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Article

Study of Bisphenol A Degradation Using Ultrasound and Additional Chemical Compounds

Alina Marilena Pahontu(Dura) ¹, Daniela Simina Stefan ^{2,*}, Laura Chiriac (Badea) ³, Ioan Calinescu ⁴, Annette Madelene Dancila ⁵ and Mircea Stefan ^{6,*}

¹ PhD student, Faculty of Applied Chemistry and Materials Science, University Politehnica of Bucharest, Romania, email: pahontu_alina@yahoo.com

² Faculty of Chemical Engineering and Biotechnologies, University Politehnica of Bucharest, 1-7 Polizu Street, 011061 Bucharest, Romania; daniela.stefan@upb.ro

³ National Institute for Research and Development for Industrial Ecology – INCD ECOIND, 57-73 Drumul Podu Dambovitei, District 6, 060652, Bucharest, Romania; email: laura.badea88@yahoo.com

⁴ Faculty of Chemical Engineering and Biotechnologies, University Politehnica of Bucharest, 1-7 Polizu Street, 011061 Bucharest, Romania, ioan.calinescu@upb.ro

⁵ Faculty of Chemical Engineering and Biotechnologies, University Politehnica of Bucharest, 1-7 Polizu Street, 011061 Bucharest, Romania, madelene.dancila@upb.ro

⁶ University Titu Maiorescu, Pharmacy Faculty, No., 22 Dâmbovnicului Street., District 4, 040441, Bucharest, Romania; email: stefan_apcpm@yahoo.com .

* Correspondence: DSS, daniela.stefan@upb.ro; MS, stefan_apcpm@yahoo.com

Abstract: Bisphenol-A (BPA) represents an important co-monomer for obtaining polycarbonate, epoxy resins, flame retardants, in paint, and other chemicals products. Products containing BPA are widely used, and thus, we can find it in the environment: in the air, in the soil, in natural surface water and in sediments, underground water in landfills, and in wastewater. BPA disturbs human and animals' health. This influences the enzymatic, androgenic, neurological, liver and reproductive systems at different stages of human life: like in fetal stage, children and adults' stages. Taking these inconveniences into account, it is very important to remove BPA from water. Ultrasonic technology can be considered a very sustainable and efficient method to remove BPA from water. The advantages of this method is easy to implement on existing water treatment and purification facilities, it does not produce residual compounds that produce sludge, the time required for degradation is of the order of 1-2 hours and the level of degradation is very high. In this work, we presented the studies on the efficiency of ultrasonics under air atmosphere on the degradation of BPA. The influence of the frequency and of some additional compounds such as carbon tetrachloride, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (FS), and ethyl anthraquinone (EAC) was studied. Three different frequencies were used: 1146 KHz, 864 KHz, 580 KHz, at a power of 50 W. It was identified the efficiency of BPA degradation over a period of 60 minutes, with sampling every 15 minutes. Using the LC-MS/MS technique, the degradation compounds were identified that result from the application of ultrasound processes. Pathways of BPA degradation were also proposed. The use of additives such as CCl_4 , FS, and EAC have a positive effect on the BPA degradation process assisted by ultrasound. After 60 minutes of exposure, the degradation capacities reach values between 50% and 75%, and after a 15-minute exposure they reach values between 23% and 55% and mineralization capacities values reach between 20 and 35%. The presence of organic compounds such as CCl_4 and EAC have a more pronounced stimulating action than FS, and EAC has the highest mineralization capacity, which represents around 75% of the degradation capacity.

Keywords: Bisphenol A; removal from water; ultrasound methods; additional compounds; degradation efficiency; mineralisation efficiency

1. Introduction

Bisphenol-A (BPA) represents an important co-monomer for obtaining polycarbonate, epoxy resins, flame retardants, in paint and other chemicals products [1,2]. Products containing BPA are widely used, and thus, we can find it in the environment: in the air, in the soil, in natural surface water and sediments, underground water in landfills and in wastewater [2]. BPA disturbs human and animals health[3-6]. This influence the enzymatic, androgenic, neurological, liver and reproductive systems at different stages of human life: like in foetal stage, children and adults' stages [7,8]. BPA causes disorders of the reproductive system in both women and men that can cause diseases such as infertility, abortions, polycystic ovaries, endometrial hyperplasia, etc. [9]. Taking these inconveniences into account, it is very important to remove BPA from water. Ultrasonic technology can be considered as a very sustainable and efficient method to remove BPA from water. The advantages of this method are: the method is easy to be implemented on existing water treatment and purification facilities, it does not produce residual compounds that produce sludge, the time required for degradation is of the order of 1-2 hours, and the level of degradation is very high [2,10]. Ultrasound (US) treatment of wastewater is considered an advanced oxidation process (AOP). Unlike other AOPs, ultrasound treatment does not require the addition of catalysts or oxidants [11]. Among the various AOPs, the sonochemical process is used for the degradation of organic pollutants, because of its eco-friendly properties and because it does not generate hazardous by-products during the cavitation process. Its efficiency depends on the hydrophobicity of the pollutants, and BPA is a hydrophobic compound, being suitable for US treatment [12].

The ultrasonic mechanism is mainly achieved by acoustic cavitation. It includes the formation of bubbles, the rapid growth and violent collapse of bubbles in the liquid. At this point, high temperatures and pressures rise to 5000 K and 100 Pa, are generated, fact which causes the decomposition of organic pollutants and water [2]. Through the decomposition of water molecules, highly reactive radical species as hydroxyl, hydrogen and hydroperoxide radicals are formed, which can oxidize the organic matrix [13], can destroy the molecular structure of pollutants, to achieve the degradation effect [14]. Organic pollutants are attacked by radicals with a high oxidation potential, forming compounds with lower molecular weight [15].

According to equations 1-5, the reactive radical species produced by the ultrasonic cavitation phenomenon are: [16].



In addition to radicals, the implosion of collapsing bubbles generates strong pressure waves, which are used for physical and chemical processes in wastewater treatment [15]. The diversification of free radical species can be done, for example, by adding a sonocatalyst [14]. Previous studies against the use of US for wastewater treatment question the economic viability, based on energy consumption calculations [12]. The effect of US wastewater treatment is limited by the disadvantage of energy consumption [14]. The possibility and efficiency of US application for BPA degradation have been investigated in various studies, but most of the research have been carried out using the sonochemical process as an auxiliary technology, to assist the photocatalytic, Fenton, UV, electrochemical processes [12]. Combining the US process with peroxydisulfate provided a promising advanced oxidation method for the removal of organic pollutants from aqueous solutions [17].

An effective way to improve the US treatment method to increase the degradation rate and treatment efficiency is by combining it with materials with sonocatalytic activity. The principle of US treatment is based on the attack of free radicals on the pollutant to degrade it, while the input of active sonocatalytic materials can improve the generation and enrichment of free radical species, so

that the degradation process is continuously enriched, in a natural way [14]. A Fenton-like catalyst used in combination with US technology for BPA degradation is Schwertmannite (Sch), an iron (III) oxyhydroxysulfate mineral. BPA degradation was significantly enhanced (98.0%), when the catalytic system was coupled with US (US/Sch/H₂O₂), indicating that there is a synergistic effect between US and Sch on H₂O₂ activation [16]. Due to the limited efficiency of BPA degradation by the single system with US or by oxidants without US assistance, the researchers investigated the activation of four different common oxidants by US. Following the analyses, they found that US and the investigated oxidants have a synergistic effect, obtaining the following synergy indices of the systems US-S₂O₈²⁻, US-H₂O₂, US-HSO₅⁻ and US-IO₄⁻ 1.13, 1.16, 1.25, 2.22 [13]. The study [16] indicates that the degradation reaction of BPA in the presence of US and Sch occurs in two stages, consisting of an induction period, followed by a rapid degradation period, according to a pseudo first-order kinetic process. The degradation efficiency was affected by several operating parameters, especially pH, catalyst dosage, temperature, H₂O₂ concentration. The optimum pH was 3, lower or higher values leading to decreased degradation efficiency. Increasing the dosage of Sch from 0.1 to 1 g/L was effective, but an increase to 2g/L did not lead to the improvement of the process, the increase in temperature led to the increase in the reaction rate in stage II, and the concentration of H₂O₂ was maximally effective at 15mM, lower values were not effective, and higher values inhibited degradation.

From previous research, it was found that ultrasonic degradation was effective at a higher frequency. Investigating the factors affecting the ultrasonic degradation rate of BPA [11], stated that dissolved oxygen, higher ultrasonic frequency in range 300-500 KHz is most efficiently [2], higher power favored BPA degradation, while the presence of HCO₃⁻, HA prevented BPA degradation, and Cl⁻ showed a minor influence. Investigating the effect of operating parameters on BPA degradation efficiency, it was found [7] that degradation was stimulated by increasing ultrasound power (38.87-97.17W), temperature (30-70°C), and initial PDS concentration (peroxydisulfate) (1.71-17.11). Determining the significance of these operational parameters in BPA degradation, their importance was estimated in the following order: temperature 46.83%, initial PDS concentration 40.54%, ultrasound power 12.63%.

The researchers' studies demonstrate that US irradiation is a promising way to effectively treat BPA in aqueous solution under optimal operating conditions – US frequency, power intensity, addition of oxidants, impact of different additives, quickly and without negative side effects.

In this work, we presented the studies on the efficiency of ultrasonics under air atmosphere on the degradation of BPA. The influence of the frequency and of some additional compounds such as carbon tetrachloride, FeSO₄ 7H₂O, and ethyl anthraquinone was studied. Three different frequencies were used: 1146 KHz, 864 KHz, 580 KHz, at a power of 50 W. It was identified the efficiency of BPA degradation over a period of 60 minutes, with sampling every 15 minutes.

Also, using the LC-MS/MS technique, there the degradation compounds that result from the application of ultrasound processes were identified. Pathways of BPA degradation were also proposed.

2. Materials and Methods

2.1. Chemicals and equipments

Chemical reagents used for experiments Bisphenol A (purity > 99.9 %), ethanol (99%), carbon tetrachloride (purity > 99.9 %, CCl₄) ferrous sulphate heptahydrated (FeSO₄ 7H₂O), methanol (HPLC grade) and acetic acid, etil anthraquinone, sulphuric acid were acquired by Sigma-Aldrich (Germany). All the rest of reagents used in the experiment were of analytical quality. High purity water was obtained in house, using an ultrapure water system, from Merck Millipore (Burlington, Massachusetts, US).

Ultrasonic system

A Meinhardt multifrequency ultrasound system composed of a frequency generator (580, 684 and 1146 kHz), a power applicator and an ultrasonic transducer was used. The metal reactor is connected to the transducer through a flange and is provided with a jacket through which coolant from a thermostat circulates. The system diagram is presented in Figure 1

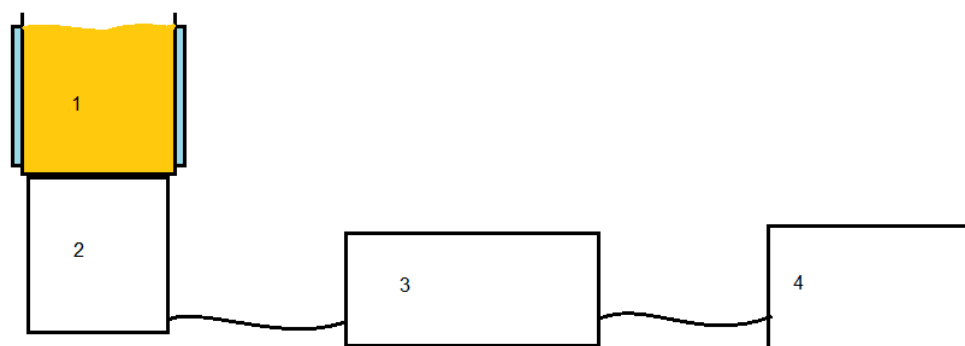


Figure 1. Schematic diagram of the experimental apparatus (Meinhardt Multifrequency system): 1 – US reactor – water jacketed; 2 – ultrasonic transducer; 3 – power amplifier; 4 – frequency generator 580; 684 and 1146 KHz.

2.2. Analytical methods used for BPA and intermediates resulted.

2.2.1. Analytical conditions used for BPA determination

The experiments for BPA quantification were carried out using Agilent 1260 series LC system (Agilent, Waldbronn, Germany) coupled with an Agilent 6410B triple-quadrupole mass spectrometer with electrospray ionization source (ESI). Luna C18 type (150 × 2.0 mm; 3.0-μm particle size) chromatographic column, maintained at 35°C was used. The mobile phase consisted of 0.01 % acetic acid in ultrapure water (A) and Methanol (B) 30/70 v/v, in isocratic mode, at a flow rate of 0.15 mL/min. The injection volume was 1 μL. BPA detection was performed in MRM (Multiple Reaction Monitoring) mode, monitoring two mass transitions: 227 → 212 and 227 → 133. MS parameters established for the BPA quantification were: cell accelerator voltage (1V), fragmentor voltage (150V), collision energy (15V), and dwell time (250msec). The BPA elution was performed in less than 6 min. ESI operational parameters: capillary voltage (6000V), drying gas temperature (300°C), drying gas flow (7 L/min) and nebulizer pressure (40 psi).

2.2.2. Analytical conditions used for the identification of the degradation products

Determination of unknown degradation products of BPA was executed using LC-MS/MS technique. The injection volume was 5 μL. The Luna C18 chromatographic column temperature was set at 20°C. The mobile phase consisted of 0.01% acetic acid in ultrapure water (A) and Methanol (B) 40/60 v/v, in isocratic mode, at a flow rate of 0.15 mL/min and a stop time of 15 min. Data were gathered in the enhanced mass spectra mode, between 50 and 350 Da. Full-scan chromatograms were registered, using the ESI source in negative mode. ESI operational parameters: capillary voltage (6000V), drying gas temperature (300°C), drying gas flow (7 L/min) and nebulizer pressure (40 psi).

2.2.3. Quality assurance and quality control

All samples were analyzed in duplicate. An etalon and a blank sample were injected at each test sequence. The method linearity was evaluated between 0.015 – 25 mg/L, using six calibration points (0.015, 0.01, 0.5, 5.0, 10 and 25 mg/L), high correlation coefficient value being obtained, $R^2 = 0.998$. Recovery was not evaluated because sample preparation required only a dilution step. The RSD values for intra-day and inter-day precision were 3.2% and 5.7%, respectively. The method accuracy was 0.92%. Limit of detection (LOD) was 0.005 mg/L, and limit of quantitation (LOQ) was 0.015 mg/L,

respectively. The measured uncertainty was determined to be 22.6%. Samples were diluted using ultra-purified water, to fit in the calibration domain. The degradation level of the BPA was determined using chemical oxygen demand analysis, COD according to the SR ISO 6060:19962.

2.4. Work Methods

Volumes as 100 mL of synthetic solution with 25 mg/L initial BPA concentration were introduced into the ultrasonic reactor under air atmosphere. The ultrasonic reactor was inserted into a cooling bath that maintains a relatively constant temperature in the range between 20 and 32°C. The influence of frequency and doses of some additional compounds such as: carbon tetrachloride, ferrous sulphate heptahydrate and ethyl anthraquinone on the efficiency of BPA degradation were studied. Three different frequencies were used: 1146 KHz, 864 KHz, 580 KHz, at a power of 50 W, in the absence and in the presence of additional compounds.

Carbon tetrachloride, CCl₄ was used in three different initial doses: 6 µL, 12 µL and 25 µL to 100 mL initial solution. The degradation efficiency is studied for 864 KHz, 580 KHz, at a power of 50 W, after 15 minutes of exposure. Another additional compound, FeSO₄ 7H₂O, FS, with 0.1 mg/L concentration, was used in two doses: 5mL /95mL initial solution and 20 mL /80mL of initial solution. The variation of efficiencies of BPA degradation in time, for each 15 minutes, time of 60 minutes, at a frequency of 580 KHz was studied. In the end, the BPA degradation efficiency was studied for a time of 60 minutes at 580 KHz for Ethyl anthraquinone with doses of 0.1, 0.2, 0.3 mL/100 mL initial solution, respectively. All the experiments have been done in duplicate; the values used in the paper represent the average value between the two runs. For optimization of the process, a comparison between all methods, all doses used for a frequency of 580 KHz, and after 15 minutes, were made.

For determined the effects of the process applied were determined the:

- efficiency of BPA degradation using the equation:

$$E = \frac{(C_0 - C_t) * 100}{C_0} \quad (1)$$

were: C_0 is the initial concentration of BPA in initial solution, mg/L, C_t is the concentration of BPA at the t moment in the system, mg/L

-efficiency of BPA mineralization using equation:

$$E_m = \frac{(C_{COD_0} - C_{COD_t}) * 100}{C_{COD_0}} \quad (2)$$

where: C_{COD_0} is the initial Chemical oxygen demand, COD, concentration for BPA in initial solution, mg/L, C_{COD_t} is the COD concentration of BPA solution at the t moment in the system, mg/L

3. Results

3.1. BPA efficiency degradation

3.1.1. Influence of US Frecvency

The results of the conducted studies showed that, for frequencies of 580 KHz and 864 KHz, and at a power of 50 W, the BPA degradation efficiency is around 38%. It can also be seen that the efficiency increases to values of 23%, 26% respectively, after the first 15 minutes, and reaches values around 32% after 30 minutes. An exposure longer than 30 minutes does not justify the energy consumption. For 1146 KHz frequency, the efficiency increases at values around 7% after 60 minutes. This means that the use of very high frequencies is not justified. In Figure 2. there are shown the BPA concentrations chromatograms superimposed for US exposure at frequencies 580 KHz, 864 KHz and 1146 KHz.

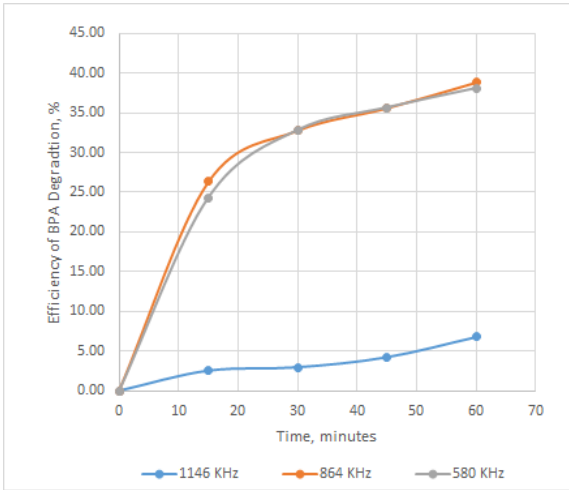


Figure 2. Influence of the US frequencies on the BPA degradation efficiency.

From the analysis of Figure 3, it can be seen that the height of the BPA peaks over time decreases to comparable values for the first two frequencies. At 1146 KHz, the height of the peak’s changes very little, which proves the poor efficiency of high frequencies in the process of BPA degradation.

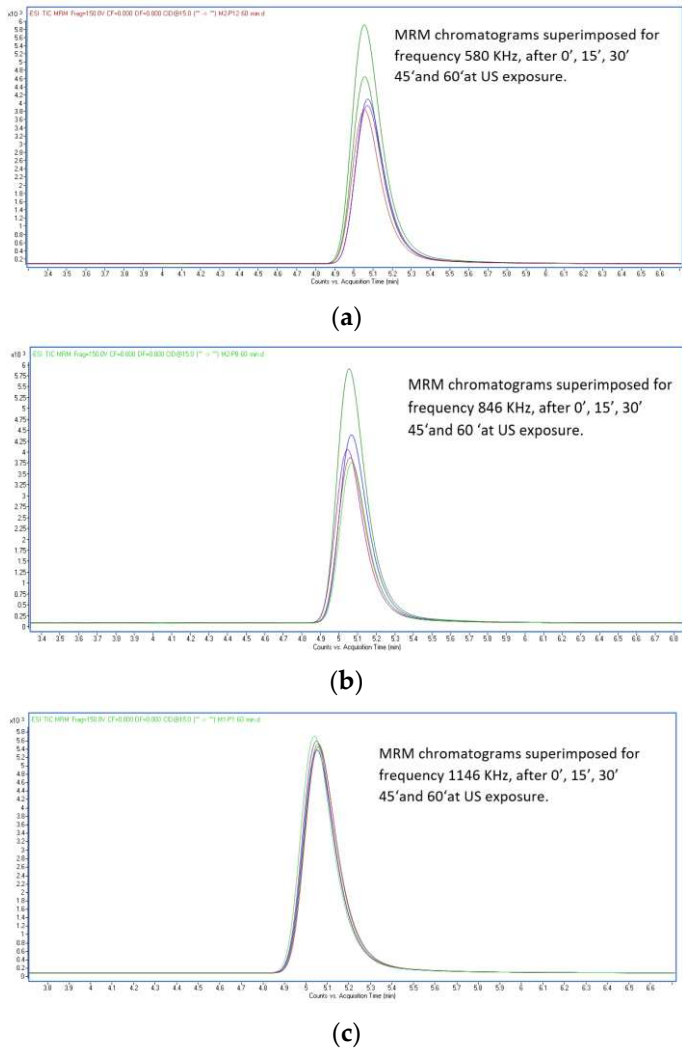


Figure 3. Concentration chromatograms superimposed at US exposure for frequencies 580 KHz, 864 KHz and 1146 KHz after 0', 15', 30' 45' and 60'.

The GS-MS/MS analysis highlighted the chemical species that appear after exposure to US. In Figure 4 it is shown the proposed pathway to BPA degradation, using US at frequencies of 580 KHz and 864 KHz, for an exposure of 60 minutes. After the first 15 minutes of exposure to US at both 580 KHz and 864 KHz, compounds such as monohydroxylated bisphenol A and dihydroxylated bisphenol A appear in the system, which prove the oxidizing action of the hydroxyl radical. This is added to the aromatic nucleus, forming vicinal Di hydroxides or Tri hydroxides [18], then vicinal carbonyl compounds, hydroperoxides following the splitting of the aromatic nucleus. It results in dicarboxylic acids that fragment to carboxylic acids, with small chains of carbon atoms such as acetic acid, formic acid, oxalic acid [19]. Another compound that results in the first 15 minutes is p-benzyl, p-phenyl isopropane, toxic for the environment [20], and which must be subjected to advanced oxidation. After 30 minutes of exposure to the US, fragments such as 4 isopropenyl phenol and 4-hydroxyacetophenone appear. These compounds are toxic compounds, relatively difficult to biodegrade in the environment, that must be oxidized further to non-toxic compounds [21-23].

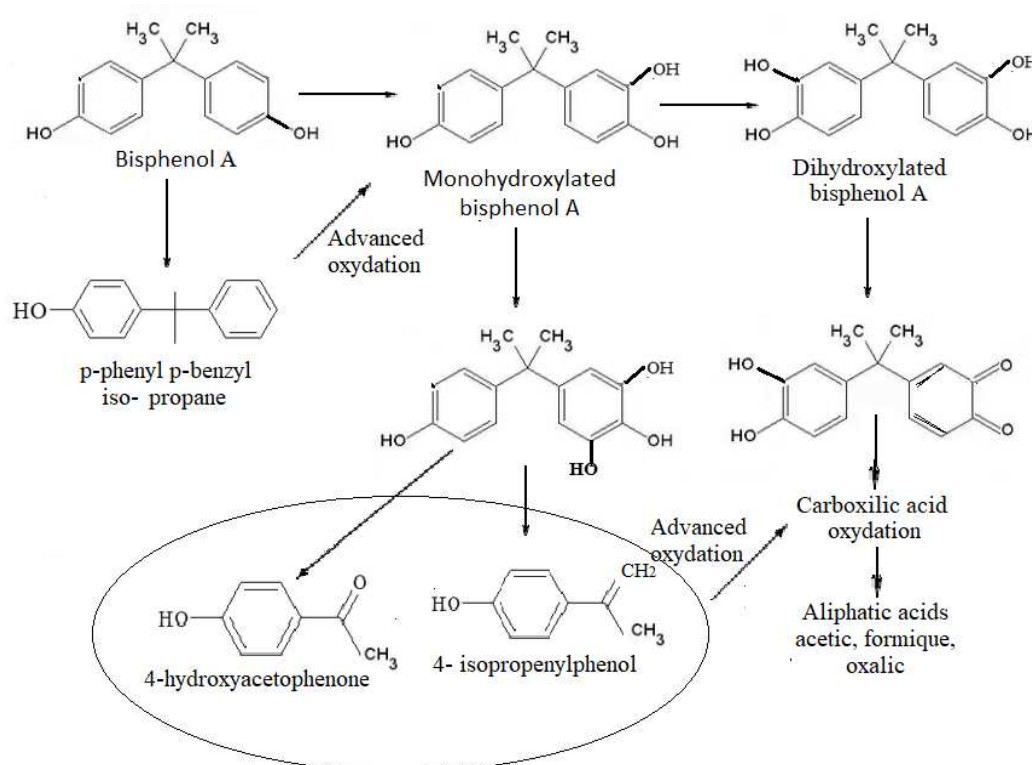


Figure 4. The proposal pathway to BPA degradation using US at frequencies of 580 KHz and 864 KHz, for an exposure of 60 minutes.

3.1.2. Influence of CCl₄ additional compounds

The use of carbon tetrachloride as an additional substance at US exposure with frequencies of 580 KHz and 864 KHz, and the power of 50 W, for 15 minutes, has a positive effect on the degradation efficiency of BPA. The BFA degradation efficiency increases from values of 25% at a dose of 0 μL to values around 55% at a dose of 6 μL CCl₄ per 100 mL solution with BFA, from values around 70% at a dose of 25 μL (see Figure 5). In Figure 6 the degradation efficiency of BPA was compared with the efficiency of the mineralization process. It can be observed that only 35% of the initial amount of BPA, which represents half of cantity degraded, managed to mineralize to carbon dioxide and water, in the first 15 minutes of exposure, to US with a frequency of 580 KHz, and P=500 W.

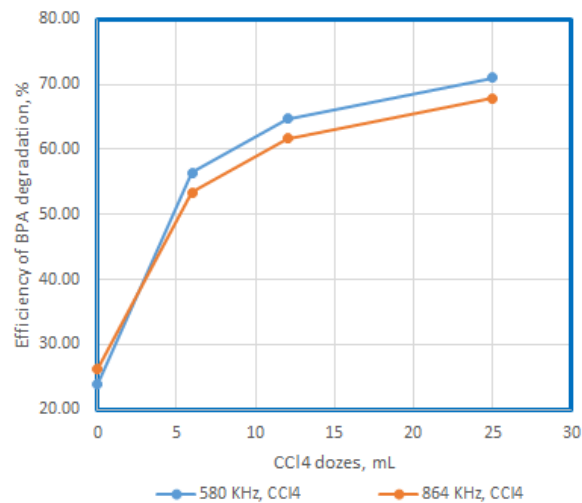


Figure 5. Efficiency of BPA degradation at US exposure at 580 KHz and 864 KHz, in presence of CCl₄, for 15 minutes.

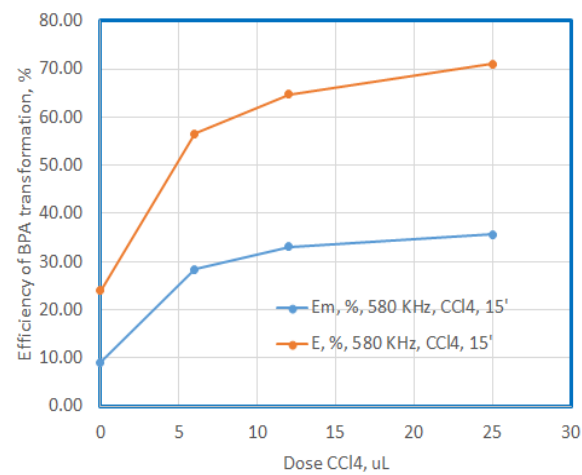


Figure 6. Efficiency of BPA degradation and mineralization at US exposure with 580 KHz, in presence of CCl₄, for 15 minutes .

Figure 7 shows a proposal pathway to BPA degradation using US at frequencies of 580 KHz and 864 KHz, for an exposure of 15 minutes in the presence of CCl₄.

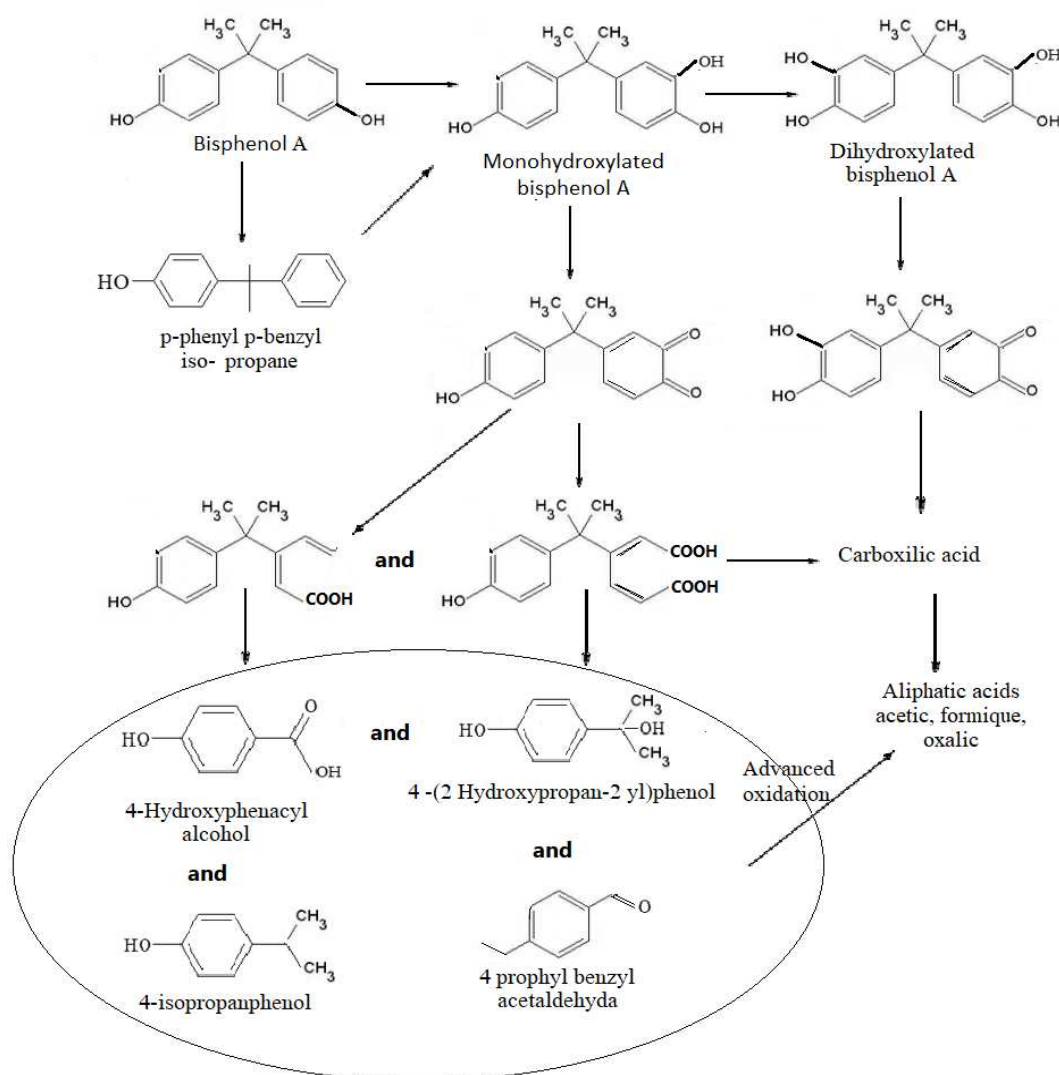


Figure 7. The proposal pathway to BPA degradation using US at frequencies of 580 KHz and 864 KHz, for an exposure of 15 minutes in presence of CCl_4 .

It was identified that exposure to US radiation in presence of carbon tetrachloride favors the formation of hydroxyl and hydroperoxyl oxidizing species. In the first 15 minutes, oxidized species such as monohydroxylated bisphenol A [24], and dihydroxylated bisphenol A [25], vicinal dihydroxy and dicarbonyl compounds [26], mono- or di-carboxylic compounds [27], resulting from the splitting of one of the aromatic ring are formed. They are degraded step by step, into carboxylic acids with a small number of carbon atoms, and other components such as 4-Hydroxyphenacyl alcohol, 4-(2-Hydroxypropan-2-yl)phenol, 4-isopropanphenol, 4-propyl benzyl acetaldehyde, partially oxidized compounds, with lower or higher toxicity [20,28], which must be oxidized further. Also it is formed P-phenyl-p-benzyl-isopropane a reduced, a very toxic compound, which must be oxidized further [29]. The positive effect of CCl_4 is highlighted by the fact that, in the resulting mixture of compounds, more species with a more advanced level of oxidation are formed in a short time, than in the case of US exposure without additional compounds.

3.1.3. Influence of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, FS, additional compounds

After 60 minutes of exposure to US at 580 KHz and at different doses of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ with a concentration of 0.1 mg/L, it can be observed in Figure 8.

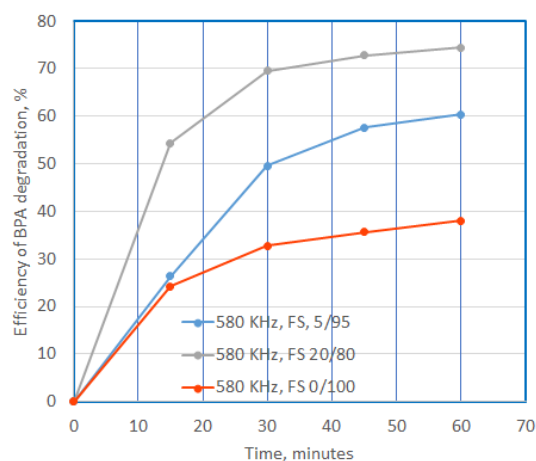


Figure 8. Efficiency of BPA degradation at US exposure in presence of SF, additional compounds, with a concentration of 0.1 mg/L, in time.

The degrees of degradation of BPA were reached around 60% and 72%, for a dose of 5 mL/95 mL and 20 mL/80 mL initial solution, respectively. After 30 minutes, the degradation capacity reaches around 50% and 70% for the two doses, respectively. This proves that FS has a beneficial effect on BPA degradation. The mineralisation efficiency increase to values around 9 % in absence of additional compounds, at 14% and 24 % respectively, for the two doses of FS, after 15 minutes of exposure (see Figure 9).

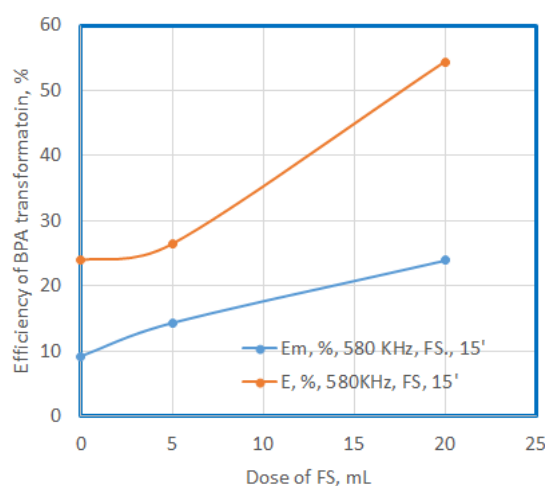


Figure 9. Efficiency of BPA transformation at US exposure in presence of SF, additional compounds, after 15'.

Figure 10 shows a proposal pathway to BPA degradation, using US and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ as additional compounds at frequencies of 580 KHz. The presence of FS increases the US effects. The pathway of the BPA degradation in the first steps involves the formation of the same compounds as in the presence of CCl_4 , the difference appears in terms of intermediate degradation compounds that are formed after the first 15 minutes of contact and in greater numbers.

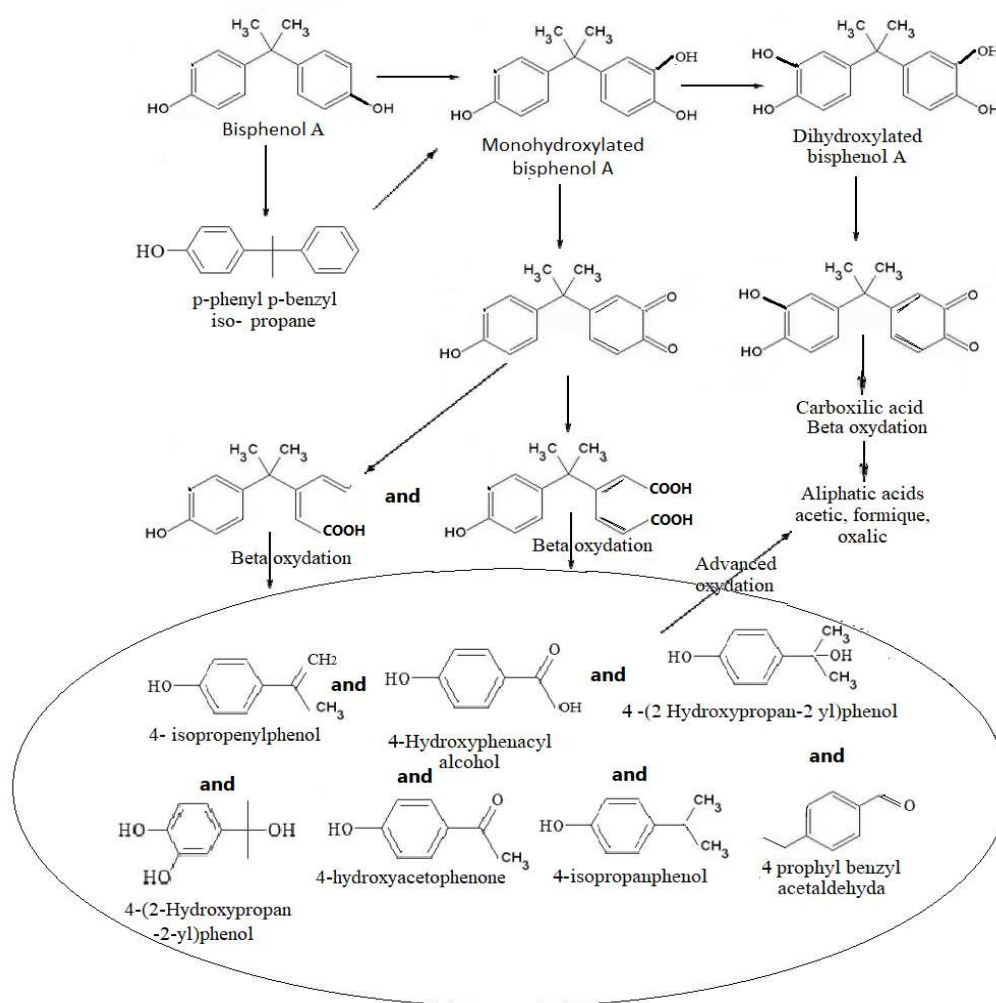


Figure 10. The proposal pathway to BPA degradation, using US and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ with concentration 0.1 mg/L, as additional compounds at different doses, and at frequency of 580 KHz for an exposure of 60 minutes.

3.1.4. Influence of ethyl anthraquinone, EAC, additional compounds

Doses of 0.1, 0.2, 0.3 ml of EAC were added over the 100 ml of BPA solution with a concentration of 25 mg/L,

US effect is amplified by EAC at 580 KHz. Thus, as the doses increase, the degradation efficiency of BPA also increases from approximately 39% in the absence of EAC, after 60 minutes, to over 64%, 68% and 72%, respectively (see Figure 11).

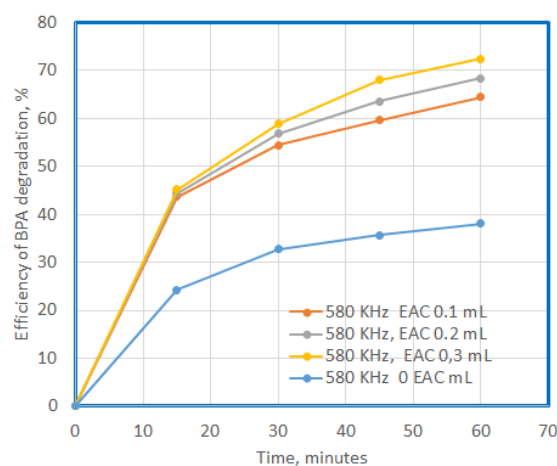


Figure 11. Efficiency of BPA degradation at US exposure in presence of EAC, in time.

Analyzing Figure 12, one can see the stimulatory effect of EAC on BPA degradation after 15 minutes of exposure, compared to the mineralization capacity. Increasing the dose of EAC causes the mineralization efficiency to increase to 32%, for a dose of 0.3 ml of EAC, while the degradation capacity remains relatively constant, around 45%, for the first 15 minutes of exposure.

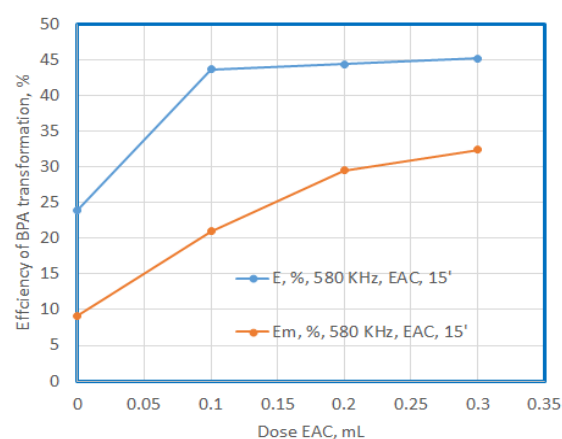


Figure 12. Efficiency of BPA transformation at US exposure in presence of EAC after 15' exposure.

This shows that approximately 70% of the intermediate compounds that are formed have been mineralized. The presence of EAC favors the formation of larger amounts of oxidizing species that favor mineralization.

The proposal pathway to BPA degradation using US and EAC as additional compounds at frequencies of 580 KHz in the Figure 13, is similar with the previous proposal pathway, because GS-MS/MS methods identified the same compounds as in this case.

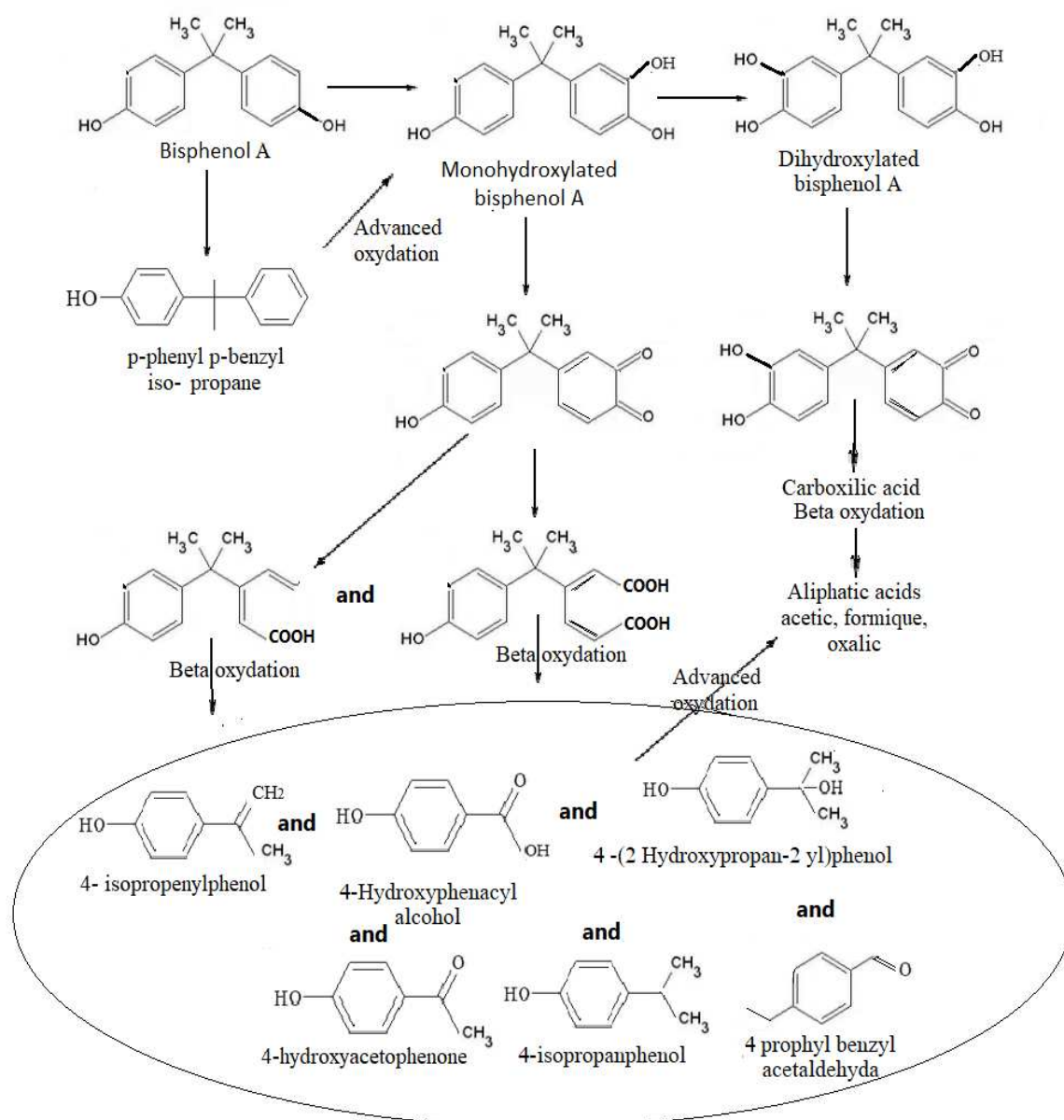


Figure 13. The proposal pathway to BPA degradation using US and EAC, as additional compounds at different doses and at frequency of 580 KHz for an exposure of 60 minutes.

4. Discussions

To optimize the process, the use of US with a frequency of 580 KHz, after a 15-minute exposure was chosen, as a comparison term. Figures 14 and 15 show the comparative values of the degradation efficiency and the mineralization efficiency for all the situations presented previously.

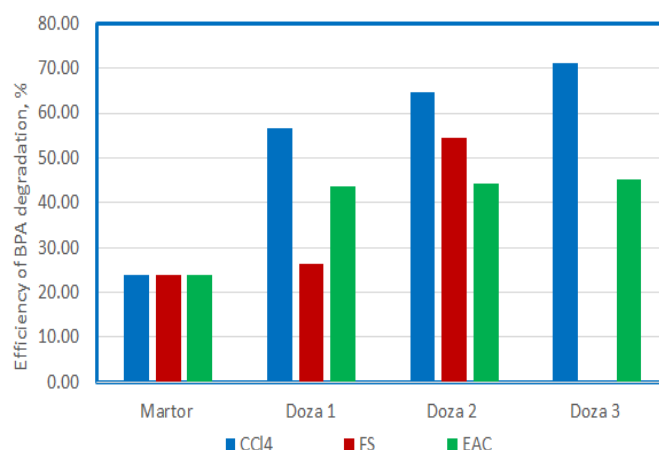


Figure 14. The comparison between the degradation efficiency of BPA at 15 minutes of US exposure and different additional compounds.

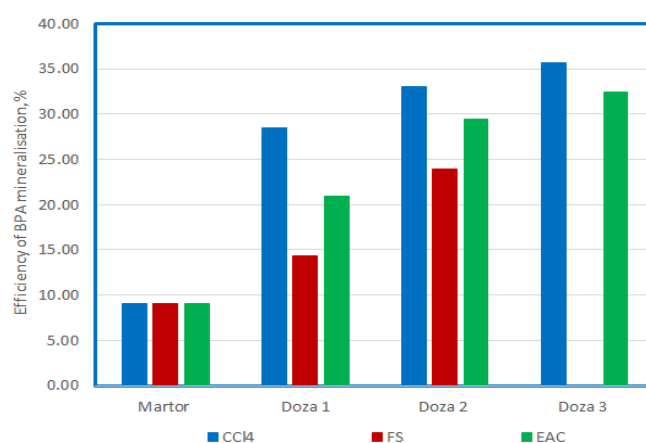


Figure 15. The comparison between the mineralisation efficiency of BPA at 15 minutes of US exposure and different additional compounds.

The use of ultrasound with high frequencies of 580 and 864 KHz and P 50 W determines degradation in proportion of 23%, and mineralization in proportion of 9% for BPA present in solutions with the initial concentration of 25 mg/L. The best degradation efficiency is obtained when using carbon tetrachloride, and the efficiency increases with the increase of the doses used, in the order of 58%, 64 and 70%. In this situation, the demineralization capacity increases from 28%, to 33% and 36%, which means that almost half of the amount that degrades reaches mineralization.

The use of FS increases the efficiency of degradation and mineralization as the dose used increases, reaching values of 28% and 54%; and 14% and 24%, respectively. The mineralization capacity is also almost half of the degradation capacity.

In the case of the use of EAC, it can be observed that the increase in the dose does not cause a sharp increase in the degree of degradation, it remains at values around 45%, while the mineralization capacity increases at values of 20%, 29% and 35% respectively as the dose increases. It seems that the use of doses of 0.3 mL of EAC causes an increase in the degree of mineralization to approximately 75% of the degradation capacity.

5. Conclusions

The use of ultrasound is a reliable method of degrading organic compounds in general and BPA in particular, taking into account the fact that ultrasound devices can be easily installed on already existing treatment/purification installations.

As a result of the degradation processes, there is no sludge that affects the subsequent stages of the treatment/purification process.

The use of additives such as CCl_4 , FS, and EAC have a positive effect on the BPA degradation process assisted by ultrasound. After 60 minutes of exposure, the degradation capacities reach values between 50% and 75%, and after a 15-minute exposure they reach values between 23% and 55%, and mineralization capacities between 20 and 35%. The presence of organic compounds such as CCl_4 and EAC have a more pronounced stimulating action than FS, and EAC has the highest mineralization capacity, which represents around 75% of the degradation capacity.

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