaceuticals.

Based on the research conducted, the following conclusions were drawn:

- The subjecting the pharmaceuticals to exposure in the ultrasonic field affected the

concentration value of the tested substances (for each tested overblowing time).

- It was observed. that the exposure of pharmaceuticals to the ultrasonic field contributed to changes in the concentration of the tested substances (for each tested supersonic time). The longer the sample exposure time in the ultrasonic field was used, the decrease in toxicity was more significant: from 83–91% for 120s sonification. up to 94–99% for 240 s exposure.
- Ketoprofen - the most favorable exposure time of 240s. a reduction in the concentration value of ketoprofen was recorded from 12 mgL^{-1}, for unmodified samples, to 0.1 mgL^{-1}, indicating a decrease in concentration of about 99.16%
- Diclofenac – the most favorable exposure time of 240 s. there was a reduction in the concentration value of diclofenac from 14.2 mgL^{-1}, for unmodified samples, to 0.1 mgL^{-1} for samples subjected to 240 s sonification, indicating a decrease in concentration of about 99%.

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