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Department of Materials and Environmental Technology

ENHANCED SONOCHEMICAL DEGRADATION OF CHLOROPHENE

KLOROFEENI INTENSIIVISTATUD SONOKEEMILINE LAGUNDAMINE

MASTER THESIS

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AUTHOR'S DECLARATION

Hereby I declare, that I have written this thesis independently.
No academic degree has been applied for based on this material.
All works, major viewpoints and data of the other authors used in this thesis have been referenced.

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PREFACE

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Valeria Budarova

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List of Abbreviations

AOPs	advanced oxidation processes
BDD	boron-doped diamond
CP	chlorophene
DBPs	disinfection by-products
DOC	dissolved organic carbon
DR	2-deoxy-D-ribose
ECs	emerging contaminants
EI	electron-impact ionization
EU	European Union
GC-MS	gas chromatography-mass spectrometry
HAAs	haloacetic acids
HPLC	high performance liquid chromatography
IC	ion chromatography
K_{ow}	n-octanol/water partition coefficient
LD_{50}	lethal dose, 50%
LOEL	low observed adverse effect level
m/z	mass-to-charge ratio
MDA	malondialdehyde
NIST	National Institute of Standards and Technology
NOEL	no observed adverse effect level
REDOX	reduction-oxidation reaction
TBA	2-thiobarbituric acid
t-BuOH	tert-butanol
TCA	trichloroacetic acid
THMs	trihalomethanes
TOC	total organic carbon
US	ultrasound
USEPA	United States Environmental Protection Agency
UV	ultraviolet
VOCs	volatile organic compounds
w/v	weight per volume

Introduction

The pollution of water bodies with disinfection and personal care products is of a major concern as most of these compounds are toxic and resistant to biodegradation. Chlorophene (CP) is a widely used disinfectant, which is commonly applied in hospitals, households and livestock breeders. Because of its widespread application, chlorophene is inevitably discharged into the environment. Due to its low biodegradability chlorophene could enter surface and ground waters. That results overwhelmingly in long-term negative consequences to aquatic biota and thus could upset the balance of ecosystems. In view of this, there is interest in new technologies to remove chlorophene from the environment.

Advanced oxidation processes (AOPs) are successfully used for the treatment of contaminated water with chlorophenols. They attract increasing interest due to the high oxidization capacity of hydroxyl radicals (HO•). This radical is able to decompose organic compounds presented in water systems to readily biodegradable and less toxic compounds. Hydroxyl radicals can be produced using various methods, such as electrolysis, ozonation, ultraviolet radiation etc.

In recent years, the mechanical energy in the form of ultrasonic vibration has been considered as a novel potential source for generation of •OH. This chemical reactivity is produced via cavitation bubble collapse under the extreme conditions within the gaseous phase (Mason and Lorimer, 2002). As a result of water decomposition highly reactive species like hydroxyl (HO•) and hydroperoxyl (HO$_2$•) radicals are released into the solution resulting in oxidation of organic pollutants. The cavitation bubbles are formed in turn through the sequence of compression and rarefaction cycles in liquid media induced by powerful ultrasound.

In the present work, chlorophene was chosen as a model contaminant to study the sonochemical degradation of organic pollutants using different enhancement methods such as Fenton-mediated processes or H•-scavenging by the addition of carbon tetrachloride (CCl$_4$). The treatment with the mere Fenton process and its combination with sonolysis were compared. The enhancements of chlorophene degradation rate in the presence of CCl$_4$ as H - radical scavenger was also evaluated.

The concentration of chlorophene was analyzed on high performance liquid chromatography (HPLC). Ion chromatography (IC) and gas chromatography-mass spectrometry (GC-MS) were used to identify intermediates during chlorophene degradation and according to that the possible reaction pathway was proposed.

1 Literature Review

1.1 Chlorophene and its application

Chlorophene (o-benzyl-p-chlorophenol) is a halogenated phenolic compound, which is referred to the group of chlorophenols. It is manufactured in the USA by Monsanto Company under the trade name Santophen® 1 germicide and by several other manufacturers in Europe (Figure 1) (Werner *et al.*, 1983). For the first time it was registered in the United States in 1948 as disinfectant. Chlorophene has sodium and potassium salts, which are used as tuberculocides, virucides and fungicides (USEPA, 1995). The United States Environmental Protection Agency (USEPA) considered chlorophenols as a particular group of priority toxic pollutants (Rayaroth *et al.*, 2015).
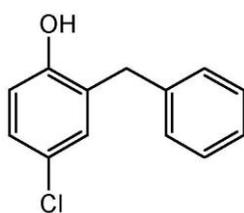
Figure 1. Structural formula of the o-benzyl-p-chlorophenol

Chlorophenols are organic compounds, widely used as preservatives or disinfectants for wood, paints, vegetable fibers and leather. Also they are applied as raw materials or synthesis intermediates in the production of dyes and pharmaceuticals (He *et al.*, 2011). Their application as disinfectants also known for farm premises, poultry houses, food processing plants, eating establishments, and federally inspected meat and poultry processing plants (USEPA, 1995).

Chlorophene is used in combination with other disinfectants in hospital and household disinfectant preparations and for general cleaning (Yamarik, 2004). Ortho-benzyl-para-chlorophenol and its salts supress the development of a range of bacteria, fungi, algae, and viruses. It is used as antimicrobial for swimming pool water related surfaces such as decks, and other hard-surface areas surrounding swimming pools refuse/solid waste sites, air washer water systems, evaporative condenser water systems and industrial processing water, and commercial/industrial water cooling systems (USEPA, 1995). In cosmetics and personal care industry, chlorophene is used in the production of hair tonics and other hair grooming aids, as well as foot powders and sprays. It prevents bacterial growth, and thus protects cosmetics and personal care products from spoilage (Cosmetics Info, 2017). According to the Cosmetics Directive of the European Union, the maximum permissible concentration of chlorophene in cosmetic ingredients is 0.2% (Yamarik, 2004).

1.1.1 Chemical and physical properties of chlorophene

Chlorophene is produced from sodium or potassium pentoxide and benzyl chloride followed by chlorination of the resulting o-benzylphenol. Chemical and physical properties of chlorophene are shown in Table 1.

Table 1. Several chemical and physical properties of chlorophene

Parameter	
CAS number[1]	120-32-1
IUPAC name[1]	2-benzyl- 4-chlorophenol
Molecular formula[1]	$C_{13}H_{11}ClO$
Molar weight[1]	218.69 g/mol
Density[1]	1.186 to 1.190 g/cm^3
Appearance[1]	Off-white to pale yellow solid with a slight phenolic odor
Melting point[1]	48.5 ℃ to 49.0 ℃
Boiling point[1]	160 ℃ to 162 ℃ or 175 ℃
Solubility in water at 16 ℃ [2]	<1 mg/mL
K_{ow} [2]	3.99
TOC content of 100 mg/L[2]	68.6 mg/L

1 – Yamarik, 2004; 2 – He et al., 2011

Despite chlorophene possesses high chemical stability, it becomes dark with age. It is noncorrosive to metals but has complex reactions with transitional metals and changes the color when exposed to sunlight. Chlorophene is relatively hydrophobic, as it has a low n-octanol/water partition coefficients (K_{ow}) with value of 3.99 (He *et al*., 2011). This coefficient increases with chlorination demonstrating the tendency for bioaccumulation. The acidity of chlorophenols increases as the number of chlorine substitutions increases (Yamarik, 2004; Olaniran and Igbinosa, 2011). Almost all chlorophenols are in the solid state at room temperature except 2-chlorophenol, which is liquid. Ortho-benzyl-para-chlorophenol is essentially insoluble in water, moderately soluble in acetone (100 mg/mL), and freely soluble in ethanol. The sodium or potassium salts of chlorophenols are

up to four orders of magnitude more soluble in water than the parent compounds (NTP, 1994; He *et al*., 2011; Olaniran and Igbinosa, 2011). This chemical is combustible (CAMEO Chemicals, 2017).

1.1.2 Chlorophene sources, distribution and fate in the environment

Chlorophene is inevitably discharged into the environment as a result of chemical and pharmaceutical industry activities. The potassium and sodium salts of chlorophene degrade rapidly into the subsequent carboxylic acid in the environment. The chemical is considered as nontoxic to birds, but highly toxic to freshwater fish and aquatic invertebrates (Igbinosa *et al*., 2013; USEPA, 1995). Because of its lipophilicity it can be transported through the cell membrane and bioaccumulate in aquatic organisms. Chlorophene is harmful for human health due to its potential carcinogenic and mutagenic properties, and high toxicity (Olaniran and Igbinosa, 2011).

Chlorophenols tend to accumulate in soil and water. They have been found in wastewater, sludge products, surface waters, and groundwater. Other sources of contamination are accidental spills, hazardous waste disposal sites, storage tanks, or municipal landfills. In addition, chlorophenolic compounds are formed during the combustion of organics such as municipal waste. Chlorophenols are poorly biodegradable, and therefore they remain in the environment for long periods. Biocides such as chlorophene are introduced into the environment by wastewater effluents from pulp bleaching process using elemental chlorine, water disinfection or even waste incineration (He *et al*., 2011; USEPA, 1995; Olaniran and Igbinosa, 2011). The widespread presence of chlorophenolic compounds in the environment is also related to the production, use and degradation of numerous herbicides and pesticides, such as chlorobenzenes and chlorinated cyclohexanes (Figure 2) (Igbinosa *et al*., 2013).
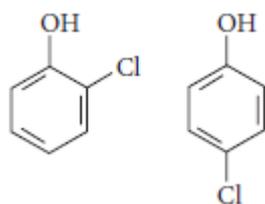

Figure 2. Chlorobenzene and chlorinated cyclohexane

Chlorophene has been detected in concentration of 50 mg/L in activated sludge and up to 10 g/L in sewage treatment plant effluents and rivers (Shi *et al*., 2016).

1.1.3 Toxicity and carcinogenicity of chlorophene

The results of experiments on animals suggest that chlorophene could be as a hidden sensitizer (Stouten and Bessems, 1998). This chemical belongs to the III category for acute oral (500 - 5000 mg/kg) and dermal toxicity (2000 - 20000 mg/kg), and to the IV category for acute inhalation toxicity (> 20 mg/liter). It is severely irritating to the eye (Category I), and is corrosive with repeated contact to the skin (USEPA, 1995).

The acute oral LD_{50} of chlorophene for rabbits and rats was determined to be from 1.4 ml/kg to 8.8 g/kg. All mice and guinea pigs died after being exposed with chlorophene doses of 4.0 and 3.0 g/kg, respectively. Rats exposed to 13.2 mg/l chlorophene for 6 h in an inhalation study had no toxic signs and none of the animals died. Chlorophene was severely irritating to rabbits in most dermal irritation studies. The acute dermal LD_{50} of chlorophene in rabbits was > 3.2 g/kg after 24 h exposure. In most ocular irritation studies, chlorophene was considered as very irritating to the eye (Yamarik, 2004).

Yamarik (2004) studied a short-term toxicity with chlorophene at 500 and 1000 mg/kg. At these concentrations F344W rats and B6C3Fl mice were losing weight and decreasing food consumption. The rats appeared more sensitive to chlorophene than the mice. Moreover, male rats were more sensitive than female rats. The NOEL (No Observed Adverse Effect Level) and LOEL (Low Observed Adverse Effect Level) of chlorophene for rats were 120 and 240 mg/kg/day. In a 2-year carcinogenicity study, all doses of chlorophene increased kidney weight in male and female rats. Mice also decreased survival time and kidney weights but increased liver weight. No any clear evidence of chlorophene carcinogenic activity in rats and mice were found. Also, chlorophene is not considered to be a genotoxic compound (Stouten and Bessems, 1998).

From experiments with male F344 rats it was concluded that o-benzyl-p-chlorophenol is not completely absorbed from the gastrointestinal tract in rats but it is well absorbed across the skin of rats. In F344 rats, isotope-labelled chlorophene was rapidly distributed to organs and tissues. Chlorophene and its metabolites (glucuronide or sulfate ester) were also rapidly excreted in urine and feces (i.e. 90% or more within 3 days). Oral administration did not induce embryotoxic effects. However, administration to maternal animals during lactation caused decreases in pup survival indices at doses of 150 but not 50 mg/kg body weight (Stouten and Bessems, 1998).

Experiments on New Zealand white rabbits determined that a 50% mortality rate occurred at 150 mg/kg/day and a 100% mortality rate occurred at 200 and 300 mg/kg/day. There was not observed maternal toxicity at any dose (Yamarik, 2004).

The chemical applied at a concentration of 10% or greater is a primary irritant to skin and mucous membranes (NTP, 1994). In chronic studies, chlorophene causes increases in kidney nephropathy and has been classified as a possible human carcinogen (USEPA, 1995). Human exposure to chlorophenols takes place by skin absorption, inhalation or oral ingestion (Olaniran and Igbinosa, 2011). It can result in irritations of the respiratory tract and eyes. Higher doses can induce convulsions, shortness of breath, coma, or even death. The number and position of the Cl atoms, and the concentration in a particular environmental compartment determine the toxicity of chlorophenols (Ivanciuc *et al*., 2006).

1.2 Sonochemistry

Sonochemical engineering is a scientific area that studies the application of sonic and ultrasonic waves to the chemical processing. It is known that sonolytic treatment of liquid matrix is able to promote chemical reactions and mass transfer. One of its application fields consists of environmental remediation and pollution prevention (Adewuyi, 2001). That undoubtedly deserves the particular attention from this standpoint, since during last several decades the state of environmental pollution has become a source of serious concern.

1.2.1 Process features

Sonochemical oxidation is generally based on acoustic cavitation ("cold boiling"), which generates localized microbubbles and supercritical regions in the aqueous phase. It includes the formation, growth, and implosive collapse of bubbles in a liquid as illustrated in Figure 3 (Wang and Xu, 2012). The microbubbles produced during the acoustic cavitation will tend to change its size until they reach the resonance size before undergoing the violent implosion. After that the bubbles produce enormous amount of heat, pressure and various free radicals within the aqueous media. These primary radicals are responsible for the following synergistic effect. They initiate additionally the production of secondary radicals and the degradation of contaminants presented in its aquatic environment. The bubbles act as centers for the occurrence of chemical reactions (Sathishkumar *et al*., 2016).
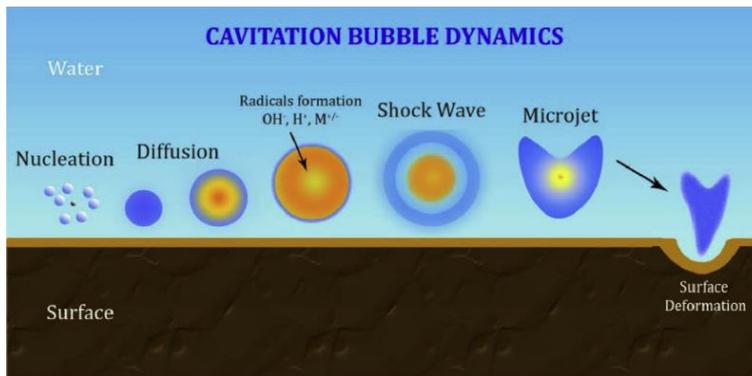
Figure 3. The process of acoustic cavitation and its effect (Pokhrel et al., 2016)

Ultrasound (US) is defined as a fluctuation of waves at frequencies above 16 kHz (16 000 cycles per second), which is inaudible by the average person. Ultrasonic energy irradiates the liquid media and produces an alternating adiabatic compression and rarefaction cycles as demonstrated in Figure 4. As a result of the negative pressure caused by the rarefaction cycle, the microbubbles are formed. These microbubbles contain vaporized liquid or dissolved gases in liquid (Adewuyi, 2001).
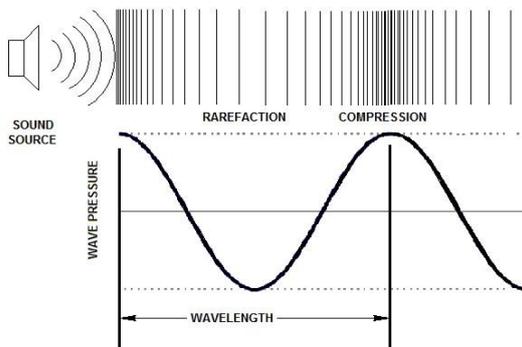
Figure 4. Rarefaction and compression of sound wave (Merouani et al., 2015)

The frequency has significant effect on the cavitation process because it changes the critical size of the cavitational bubble. For example, at very high frequencies the negative pressure is insufficient to initiate cavitation. In addition, the cavitational effect can be reduced due to the compression cycle that occurs much faster than the time necessary for the microbubble to collapse. On the other hand, when the negative pressure applied to the liquid is very large, the average distance between the molecules would exceed the critical molecular distance necessary to hold the liquid intact. As a result, the liquid will disintegrate to form cavities made of vapor and gas-filled microbubbles (Wang and Xu, 2012). Lower frequency ultrasound produces more violent cavitation, leading to higher localized temperatures and pressures. Higher frequencies may lead to higher reaction rates due to the increased number of free radicals (Adewuyi, 2001).

Ultrasound induced oxidation reactivity depends on the physical and chemical characteristics of the pollutants in the various reaction zones and the rate at which the compounds are removed (Ondruschka *et al.*, 2000). Solvents with high vapor pressure, low viscosities and surface tensions are more ready for sonolytic degradation. The intermolecular forces in the liquid need to be cleaved in order to form the bubbles. The solubility of the gas in the liquid used is also an important aspect: the more soluble is the gas, the more likely it is to diffuse into the cavitation bubble. Dissolved gases form the nuclei for cavitation (Adewuyi, 2001).

1.2.2 Reaction mechanism

Among the different theories of sonochemistry, the "hot spot theory" is widely accepted in explanation of sonochemical reactions in the field of environmental protection technologies. It suggests that the bubble collapse is very rapid and the compression of the gas and vapor inside the bubble has the adiabatic characteristics (Wang and Xu, 2012). The presence of dissolved gas near the "hotspots" are responsible for the generation of highly reactive radicals (Sathishkumar *et al.*, 2016).

"Hot spot theory" considers a sonochemical reactions to be highly heterogeneous in which reactive species and heat are produced from a well-defined microreactor. In the "structured hot spot" model shown in Figure 5, there are mainly three reaction zones: (1) a hot gaseous nucleus in which temperature and pressure are extremely high; (2) an interfacial region with radial gradient in temperature and local radical density; and (3) the bulk solution at ambient temperature (Adewuyi, 2001).
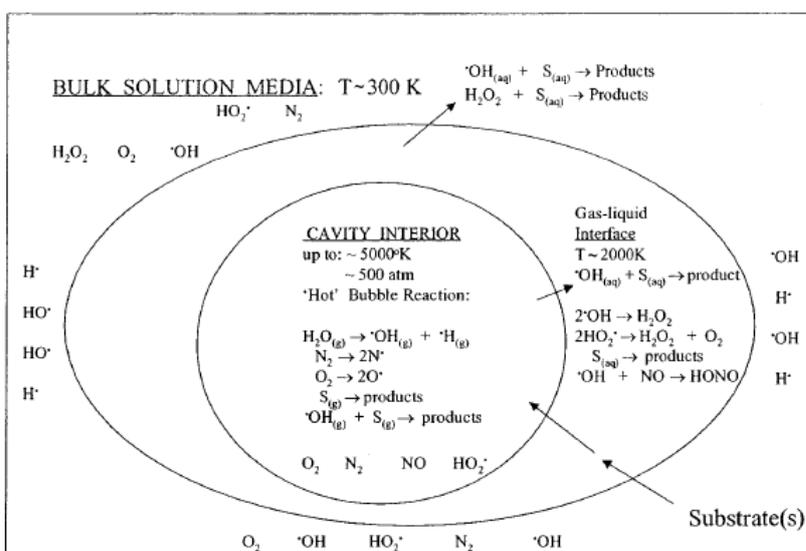
Figure 5. Three reaction zones in the cavitation process (Adewuyi, 2001)

Reactions can occur at the interface of the bubble and in the surrounding liquid. The collapse of microbubbles leads to extremely high local temperature of about 5000 K and pressure of 1000 atm (Adewuyi, 2001). Although these extreme conditions are very short-lived, they cause the dissociation of the water and provide the activation energy required for the bond cleavage. As a result, highly reactive species are formed inside the cavitation bubble as given in Eq. (1) (Rayaroth et al., 2015). Free radicals such as hydroxyl (HO•) and hydrogen (H•) are capable of initiating many red-ox reactions. These reactions with inorganic and organic substrates are fast and often near the diffusion-controlled rate (Adewuyi, 2001). The substrate reacts either with HO• or undergoes pyrolysis (Wang and Xu, 2012). The radicals react either with each other resulting in recombination reactions and form new molecules and radicals or diffuse into the bulk liquid serving there as oxidants.

$$H_2O \;)))) \rightarrow HO\bullet + \bullet H \tag{1}$$

The second reaction zone is located in the gas-liquid interface, which surrounds the imploding cavity. The temperature in this site can reach ca 2000 K during cavity implosion. In this layer both pyrolysis and free radical reactions (involving HO• derived from the decomposition of H_2O) occur. Reactions are similar to that of gaseous phase. In the absence of HO• scavengers, the main product of the sonolysis of water is H_2O_2 (Eq. 2) (Wang and Xu, 2012). For example, in case of surface active compounds sonolytic degradation they tend to accumulate in the interface region and therefore, are more likely oxidized in this region by generated oxidizing species.

$$HO\bullet + \bullet OH \rightarrow H_2O_2 \tag{2}$$

In the bulk liquid, no primary sonochemical activity takes place, although subsequent reactions with ultrasonically generated intermediates may occur. A small number of free radicals produced either in the cavities, or at the interface may introduce into the bulk-liquid phase and react with the substrate. The reactions are basically between the substrate and HO• or H_2O_2 (Adewuyi, 2001; Wang and Xu, 2012).

Sonolysis of water produces H_2O_2 and hydrogen via the reactions of hydroxyl radicals and hydrogen atoms (Eq. 2-7). In the presence of oxygen which acts as a scavenger of hydrogen atom the suppression of the recombination of •H and HO• takes place and the hydroperoxyl radical (HO$_2$•) is additionally formed (Eq. 4) (Adewuyi, 2001). This oxidizing agent generates finally hydrogen peroxide. These radicals can react with dissolved organic compounds by hydroxylation and by oxidation in the presence of air or oxygen (Naddeo *et al*., 2014) (Eqs. 3-7).

$$H\bullet + H\bullet \rightarrow H_2 \tag{3}$$

$$H\bullet + O_2 \rightarrow HO_2\bullet \tag{4}$$

$$HO_2\bullet + HO_2\bullet \rightarrow H_2O_2 + O_2 \tag{5}$$

$$HO_2\bullet + HO_2\bullet \rightarrow H_2O + 3/2O_2 \tag{6}$$

$$H\bullet + HO_2\bullet \rightarrow H_2O_2 \tag{7}$$
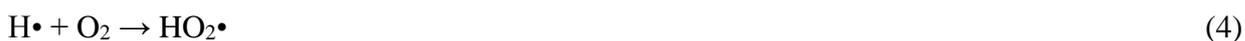
Thermal dissociation of oxygen molecule may also occur, leading to the generation of additional hydroxyl radicals (Eqs. 8-9).

$$O_2 \rightarrow 2O\bullet \tag{8}$$

$$O\bullet + H_2O \rightarrow 2HO\bullet \tag{9}$$

1.2.3 Advantages and disadvantages over the other methods

Sonolysis has a number of preferences over the other advanced oxidation processes (AOPs). It is considered mainly as clean and safe technology. Moreover, comparing to other AOPs the sonolytic water treatment creates conditions for pyrolysis to occur (Rayaroth *et al*., 2015) which is of a high importance in case of persistent organic pollutants. The shorter reaction cycles and the use of cheaper reagents are also among the basic sonolysis advantages. In addition, sonication improves mass transfer and for example its application in combination with the Fenton process is expected to reduce chemicals usage resulting in minimizing of sludge formation and related expenses for its disposal and utilization. The physical effects of ultrasound can enhance the reactivity of a catalyst by enlarging the surface area or accelerate a reaction by proper mixing of reagents. The chemical effects of ultrasound enhance reaction rates because of the formation of highly reactive radical species formed during cavitation (Adewuyi, 2001). Sonolysis is useful in case of wastewater types with low light penetration and it is also economically profitable for treatment of small wastewater volumes (Hu and Apblett, 2014). Ultrasonic reactors are compact and flexible with low capital costs. Ultrasound process can provide the removal of different kind of microorganisms including pathogens from water. The rates of microbiological processes inactivation are usually high, so the effective disinfection is easily achieved (Naddeo *et al*., 2014).

Here should note that mere ultrasonic irradiation is ineffective for the degradation of various environmental contaminants especially for the hydrophilic contaminants. The process requires a solid support for the effective interaction of the environmental pollutants with the various radicals

produced during the sonolysis. Among the other basic disadvantages of ultrasound application are the increase of the water turbidity and the lack of prolonged disinfection capacity, as the disinfection lasts only as long as ultrasound is applied. Design criteria is still being developed in order to rationalize these systems for application to full-scale plants. Ultrasound allows the economic treatment only for small volumes, mainly due to the high energy consumption related to ultrasound generation (Naddeo *et al*., 2014). In addition, there are high maintenance and replacement costs for the corresponding equipment (Hu and Apblett, 2014).

However, its combination with other AOPs enhances certainly the production of powerful non-selective radicals which improve the degradation process and avoids the secondary pollution. Moreover, the combinations of ultrasound with other AOPs are economically more attractive for the environmental purification (Sathishkumar *et al*., 2016). High synergy is appeared in combination with conventional disinfection treatments such as O_3, Cl_2, or UV.

1.2.4 Practical application and technological setup

The ultrasonic power is known to be applied in a variety of industry fields. Ultrasonic irradiation is successfully used in the degradation of many organic compounds and for disinfection purposes (Hu and Apblett, 2014; Naddeo *et al*., 2014). Therefore, ultrasonic energy has found its application in removal of contaminants from air and in degradation of toxic compounds in water and soil. The environmental sonochemistry is a rapidly growing area that deals with the destruction of organics in aqueous solutions (Adewuyi, 2001). Also, the ultrasound can be used in separation of gases because smaller molecules tend to pass the ultrasound field region faster than bigger ones.

In biology and biochemistry, ultrasonic power is applied for homogenization and cell disruption in order to release cells contents for further studies. In mechanical engineering ultrasound has been used to assist drilling, grinding and cutting. It is particularly useful for processing of hard brittle materials e.g. glass, ceramics. Other uses of ultrasound power are welding (both plastics and metals) and metal tube drawing. Pulse/echo techniques are used in the location of mineral and oil deposits and in depth gauges for seas and oceans. In addition, under the influence of ultrasound pigments and solids can be easily dispersed in paint, inks and resins.

Ultrasonic imaging (2-10 MHz) is used, particularly in obstetrics, for observing the foetus and for guiding subcutaneous surgical implements. In physiotherapy, lower frequencies (20-50 kHz) are used in the treatment of muscle strains, disintegration of blood clots and cancer treatment. In dentistry, ultrasound is applied for cleaning and drilling of teeth, also for curing glass ionomer fillings.

Ultrasound is known to generate extremely fine emulsions from mixtures of immiscible liquids. Ultrasonic homogenization has been used for many years in the food industry for the production of tomato sauce, mayonnaise and other similar blended items. In chemistry, such emulsions provide enormous interfacial contact areas between immiscible liquids and thus the potential for greater reaction between the phases. This can be particularly beneficial in phase transfer catalysis (Mason and Lorimer, 2002).

Figure 6 demonstrates the examples of sonolytic reactors installations which have been successfully employed for different studies. The ultrasonic probe is suitable to treat relatively small volumes of liquid with the ultrasound irradiation being localized around the emitting horn. In industry the ultrasonic baths where US irradiation is distributed through the tank are widely used. Unlike the bath-type reactors type, the plug-flow reactor consists of ultrasound transducers immersed into the liquid, where the transducers are not in direct contact with the liquid phase. Moreover, it can treat larger volumes than the probe or the bath. The flow cell is a unique system that works under pressure and the water inside is sonicated all around (Naddeo et al., 2014).
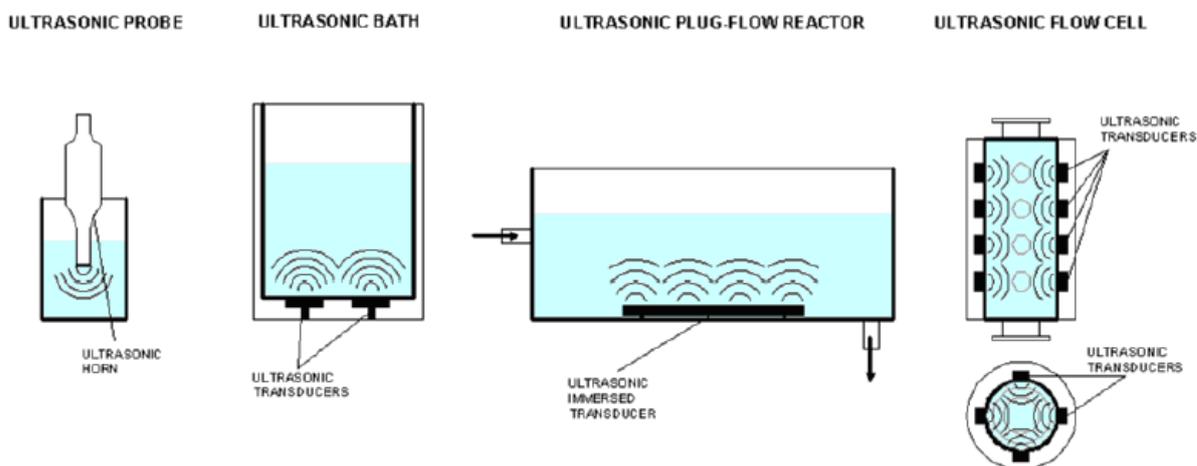
Figure 6. Several types of reaction systems

The simplest method of increasing the amount of ultrasonic power is to introduce the ultrasonically vibrating tip of a sonic probe directly into the reaction mixture. Such sonicator is made up of three major components: generator, converter and probe (or horn). The generator provides electronic pulses, which are transformed into mechanical vibrations by the converter. The acoustic horn conducts and amplifies the vibrational energy from the transducer into the reaction. A typical sonochemical setup is shown in Figure 7.

Figure 7. A simple sonochemical setup (Laboratory - Equipment, 2017)

1.3 Chlorophene degradation processes

Advanced oxidation processes (AOPs) are widely used for eliminating organic pollutants from water. In this case, micro-pollutants react with hydroxyl radicals (HO•), forming organic intermediates, carbon dioxide, water and other inorganic ions. Advanced oxidation processes involve UV/H_2O_2 photolysis, Fenton and photo-Fenton, ozonation, photocatalysis, sonolysis, and electrochemical advanced oxidation processes. All these AOP-based treatment technologies can be used for degradation of chlorophene (Rayaroth *et al*., 2015). The effective removal of chlorophene from water has been achieved by photochemical degradation, ozone oxidation, electro-Fenton degradation, oxidation by manganese oxides, and chlorine disinfection (Shi *et al*., 2016). Several chlorophene degradation methods are presented below.

1.3.1 Fenton and electro - Fenton

One of the most popular AOP for the treatment of acidic waters is the Fenton's reagent. A mixture of Fe^{2+} and hydrogen peroxide is added to the contaminated water to produce HO• and Fe^{3+} according to the classical Fenton's reaction (Eq. 10) (Sirés *et al*., 2007):

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO\bullet + OH^- \tag{10}$$

This method becomes effective because reactions between •OH and organics are usually very fast. However, a part of the generated radical is lost due to its direct reaction with Fe^{2+} and H_2O_2, as shown in reactions (11) and reaction (12):

$$Fe^{2+} + HO\bullet \rightarrow Fe^{3+} + OH^- \tag{11}$$

$$H_2O_2 + HO\bullet \rightarrow HO_2\bullet + H_2O \tag{12}$$

Fe^{2+} can be regenerated in small extent from the reduction of Fe^{3+} by H_2O_2 from reaction (13), by hydroperoxyl radical ($HO_2\bullet$) from reaction (14) or by organic radical intermediates $R\bullet$ from reaction (15). $HO_2\bullet$ is an oxidant much weaker than $HO\bullet$ and can also oxidize Fe^{2+} by reaction (16).

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + HO_2\bullet \tag{13}$$

$$Fe^{3+} + HO_2\bullet \rightarrow Fe^{2+} + H^+ + O_2 \tag{14}$$

$$Fe^{3+} + \bullet R \rightarrow Fe^{2+} + R^+ \tag{15}$$

$$Fe^{2+} + HO_2\bullet \rightarrow Fe^{3+} + HO^-_2 \tag{16}$$

Among AOPs, oxidation using Fenton's reagent is an attractive treatment because of its low cost, the lack of toxicity of the reagents (i.e., Fe^{2+} and H_2O_2), the absence of mass transfer limitation due to its homogeneous catalytic nature and the simplicity of the technology (Wang, 2008).

Electro-Fenton is an indirect electro-oxidation treatment based on the combined use of hydrogen peroxide generated on the surface of cathode and iron ions as catalyst. The method includes the continuous supply of H_2O_2 to the acidic contaminated solution from the two-electron reduction of oxygen gas given by reaction (17):

$$O_2(g) + 2H^+ + 2e^- \rightarrow H_2O_2 \tag{17}$$

Fe^{2+} or Fe^{3+} is then added to the solution to generate the oxidizing agent $HO\bullet$ from Fenton's reaction (10).

Sire´s *et al*. (2007) tested four different electro-Fenton systems, where a Pt or boron-doped diamond (BDD) anode and a carbon felt or O_2-diffusion cathode were used. Electrolysis was carried out with 50 mg/l chlorophene solutions at pH 3.0, with 0.05 M Na_2SO_4 as supporting (background) electrolyte and Fe^{3+} as catalyst.

The catalytic behavior of the Fe^{3+}/Fe^{2+} system mainly depends on the cathode tested. The cells with an O_2-diffusion cathode provide a large accumulation of electrogenerated H_2O_2 while Fe^{3+} content remains practically constant. Chlorophene degradation profile decreases more rapidly with increasing the initial Fe^{3+} concentration. This leads to a higher quantity of Fe^{2+} regenerated at the cathode (18) and, subsequently, to a greater $HO\bullet$ production from Fenton's reaction (10).

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \tag{18}$$

In the Pt/O_2 diffusion cell decay rate of chlorophene is higher and faster than in the BDD/O_2 diffusion cell but chlorophene is poorly mineralized because the final Fe^{3+}–oxalate complexes are difficult to oxidize with HO•. These complexes are completely mineralized at a BDD anode at high current due to the great production of reactive HO• on its surface.

On a carbon felt cathode was found a more positive action of the Fe^{3+}/Fe^{2+} system due to the much faster regeneration of Fe^{2+} at its surface leading to much greater HO• production. The removal rate of chlorophene is always lower in the cells with BDD than with Pt, because Fe^{2+} is less accumulated since it is also oxidized with peroxodisulfate generated at the BDD anode.

The efficiency for the degradation process in the cells increase in the order: Pt/O_2 diffusion < BDD/O_2 diffusion < BDD/carbon felt < Pt/carbon felt. These results showed that electro-Fenton is a possible environmentally friendly technology for the remediation of wastewaters containing chlorophene.

1.3.2 Photolysis and UV/H_2O_2

Among the other water purification techniques are the photolytic processes based on ultraviolet (UV) irradiation of organic pollutants contaminated water, which is known as very effective for groundwater and drinking water remediation. UV-treatment is also effective in water disinfection (Benitez *et al*., 2013; Summerfelt, 2003).

Benitez *et al.* (2013) studied the photodegradation of five frequently detected in wastewater emerging contaminants including chlorophene by mere UV radiation and UV radiation combined with H_2O_2. The radiation source was a low pressure mercury vapor lamp with an electrical power of 15 W. In order to achieve the pH in the range 3 - 9, the solutions were previously buffered with a phosphate buffer (10 mM). Some experiments were performed with the presence of *tert*-butanol (*t*-BuOH, 0.01 M) which was added as HO• radical scavenger.

Research showed that chlorophene is well degraded by a monochromatic UV radiation at 254 nm at different pH values. The presence of *t*-BuOH in the solutions decreased the degradation rates, especially at pH 3 and 5. The combined UV/H_2O_2 process provided a significant increase in the reaction rates, as a result of the generation of hydroxyl radicals which can oxidize organic compounds more effectively. The evolution of the toxicity by single UV radiation was studied in a group of experiments performed at pH = 7. This toxicity was evaluated by measuring changes in the natural emission of the luminescent bacteria *Vibrio fischeri* in samples collected at different irradiation times. The results showed an initial increase of toxicity in all cases. The toxicity took a downward turn as the intermediates were degraded to less toxic products.

1.3.3 Ozonation and UV/O$_3$

Ozone is an efficient oxidant for the purification of surface and drinking waters because, in addition to the direct reaction with the organic pollutants, it produces another strong oxidant, the HO• radical. Thus, ozonation processes include both, molecular ozone and HO• radical oxidation pathways (Benitez *et al*., 2013).

Benitez *et al*. (2013) carried out two different groups of ozonation experiments of chlorophene. The direct reaction between ozone and chlorophene was conducted at homogeneous conditions. Metoprolol was used as a reference compound. The initial concentration for both substances was 10 µM. *Tert*-butyl-alcohol (0.1 M) was also added to the solution as HO• radical scavenger. The solutions were buffered with a phosphate buffer in order to achieve pH values in the range 3–11. Each run was initiated by injecting a variable volume of the ozone stock solution, necessary to achieve the desired initial O$_3$ dose into the flask. The identification of by-products was performed in heterogeneous conditions and without buffering. Ozone was produced from an air stream in an ozone generator. Then, it was continuously bubbled into the solutions through a gas-dispersion plate located at the bottom of the reactor. Samples were analyzed by a HPLC system.

The results showed that ozone is a possible alternative for the degradation of chlorophene due to the high values of the contaminant degradation rate constants and the generation of less toxic intermediate products as well as due to the less toxicity of the degradation products. Ozonation can be successfully used to oxidize the emerging contaminant, achieving both disinfection and water quality improvements in short or moderate reaction times, depending on the pH conditions.

He *et al.* (2011) investigated chlorophene degradation by combined ultraviolet irradiation and ozonation (UV/O$_3$). The study demonstrated that UV enhanced ozonation has a synergistic effect in treating chlorophene comparing to that performed separately. The optimal reaction mixture pH was 8.0. A better degradation rate was observed for a low initial chlorophene concentration. The ozone dosage and UV intensity increase resulted in a higher TOC removal. All of the intermediates in the UV/O$_3$ process can be decomposed and oxidized to formic, acetic or oxalic acid. Combined UV and ozone treatment is promising for the degradation of chlorophenols. However, the presence of other constituents in wastewater, i.e. the matrix effect will reduce the reaction rate. Further studies should focus on specific application fields to identify a balance between the treatment cost and efficiency for use in industry.

1.3.4 Chlorination and bromination

Chemical oxidants are commonly used in water treatments because of their high efficacy in destruction of micropollutants. Although chlorine (Cl_2) as gaseous chlorine or hypochlorite are considered as less reactive than ozone, they have been also frequently used in water treatments. Chlorine hydrolyzes in water and forms hypochlorous acid (19):

$$Cl_2 + H_2O \rightarrow HOCl + Cl^- + H^+ \tag{19}$$

Hypochlorous acid is a weak acid that dissociates in aqueous solutions (20):

$$HOCl \Leftrightarrow ClO^- + H^+ \tag{20}$$

In the pH range between 6–9 (typical of water treatment conditions), hypochlorous acid and hypochlorite are the main chlorine species presented in water. Besides its low cost, the great advantage of chlorine is the reaction with numerous inorganic and organic micropollutants. However, its main disadvantage is the formation of possible harmful disinfection by-products (DBPs), such as halogenated organic compounds, some of which exhibit a potentially carcinogenic activity, e.g. trihalomethanes (THMs) and haloacetic acids (HAAs).

Bromination reactions in the oxidation of water pollutants have also deserved an increasing interest, especially in waters with a high bromide (Br^-) content. In general, the oxidation of bromide with hypochloride leads to the formation of aqueous bromine (21) (Acero *et al.*, 2013):

$$HOCl + Br^- \rightarrow HOBr + Cl^- \tag{21}$$

Acero *et al.* (2013) investigated chlorination and brominaton kinetics of emerging contaminants (ECs) during wastewater and drinking water treatment. In addition, they explored disinfection by-products formation, mainly THMs. For this purpose, chlorination experiments were conducted at 20 °C and natural pH of the waters (in the range pH 7.4–8.3).

According to the results, chlorine is efficient for the removal of chlorophene. Moreover, the additional presence of bromide could also enhance the degradation of ECs. The total THMs concentration increased continuously with the increase in the chlorine dose, being in all cases below 100 µg/L (the maximum value permitted by EU regulations in drinking water).

1.3.5 Oxidative transformation by manganese oxides (MnO_2)

Oxides of Mn, Fe, and Al are usually found in soils and sediments. They promote abiotic reactions of organic pollutants via hydrolysis, oxidation, or reduction. Manganese (hydr)oxides are probably

some of the most important natural oxidants, which oxidize and promote polymerization of phenolic compounds (Zhang and Huang, 2003).

Zhang and Huang (2003) studied oxidative transformation of chlorophene with manganese dioxide (MnO_2). Reactions were initiated by adding a small amount of the organic reactant stock to suspensions containing manganese oxide. A condition of pH below 7 was maintained due to mild acidic conditions are common in many soils.

This investigation demonstrated high susceptibility of chlorophene toward oxidation by manganese oxides and significantly fast reaction rates. However, the reaction rate could be reduced by other elements being in natural water and soils. Natural organic matter and dissolved metal ions competitively contact with oxide surfaces. Nevertheless, oxidative transformation by manganese oxides is likely an important process for chlorophene oxidation in the soil-water environment. Formation of heavier and more hydrophobic products via dimerization and polymerization will decrease the mobility of these antibacterial agents and potentially decrease the biological effects when the larger products become less available for aquatic organisms.

1.3.6 Laccase-catalyzed removal of the antimicrobials from water

Shi *et al*. (2016) explored the laccase-catalyzed removal rates of chlorophene in a batch system at varying initial enzyme activities. Laccases are blue copper-containing oxidase enzymes that catalyze a wide range of aromatic compounds. Laccases use dissolved molecular oxygen as the electron acceptor. Thus, it is not toxic to microorganisms, animals, and humans. It has been reported that laccase treatment could be effective for the removal of various emerging micropollutants from water/wastewater. Laccase is capable of polymerizing phenols with high efficiency and generating products of a molecular size large enough to precipitate from water.

All laccase-catalyzed reactions were incubated on a rotary shaker at room temperature. The solutions for the reaction were buffered (pH 6.0). Laccase was added to the reactor as the last component to initiate the reaction. Laccase activity was relatively constant during the reaction. For the prevention of reaction, reactor was dosed with 2 mL of methanol.

The results demonstrated that emerging antimicrobials such as chlorophene could be effectively transformed and removed from water by laccase-catalyzed reaction processes. Acute toxicity tests showed that the toxicity caused by chlorophene was effectively eliminated by the laccase-catalyzed reaction. It was also found that humic acid behave as a scavenger of the free radical intermediates produced from reactions between laccase and the substrates. Consequently, it could interrupt the transformation of chlorophene. These findings state appropriate application of the

laccase-mediated to control chlorophene and other trace-level contaminants of a similar nature in water treatment practice.

1.3.7 Biological degradation

Swisher and Gledhill (1973) determined the range of biodegradation of o-benzyl-p-chlorophenol in river water, sewage, and activated sludge. Biodegradation was estimated colorimetrically. The river water being spiked with 0.1 mg/L of chlorophene and stored in the dark at room temperature was degraded within 6 days. Sewage was shaken on a rotary shaker for 4 days. 0.5 and 1.0 mg/L of antimicrobial were added. These concentrations of chlorophene were degraded in 1 day. Activated sludge was gradually acclimated by accumulative feeding of chlorophene. Biodegradation was assessed by measuring disappearance of dissolved organic carbon (DOC). It has been achieved 80% biodegradation of 1.0 mg/L chlorophene in 8 h and 100% in 24 h.

Based on the results of these studies, biodegradation of chlorophene (of present levels) in the biological systems should present no significant environmental problems.

2 Materials and Methods

2.1 Chemicals and reagents

All chemicals used (chlorophene, *tert*-butanol, tetrachloromethane, 2-deoxy-D-ribose, 2-thiobarbituric acid, trichloroacetic acid, 1,1,3,3-tetraethoxypropane, ferrous sulphate heptahydrate, ferric sulphate nonahydrate, hydrogen peroxide, H_2O_2 ($\geq$30% w/w)) were purchased from Sigma-Aldrich (Germany). Reagents were of analytical grade at greater than 95% purity, used without further purification. The working solutions were prepared using ultrapure water obtained from a Millipore ultrapure water UV-system (Simplicity®, EMD Millipore Corporation, Billerica, MA, USA).

2.2 The experiment setup and operation conditions

Sonochemical degradation of chlorophene was performed using an ultrasonic system (Fig. 8). The apparatus consisted of a 200-mL cylindrical glass reactor, a Bandelin Sonopuls HD 3100 ultrasound generator (100 W) at a frequency of 20 kHz, ultrasonic transducer, probe VS-70T (13 mm diameter), temperature sensor, inner and external cooling system. The probe made from titanium alloy ($TiAl_6V_4$) was immersed into the solution at the depth of 20 mm. To maintain the reaction temperature at 22 $\pm$ 2 °C a cylindrical glass reactor was equipped with two different cooling systems. Spiral glass-cooler with circulating tap water was immersed into the solution and on the outside of the reactor the water jacket was placed. Moreover, to maintain the constant temperature of the reaction mixture tap water was cooled by ice cubes before the subsequent supply to spiral-cooler. The temperature of the reaction mixture was measured by integrated to the ultrasound generator temperature sensor. The total ultrasound irradiation time was 120 min. Aliquots of 1.0 mL were withdrawn during the experiment at regular times for the following analysis (0, 5, 15, 30, 45, 60, 75, 90, 105, 120 min).

In the present study, water was spiked with chlorophene to obtain its initial concentration of 10 µM. Solution pH was regulated to 3.0 because the acid environment is favorable for the Fenton process. For this purpose a 0.5-M sulfuric acid solution was used. In order to combine sonolysis with the Fenton reaction, hydrogen peroxide (H_2O_2) and iron catalysts (Fe^{2+} or ferrioxyhydroxide) were added in the beginning of the experiment with simultaneous switching on of ultrasound generator.
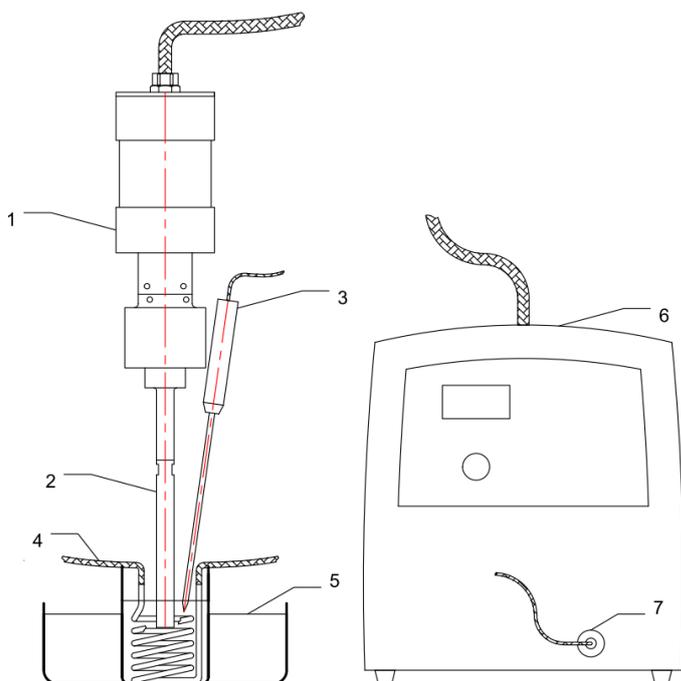
Figure 8. The principle scheme of ultrasound assembly for degradation of chlorophene. 1- ultrasonic transducer, 2- probe VS-70T, 3- temperature sensor, 4-inner spiral cooler, 5- external water jacket, 6- ultrasound generator, 7- temperature sensor port

Sludge (ferrioxyhydroxide) was synthesized by mixing of sodium hydroxide and ferric sulphate solutions according to stoichiometric ratio obtained from the reaction (22):

$$Fe_2(SO_4)_3 + 6NaOH \rightarrow \underline{2Fe(OH)_3\downarrow} + 3Na_2SO_4 \tag{22}$$

The resultant precipitate and sodium sulphate were separated from each other by means of filtration and washing out of supernatant, i.e Na_2SO_4 solution. The first one was dried further at 105 °C for 2 h. The initial concentration of obtained sludge in all the sonochemical experiments was 50 mg/L.

The Fenton oxidation process was stopped by adding of 1 mL of freshly prepared 0.1-M Na_2SO_3 solution to 1 mL of sample. The initial concentration of H_2O_2 varied from 50 to 200 μM. The molar ratio of Fe^{2+}/H_2O_2 was maintained at 1/10, which was found to be optimal for chlorophenols degradation (Bolobajev *et al.*, 2016).

In some experiments, *tert*-butanol (*t*-BuOH) or 2-deoxy-Dribose (DR) in concentration of 5 mM were added as HO• scavengers. Also, H•-scavenging by CCl_4 (60 μM) was used to enhance the sonolytic oxidation.

2.3 Analytic methods

The concentration of chlorophene in each sample after sonication was determined by a high performance liquid chromatograph (YL-Instrument 9300, Young Lin Instrument Corporation, Hogye-dong, Anyang, Korea) equipped with a Waters Bridge (150 mm × 3.0 mm inner diameter) C18 (3.5 μm particle size) column. The mobile phase was a mixture of 30% eluent A (0.1% acetic acid in ultrapure water), and 70% eluent B (acetonitrile) at 0.2 mL min^{-1}. Detection was performed at 280 nm because at this wavelength chlorophene has maximum light absorbance. The total analysis time was 15 min. The injected sample volume was 20 μL.

The HO• concentration in the reaction mixture was measured spectrophotometrically according to the deoxyribose method by Halliwell *et al*. (1987). This method is based on the degradation of deoxyribose under the influence of HO• with further formation of malondialdehyde (MDA). The last one reacts then with 2-thiobarbituric acid (TBA) producing a pink chromophore (TBA-MDA reaction product) that has the maximum light absorbance at 532 nm. Thus, a 2.8-mM DR solution was oxidized by HO• generated by sonolysis or Fenton's reagent at similar treatment conditions to that of CP degradation. At regular time intervals, 1 mL of the sample was taken from the reactor and placed into the test tube with a 1.25 mL of a 2.8-% (w/v) trichloroacetic acid (TCA) solution to terminate the radical oxidation process. Then, 1.25 mL of TBA (1% w/v) was added and the reaction mixture was heated to 90-100 °C for 20 min. The absorbance of resultant pink chromophore was determined in a 1-cm path length cuvette at 532 nm using a Heλos ultraviolet-visible spectrophotometer (Thermo Electron Corporation, Beverly, MA, USA). The quantification of HO• formed was performed using MDA standards prepared via hydrolysis of 1,1,3,3-tetraethoxypropane in 0.1 N HCl.

H_2O_2 in the reaction mixture was analysed photometrically at 410 nm as a complex of H_2O_2 with Ti^{4+} (Eisenberg, 1943). The method is based on photometric measurement of the color intensities of hydrogen peroxide solutions treated with titanium sulfate reagent. The yellow-colored complexes produced in the reaction is due to the formation of pertitanic acid. The reaction equation is presented below (23):

$$Ti^{4+} + H_2O_2 + 2H_2O \rightarrow H_2TiO_4 + 4H^+ \tag{23}$$

For the determination of residual H_2O_2 formed during the sonolysis 2.25-mL aliquot was withdrawn from the reactor at regular time and transferred into the test-tube where 0.25 mL of Ti^{4+} solution was previously added. Each point of measurement occupied two tubes: zero and defined solutions. The calibration curve for residual H_2O_2 was also observed using standards at different

concentrations of H_2O_2. For this purpose 0.5 mL of Ti^{4+} solution and 4.5 mL of standard or water (in case of the blank solution) were added into the test tube for analyses.

Chloride ion (Cl^-) was detected using an ion chromatograph (761 Compact IC, Metrohm) equipped with a suppressed conductivity detector and a Metrosep A Supp 5 (150 mm × 4.0 mm inner diameter) analytical column.

All the experiments were duplicated. The standard deviation of the results was less than 5%.

The preparation of samples for identification of oxidation intermediates was performed by liquid-liquid extraction using dichloromethane. Obtained extracts were dried with Na_2SO_4. 10 mL of each extract were concentrated by evaporation to 1 mL for the further analysis by GC-MS (Schimadzu, GC-2010) equipped with a Phenomenex Zebron capillary column ZB-5MS (30 m × 0.32 mm inner diameter with film thickness of 0.25 μm) and quadrupole mass-spectrometer (Schimadzu, GCMS-QP2010). Extracts (2 μL) were injected splitless to the GC with injection port temperature of 250 °C. The GC column oven program started from the initial temperature holdup at 80 °C for 2 min with the following increase from 80 °C to 180 °C at the rate of 20 °C min^{-1}. The next temperature increase was to 280 °C at the rate of 5 °C min^{-1} with the final holdup for 3 min. Mass spectra of oxidation intermediates were obtained using an electron-impact ionization (EI) mode by scanning m/z range over 40-340 with a speed of 1666 amu s^{-1}. The ion source and interface temperatures were 230 °C and 250 °C, respectively.

3 Results and Discussions

3.1 Role of HO• in sonochemical degradation of chlorophene

Sonolytic degradation in aqueous solutions involves such reaction pathways as pyrolysis and radical oxidation. Pyrolysis occurs mainly inside the cavitational bubble but radical reactions are possible at the interfacial region and bulk solution. Thus, for the existence of pyrolysis within the bubble the conversion of organic compound to the gaseous phase is required. This process needs volatile organics with high vapor pressure to be oxidized (Kotronarou *et al*., 1991). Chlorophene being non-volatile at room temperature with low vapour pressure (1.04×10^{-6} mmHg at 25°C (Werner et al., 1983)) tend to be present rather in liquid or interface region than in gaseous phase during the collapse of the cavities in sonolysis. Therefore, the formation of HO• as a result of thermal decomposition of water could be the main mechanism that leads to chemical degradation of chlorophene.

The HO• behavior in the cavitation bubble has usually two ways: the radicals react either with each other to form new molecules and radicals or diffuse into the bulk liquid to react with the substrate (Fig. 9). HO• are strong oxidants that are capable to convert resisting compounds into biodegradable forms (Juretic *et al*., 2015). In this study, hydroxyl radicals were also generated by the Fenton process in order to enhance the sonolityc treatment of chlorophene. Under an ultrasonic irradiation organic compounds in aqueous solution in turn behave differently according to their physical and chemical properties. Hydrophilic and non-volatile molecules can react with hydroxyl radicals in the bulk solution at low concentration. However, at higher concentrations of organic substrate the reaction can also take place at the interface of cavitation bubble. Contrary to that, hydrophobic and more volatile compounds can enter and de-compose inside the cavitation bubble by way of pyrolysis and radical attack (Bejarano-Pérez and Suárez-Herrera, 2008). Several studies reported that highly hydrophobic compounds tend to concentrate at the gas-liquid interface (Park *et al*., 2011) and have higher degradation efficiency due to the closer contact with oxidative species outgoing from cavitation bubble Since chlorophene is an example of hydrophobic organic compounds (K_{OW} is 3.99 (He *et al*., 2011)), its degradation occurs more likely at the gas-liquid interface of the bubbles rather than in bulk solution.
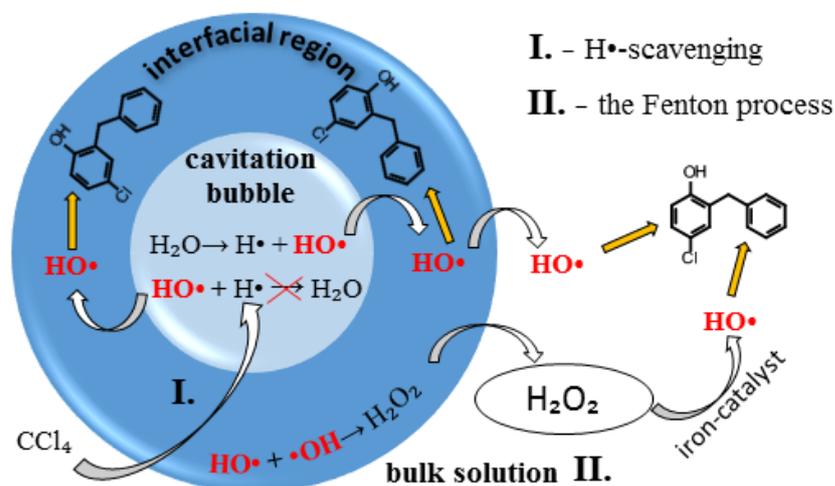
Figure 9. Participation of •OH-radicals in degradation of chlorophene

The influence of HO• on degradation of chlorophene was tested by the experiments in the absence and presence of radical scavengers. In excess of strong HO• such as DR and *t*-BuOH, the radical oxidation was almost completely suppressed. Nevertheless, the presence of H•-scavenger such as CCl_4 improved the degradation of the organic pollutant. The results of experiments performed are demonstrated in Figure 10.
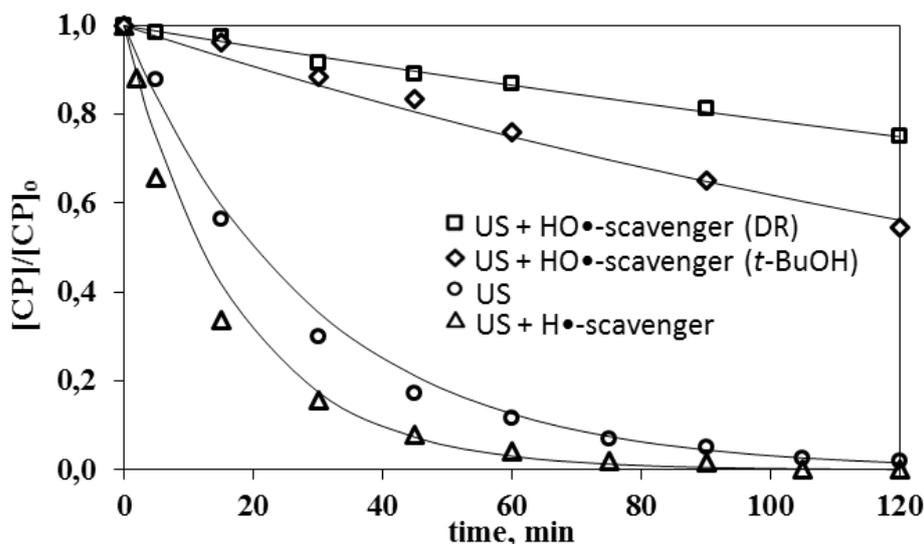
Figure 10. Degradation of chlorophene (CP) by simple sonolysis and sonolysis in the presence of CCl_4 as the H•-scavenger, deoxyribose (DR) and tert-butanol (t-BuOH) as the HO•-scavengers. (The initial concentrations of chemicals: $[CP]_0 = 10$ μM, $[DR]_0 = [t\text{-BuOH}]_0 = 5$ mM, $[CCl_4]_0 = 60$ μM)

Mathematical analysis of reaction kinetics indicated that the decomposition of CP by sonolysis and its modifications fit in the pseudo-first order kinetics (Eq. 24) (Fig. 11) with high accuracy. The explanation of that phenomenon can be expressed using the next sequence of mathematical

expressions. Suppose the degradation of CP was provided by HO• attack. In terms of reactions kinetics it can be described using Eq. 25.

$$\frac{d[CP]}{dt} = -k' \times [CP] \tag{24}$$

$$\frac{d[CP]}{dt} = -k \times [\bullet OH] \times [CP] \tag{25}$$
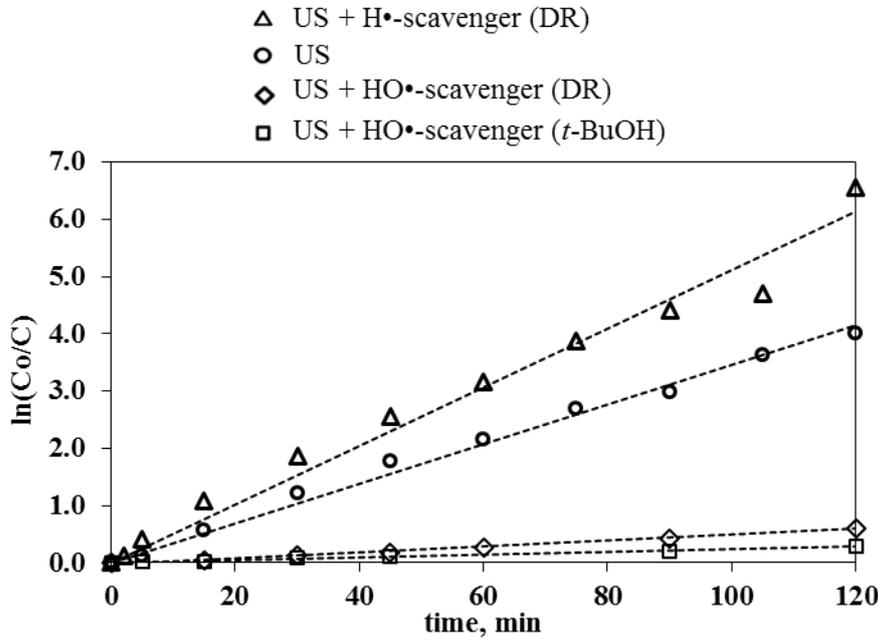
Figure 11. The example of linear dependence between $\ln(C_0/C)$ and time of treatment using sonolysis in the presence of different scavengers

Measuring a second order rate for the reaction between HO• and CP can be problematic. The concentrations of the two reactants must be followed simultaneously, which is in case of HO• technically extremely difficult. Due to the high reactivity of reactant HO• its concentration can be approximated to as substantially lower than that of CP ([HO•]<<[CP]) and moreover it remains constant (k = const) within the reaction. Therefore, Eq. 25 is approximated to pseudo-first reaction kinetics (Eq. 24) where $k' = k \times [HO\bullet]$ is the pseudo first-order reaction rate constant. The k' (Table 2) was calculated by the integration of Eq. (25) in the range from $[CP] = [CP]_0$ at $t = t_0$ to $[CP] = [CP]$ at $t = t$, obtaining equation (26).

$$\ln\left(\frac{C_0}{C_i}\right) = k' \times t \tag{26}$$

Table 2. Pseudo-first order reaction rate constant (k', min^{-1}) of CP degradation

Process	$k' \times 10^{-2}$, min^{-1}, (treatment time, min)	R^2

US	3.45	0.993
US + HO•-scavenger (DR)	0.24	0.994
US + HO•-scavenger (*t*-BuOH)	0.48	0.985
US + H•-scavenger	5.11	0.976
US + Fe(II)	3.16	0.992
Classical Fenton 50 (0-2 min)	50 (0-2 min)	
	4.57 (2-120 min)	0.989
Classical Fenton + US	50 (0-2 min)	
	6.65 (2-120 min)	0.987
US + classical Fenton + H•-scavenger	50 (0-2 min)	
	8.22 (2-120 min)	0.993
US + H_2O_2 + ferrioxyhydroxide	4.77	0.990

Considering HO•-scavenging effect of DR and *t*-BuOH it is possible to indicate the process region (liquid phase, interfacial region or gaseous phase) responsible for CP degradation. *t*-BuOH is water soluble and volatile compound thus it is capable to get into the cavitational bubble and capture •OH both inside and outside of that (Im *et al*., 2015). In contrast, DR is non-volatile and due to that it could be present only outside of the cavitation bubble. Regardless of the •OH- scavenging region, DR and *t*-BuOH remove reactive species which participate in the decomposition of the organic pollutant. Consequently, CP degradation rate decreased more than a five-fold. This fact is confirmed by a pseudo-first order reaction rate constant (Table 2) which reduced from 3.45×10^{-2} to 0.24×10^{-2} and 0.48×10^{-2} min^{-1} using DR and *t*-BuOH, respectively.

3.2 The influence of H•-scavenger on degradation of chlorophene

In the next sequence of experiments carbon tetrachloride (CCl_4) as the H•-scavenger was added into reactive solution. Weissler *et al*. (1950) reported that CCl_4 forms strong oxidizing agents under ultrasonic irradiation that are able to oxidize many species like iodide ions. In present study, the addition of CCl_4 resulted in a two-fold increase of the HO• comparing to that of simple sonolysis in 120 min of experiment (Fig. 12). Unlike chlorophene, CCl_4 belongs to the group of volatile organic compounds with the high vapor pressure (115 mmHg at 25 °C (Boublik *et al*., 1984)). Consequently, it is able to participate in the cavitation bubble interior processes (Hua *et al*., 1996; Griffing, 1950), particularly react with a hydrogen atom. The reaction between CCl_4 and H• interrupt the unproductive recombination of H• with HO• (Eq. 27) because the rate of carbon

tetrachloride degradation is very fast and moreover it increases with ultrasonic frequency (Bejarano-Pérez, Suárez-Herrera, 2008). This enhancement effect allowed releasing the additional amount of HO• into the interface and bulk solution. Therefore, the presence of CCl_4 as the strong H•-scavenger showed the enhancement effect on the formation of HO• during the sonolysis. It is confirmed by a pseudo-first order reaction constant of CP sonolytic degradation that increased from 3.45×10^{-2} to 5.11×10^{-2} min^{-1} (Table 2). Thus, this method of HO• formation enhancement in sonolytic processes can undoubtedly improve the degradation of chlorophene.

$$HO• + H• \rightarrow H_2O \tag{27}$$
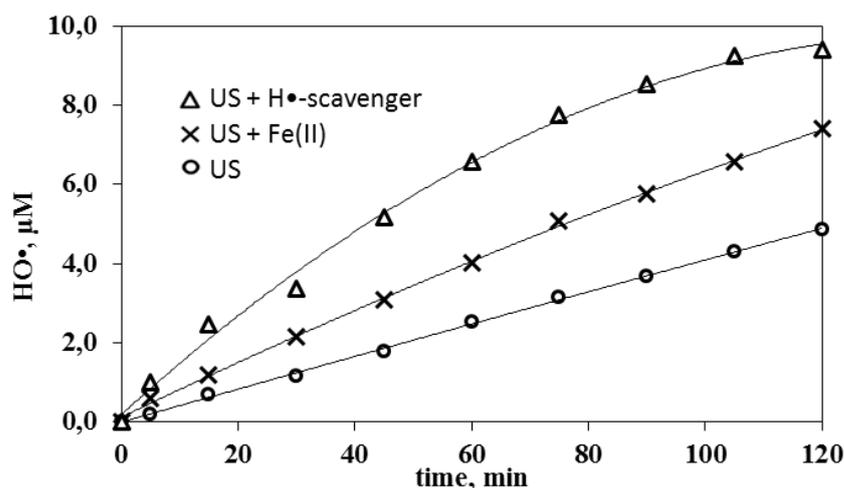
Figure 12. Formation of hydroxyl radicals (HO•) in simple sonolysis and sonolysis enhanced by the addition of Fe^{2+} and CCl_4 as the H•-scavenger

According to the chemical properties of CCl_4, its main degradation mechanism is known (Griffing, 1950) to be based on pyrolysis and hydrogen radical (H•) under ultrasonic irradiation leading mostly to carbon dioxide and chloride (Eqs. 28-33).

$$CCl_4 + H• \rightarrow HCl + •CCl_3 \tag{28}$$

$$CCl_4 \rightarrow Cl• + •CCl_3 \text{ or } Cl_2 + :CCl_2 \tag{29}$$

$$•CCl_3 \rightarrow Cl• + :CCl_2 \tag{30}$$

$$2:CCl_2 \rightarrow C_2Cl_4 \tag{31}$$

$$2•Cl \rightarrow Cl_2 \tag{32}$$

$$Cl_2 + H_2O \rightarrow HClO + HCl \tag{33}$$

In spite of the formation of some intermediate activated species as chlorine radical, trichloromethyl radical and dichlorocarbene within the process, the complete mineralization of CCl_4 could be easily achieved inside the cavitation bubble (Francony, Pétrier, 1996). Thus, this eliminates the problem of a secondary pollution appeared due to CCl_4 addition.

Although the addition of CCl_4 increased the degradation rate of organics, the practical use of that approach is of concern. Carbon tetrachloride is considered as toxic and stable organic pollutant that is degraded very slowly. According to that, its intentional addition into the wastewater might result in negative effect of environmental pollution. Chemical is released into the environment as a consequence of human activities and manufacturing processes. Particularly wastewater might be contaminated with chlorinated volatile organic compounds (VOCs) including CCl_4 by water supply with chlorination, industries, household and consumer products, chemical and biogenic reactions that occur during water and wastewater treatment (Faroon *et al*., 2005; Yang *et al*., 2014). Therefore, the probability of CCl_4 and CP co-existence in wastewater matrix is undoubtedly high. From that standpoint the H•-scavenging effect induced by CCl_4 became reasonable in terms of sonolytic oxidation improvement. Besides, could assume that a number of chlorinated VOCs behaves under ultrasonic irradiation in a similar manner and their presence in the sonolysis seemed to be attractive.

3.3 Formation of H_2O_2 in the sonolysis and its utilization in the Fenton-mediated oxidation

Another matter of interest was the formation of H_2O_2 during the sonolysis. In the end of the experiment, the concentration of H_2O_2 reached 25 μM (Fig. 13). Thus, the formation of H_2O_2 induced by sonolysis is relatively slow. Mainly, hydrogen peroxide is produced in the interfacial region of the cavitation bubble, as a result of the recombination of two HO• (Eq. 2). Although H_2O_2 is known as oxidizing agent and hypothetically is able to participate in CP oxidation, the H_2O_2 molecular oxidation is considered as unproductive.

The homolytic cleavage of H_2O_2 with the subsequent formation of HO• radicals is another approach that can easily degrade organic matter. This process is initiated using transition metals. The application of different forms of Fe^{2+} in combination with H_2O_2 is known as the Fenton reagent (Eq. 10). It is most widely applied method to generate HO• from H_2O_2. In sonolysis, the addition of Fe^{2+} to the bulk solution was aimed to utilize H_2O_2 formed for the subsequent oxidation. As can be seen in Fig. 13 that resulted in the small additional increase of HO• comparing to that of mere sonolysis.
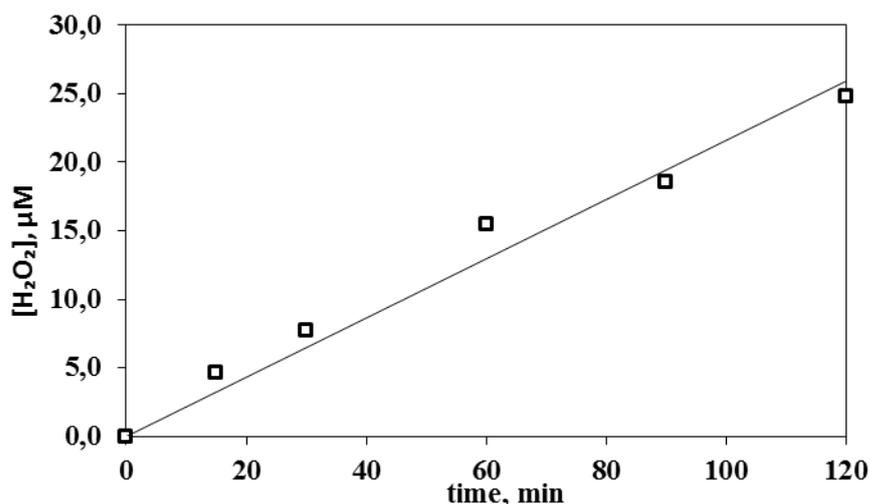
Figure 13. Formation of H_2O_2 during sonolysis at 70% of maximum (100 W) ultrasound generation power

However, the presence of catalyst causes one more unproductive reaction between Fe^{2+} and HO• (Eq. 11) where Fe^{2+} acts as HO• scavenger with further oxidizing to Fe^{3+}. Meanwhile, ferric ions can also react with H_2O_2, producing hydroperoxide radicals (HO$_2$•) which cause a second decomposition process for the pollutant. This mechanism is known as the Fenton-like reaction. It is based on the formation of unstable $Fe^{III}(HO_2)^{2+}$ complex (Eq. 34) that further decomposes to hydroperoxyl radical (HO$_2$•) and Fe^{2+} (Eq. 35). Later on, these ferrous ions (Fe^{2+}) induce the Fenton reaction and thus can be involved in the production of HO• (Eq. 10).

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{III}(HO_2)^{2+} + H^+ \tag{34}$$

$$Fe^{III}(HO_2)^{2+} \rightarrow Fe^{2+} + HO_2\bullet \tag{35}$$

Based on the reaction rate constants, Fenton oxidation ($k = 70$ $M^{-1}s^{-1}$) is faster than Fenton-like ($k = 0.001 - 0.01$ $M^{-1}s^{-1}$) oxidation (Wang, 2008). Wang (2008) discovered in the study on wastewater decolourisation that the effect of the classical Fenton was higher than that in Fenton-like in the initial stage.

Therefore, for the effective synergistic integration of the Fenton process with sonolysis the concentration of H_2O_2 should be sufficient in the initial stage of the treatment, i.e. additional dosage of H_2O_2 is probably needed, as the sonolytic H_2O_2 formation was slow.

3.4 Effect of the Fenton process on sonolytic degradation of chlorophene using different forms of iron

In this study, sonolytic treatment of chlorophene was combined with the classical Fenton process (Fe^{2+}/H_2O_2) in order to enhance the degradation rate.

At the beginning of the experiment the formation of hydrogen peroxide in interfacial region of cavitation bubble during the sonolysis was observed. Thus, Fe^{2+} was added into the reactor for the Fenton process to proceed. Analyzing Figure 12, it is resulted in a slight higher formation of HO• during the sonolysis. However, Fig. 14 shows that addition of Fe^{2+} did not influence the degradation rate of chlorophene. Obviously, the initial concentration of H_2O_2 was insufficient for the effective additional oxidation to occur.

Next, the addition of both Fe^{2+} and H_2O_2 to sonolytic process increased remarkably the degradation of chlorophene, as the Fenton reaction is known to be powerful source for generation of HO•. Moreover, the combination of the Fenton oxidation and sonolysis allowed achieving faster (in 60 min) complete degradation of chlorophene than that by the Fenton alone (Fig. 14). The subsequent addition of H•-scavenger to that combination only slightly increased the degradation rate of chlorophene, but this action did not reduce the treatment time of CP complete degradation. Thus, the combination of sonolysis, classical Fenton and H•-scavenger is not considered as appropriate method.
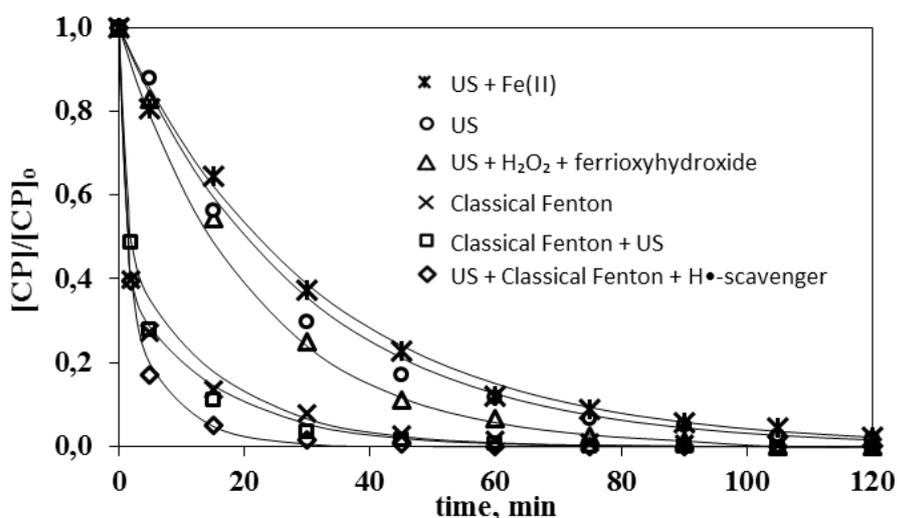

Figure 14. Combination of sonolysis, H•-scavenging by CCl_4 and/or the Fenton process for degradation of chlorophene using either soluble or insoluble forms of iron such as ferrous sulphate or ferrioxyhydroxide ($Fe_2O_3 \cdot nH_2O$). (The initial concentrations of chemicals: $[CP]_0 = 10$ μM, $[Fe^{2+}]_0 = 50$ μM, $[H_2O_2]_0 = 500$ μM, $[CCl_4]_0 = 60$ μM, $[Fe_2O_3 \cdot nH_2O]_0 = 50$ mg L^{-1})

As shown in Figure 14, the first 2 min of CP degradation by the combined sonolysis and classical Fenton process were characterized by fast phase supported by immediate burst of HO• according to Eq. 10. Then the CP degradation profile proceeded into its slow phase where the degradation behaved independent of the initial state of iron. It can be explained by the fact that the generation of HO• is followed by simultaneous oxidation of Fe^{2+} to Fe^{3+}.

Keck *et al*. (2002) described sonolysis of water in the presence of quartz particles leading to higher yields of the radicals. They concluded that solid particles changed the shape of bubbles producing larger surfaces for interaction with target compounds. In this study, insoluble ferric oxyhydroxide as solid fraction in Fenton-mediated sonolysis was proposed. Moreover, experiments were conducted at acidic conditions (pH = 3.0) which promoted slow detachment of Fe^{3+} species from ferrioxyhydroxide surface to aqueous media. The co-existence of ferric iron and H_2O_2 in solution results in the Fenton-like oxidation. The additional influence of sonolysis should obviously support ferric iron dissolution by way of solid particles disintegration via ultrasound energy. Although this application resulted in only slight increase of the degradation rate, the complete oxidation of chlorophene was achieved at least 30 min faster than that by mere sonolysis.

3.5 Chlorophene degradation by-products

The following step of this study was focused on the identification of the intermediate by-products generated during the sonication of chlorophene. In order to accomplish this objective, reaction samples were collected at regular reaction times and analyzed by the GC-MS with an electron-impact ionization mode. Then mass (m/z) spectra obtained was compared to the NIST database. This analysis allowed identifying the primary CP degradation by-products (Fig. 15). The molecular structure of oxidation intermediates indicated the degradation pathway of chlorophene. It serves as an example of classical aromatic ring opening mechanism with initial aromatic ring hydroxylation, further formation of linear polyfunctional products and final decarboxylation.
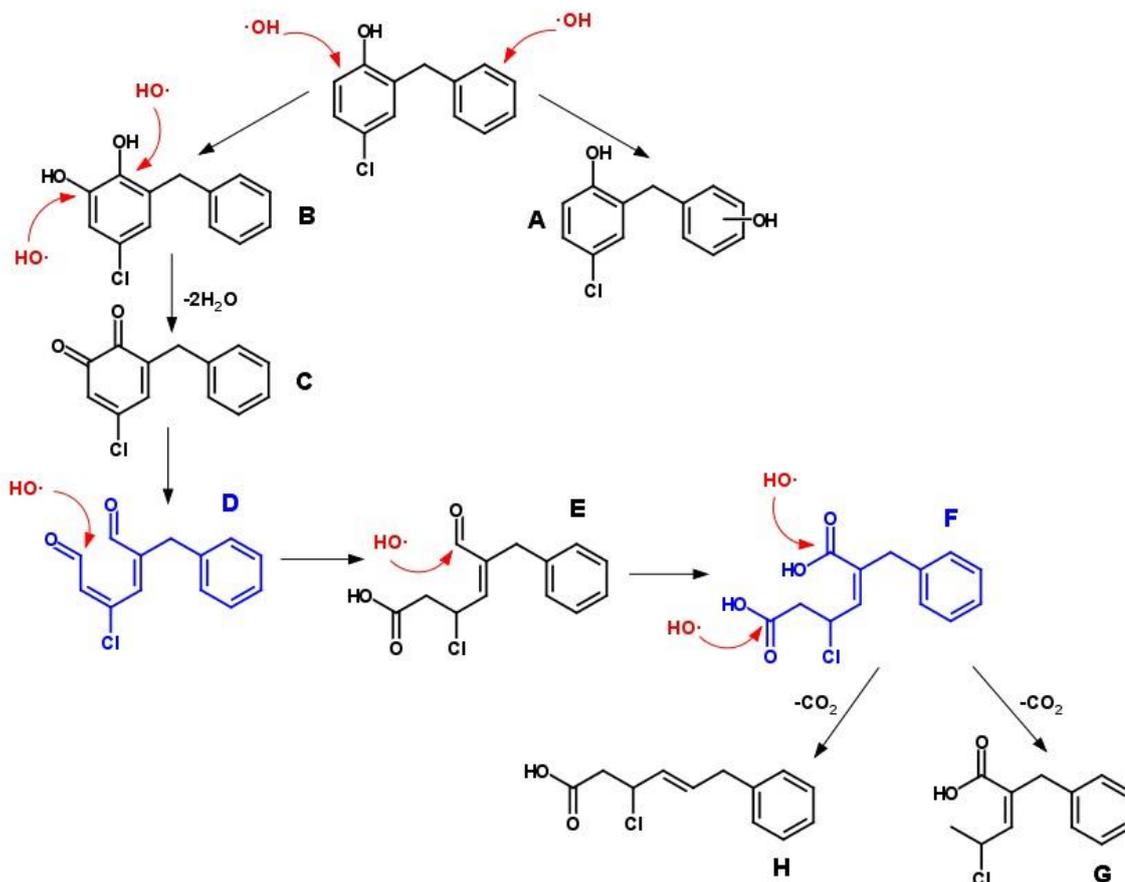
Figure 15. Proposed mechanism of chlorophene degradation. Blue-coloured compounds were not detected on chromatograms, but obviously are the precursors of identified by-products

In the initial stage of CP degradation the hydroxyl radicals attack either primary, or secondary aromatic rings. As a result of hydroxylation the isomers A (3-benzyl-5-chlorobenzene-1,2-diol) and B (4-chloro-2-[(n-hydroxyphenyl)methyl]phenol) were formed. Fig. 16 demonstrates the existence of the characteristic molecule fragments obtained in m/z spectra indicating the probable –OH position. The presence of similar isomers with unidentified structure was also observed in the study of Benitez *et al*. (2013) where CP was oxidized by ozonation. The addition of hydroxyl group to primary aromatic ring caused the following series of ring opening reactions and set the course of CP degradation pathway. The further hydroxyl radical attack directed by the position of the hydroxyl group (Benitez *et al*., 2013) caused hydroxyl-chlorophene oxidation to diketone C (3-benzyl-5-chlorocyclohexa-3,5-diene-1,2-dione). This intermediate product made the subsequent HO• attack favorable for the ring opening reactions.
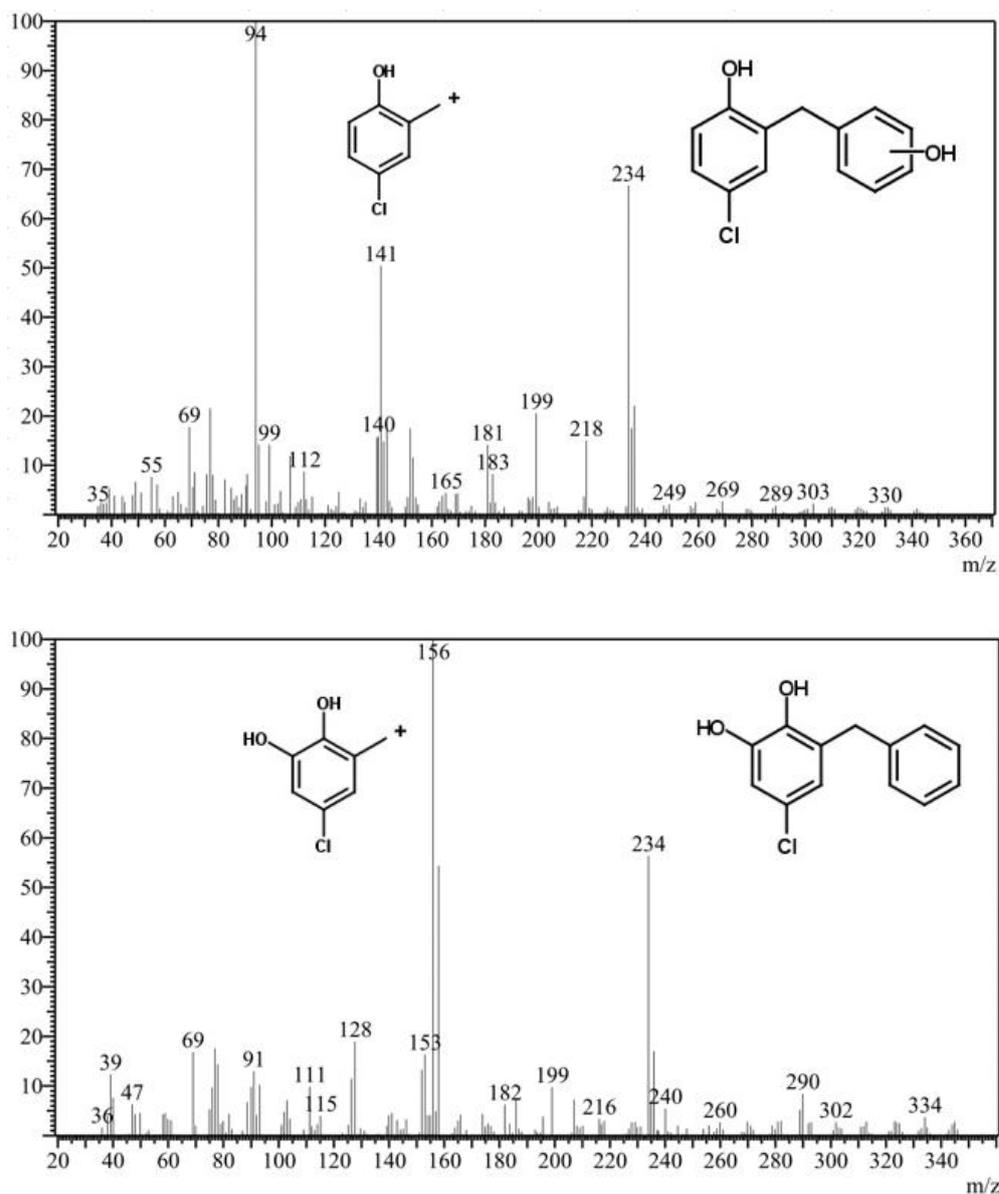
Figure 16. Characteristic fragments obtained by MS with EI allowed distinguishing the structural features of chlorophene degradation by-products, isomers A and B

A following sequence of HO• captures led to the formation of carboxylic acid E [(4Z)- 3-chloro-5-formyl-6-phenylhex-4-enoic acid] and then F [(2Z)-2-benzyl-4-chlorohex-2- enedioic acid]. Although F was not detected on the GC-MS chromatograms, compounds G [(4E)-3-chloro-6-phenylhex-4-enoic acid] and H [(2Z)-2-benzyl-4-chloropent-2-enoic acid] could be obviously formed as a result of F decarboxylation. That occurred via an attack of HO• on the carboxyl carbon.

The structural features of CP degradation by-products were distinguished. For example, the positioning of hydroxyl group (HO-) on either primary or secondary aromatic ring of isomers played the crucial role in the overall degradation pathway and raised the basis for the subsequent partial mineralization of organics through the carboxyl carbon attack by HO• and the resultant decarboxylation.

Although the ion-chromatographic analyses indicated the presence of Cl^- in concentration of 6.7 µM after 120 min of CP sonolytic degradation that corresponded to 67% of maximum dechlorination, the expected mechanism of chlorine substitution to hydroxyl group was not observed using the GC-MS.

Conclusions

In this research, the influence of different enhancement aids as H•-scavengers or the Fenton-mediated processes on the sonolytic degradation of chlorophene was studied. Due to the physicochemical properties of chlorophene it was found that pyrolysis has a negligible effect on its degradation. The removal of non-volatile chlorophene was mainly attained by HO• oxidation.

Fenton-mediated process were performed using different iron forms with and without supplementary H_2O_2. It was hypothesized that addition of iron (Fe^{2+}) into the reaction mixture would utilize H_2O_2 formed during sonolysis via the Fenton oxidation and increase therefore the efficacy of the process. However, this approach did not result in substantial change of CP degradation rate, although some small HO• formation increase was observed indeed. The reason is that H_2O_2 formation proceeded very slow and for remarkable CP degradation increase the additional dosage of H_2O_2 is probably needed. Several experiments were performed using solid surface as ferrioxyhydroxide with supplementary H_2O_2 aimed to activate sono-Fenton process. This resulted in only slight increase of the degradation rate, the complete oxidation was achieved at least 30 min faster than that by mere sonolysis. All in all, the combined sonolysis and the Fenton process (Fe^{2+}/H_2O_2) allowed achieving faster complete degradation than each treatment method alone. Obviously, the main benefit of using that combination lies on the principle that during the first two minutes of Fenton process immediate burst of HO• is occurred, while sonochemical oxidation is moderate as long as the ultrasound was applied. After the fast phase the Fenton degradation proceeded to its subsequent retardation to slow phase where the sonolytic degradation played the major role. Consequently, their combination allowed achieving better CP oxidation, i.e. the complete degradation was achieved 60 min faster than that by mere sonolysis or the Fenton oxidation.

The combination of ultrasound with carbon tetrachloride (CCl_4), used as H•-scavenger, enhanced the degradation efficiency of chlorophene. The mechanism of that relied on the series of H• captures by CCl_4, which interrupted the recombination of H• and HO• in gaseous phase of cavitation bubble. As a result, CCl_4 produced the additional amount of highly reactive HO•-radicals which allowed the more effective degradation of chlorophene. The elevated HO• generation by sonolysis in the presence of CCl_4 was confirmed by the deoxyribose method.

The identification of degradation by-products helped to determine CP oxidation pathway. The mechanism of chlorophene degradation by ultrasound involved the sequence of aromatic ring opening reactions. That resulted in formation of carboxylic acids with their following decarboxylation.

Thus, the supporting methods allowed reducing treatment time and as a result the energy consumption. The integration of such approaches into the conventional wastewater treatment plants may serve for the improved degradation of bioresistant organic emerging pollutants including disinfectants and personal care products with the similar physicochemical properties to that of chlorophene.

RESÜMEE

Käesolevas töös uuriti klorofeeni sonolüütilist lagundamist. Sonolüüsi kombineerimine H•-püüdjatega ja Fentoni reaktsiooniga võimaldas tõsta klorofeeni oksüdatsiooni efektiivsust. Arvestades orgaaniliste ainete lagundamise keemilist olemust sonolüüsil ja klorofeeni füüsikalis-keemilisi omadusi, jõuti järeldusele, et klorofeeni pürolüüsi osatähtsus on käesolevas protsessis tühine. Antud mittelenduva saasteaine lagundamine toimus peamiselt HO• oksüdeerimisega.

Fenton-tüüpi protsessi kombineerimisel sonolüüsiga kasutati erinevaid rauaallikaid, nn mittelahustuvat rauasetet ($Fe_2O_3 \cdot nH_2O$) või lahustuvaid Fe(II)-sooli. Püstitatud hüpoteesi kohaselt peaks Fe(II) lisamine suurendama klorofeeni lagundamise efektiivsust reaktsioonisüsteemis. Selle hüpoteesi aluseks oli HO• tekke määramisel saadud suurenenud HO• hulk Fe(II) lisamisel sonolüüsi reaktsioonisegusse. Paraku ei tõstnud käesolev intensiivistamismeetod märgatavalt klorofeeni lagundamiskiirust. Selle põhjuseks oli aeglane H_2O_2 teke vedelfaasis, mistõttu eeldatav klassikaline Fentoni reaktsioon H_2O_2 ja Fe(II) vahel ei osutunud efektiivseks. Uurimistöö järgmiseks etapiks olid seega eksperimendid, kus lisaks Fe(II)-le kasutati ka H_2O_2. Selle meetodi eesmärgiks oli tagada piisav H_2O_2 kontsentratsioon Fentoni reaktsiooni kulgemiseks sonolüüsi algstaadiumis, kuna on teada, et Fentoni reaktsioonil on kõrge oksüdeerimisefektiivsus väga kitsas ajavahemikus ehk peamiselt esimesel minutil. Sonolüüs tagab omakorda mõõduka oksüdeerimise kogu töötlemisaja ulatuses. Sellest tulenevalt osutus nende kombinatsioon väga efektiivseks ja tõstis märgatavalt klorofeeni oksüdatsiooni kiirust ning saavutati kiirem klorofeeni täielik lagundamine. Sonolüüsi kombineerimine $Fe_2O_3 \cdot nH_2O$ ja H_2O_2-ga ei näidanud märgatavat efekti.

Antud töös uuriti ka H•-püüdmismehhanismi, mis takistab mitteproduktiivset rekombinatsiooni kavitatsioonimullis tekkinud HO• ja H• vahel. Selle tulemusel vabaneb vesikeskkonda HO• lisakogus ning see tõstab sonolüüsi oksüdeerimisvõimet. Eksperimentides kasutati H•- püüdjana CCl_4. CCl_4 juuresolekul suurenes HO• arv. Selle tulemusel suurenes ka klorofeeni lagundamiskiirus. Siin tuleks mainida, et CCl_4 on iseenesest saasteaine ja selle kasutamine lisandina sonolüütilises veepuhastustehnoloogias on ilmtingimata mittesoovituslik. Teisest küljest esineb CCl_4 päris tihti reovees ja seetõttu on antud intensiivistamise mehhanism reaalsetes tingimustes väga tõenäoline.

Lisaks ülalpool nimetatule identifitseeriti ka klorofeeni lagundamisprodukte. Klorofeeni sonolüüsi käigus toimub aromaatse tuuma avamismehhanism, kus hüdroksüülradikaal ründab hüdroksüülrühma kõrval asetsevat süsinikuaatomit. Selle tulemusel moodustub vastav kinooni

ühend, mis määrab edaspidise oksüdeerimise käigu karboksüülhapeteni. Sellele lisaks fikseeriti ka klorofeeni laguproduktide osalise mineralisatsiooni mehhanism.

Käesolevas uurimistöös kasutatud intensiivistamismeetodid võimaldasid vähendada klorofeeniga saastatud vee töötlemisaega ja säästsid seega ka sonolüüsi energiatarbimist. Sonolüüsi kombineerimine Fentoni reaktsiooniga osutus väga efektiivseks ja on võrreldes H•-püüdjate kasutamisega perspektiivsem, kuna H•-püüdmise mehhanism eeldab vastavate orgaaniliste ühendite olemasolu reovees, mis tihtipeale on samuti toksilised nagu uuritav saasteaine. Teisest küljest näitas H•-püüdmise mehhanism ka suurt efektiivsust ning seega peaksid edaspidised uuringud olema suunatud ohutu lenduva reovee komponendi otsingule, mis tagaks vastava H•-püüdmise mehhanismi.

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