

Treatment of Bisphenol-A Using Sonication-assisted Photo-Fenton Hybrid Process: Influence of Reaction Parameters



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Sonication-assisted photo-Fenton oxidation of an endocrine disrupting compound, bisphenol-A (BPA), was studied under visible-light irradiation in the presence of a LaFeO₃ perovskite catalyst. The effects of the parameters: initial BPA concentration ([BPA]₀), H₂O₂ concentration ([H₂O₂]₀), catalyst loading, initial pH of the BPA solution, and reaction temperature were studied on the sonication-assisted photo-Fenton oxidation of an aqueous BPA solution. The optimum conditions for the oxidation were determined to be: [BPA]₀ = 10 ppm, [H₂O₂]₀ = 4.8 mM, catalyst loading = 0.75 g L⁻¹, pH = 2.6, temperature = 313 K. During all runs, sonication power of 40 W, visible lights power of 150 W+150 W, BPA solution volume (0.5 L), and stirring speed of 500 rpm were kept constant. Under these conditions, degradation of 56.3 %, COD removal of 50.9 %, and TOC removal of 15.6 % were achieved after 6 h of reaction. The small amount of iron that leached into the solution indicated high stability of the catalyst. The sonication-assisted photo-Fenton oxidation of BPA was described by the second order kinetics with an activation energy of 15.34 kJ mol⁻¹. Toxicity tests were also performed and the results revealed that the intermediates formed in the sonication-assisted photo-Fenton oxidation of BPA were less toxic compared to the parent BPA molecule at a neutral pH value. However, the same interpretation was not valid at the acidic pH of 2.6.

Keywords:

Bisphenol-A, sonication-assisted photo-Fenton oxidation, perovskite catalyst, parametric study, toxicity

Introduction

Bisphenol-A (BPA) is widely used in the plastic industry to produce epoxy resins and polycarbonate polymers. Hence, BPA is found in plastic food containers, food-can linings, water bottles, and so on.

BPA is released into ground water not only from the discharges of effluent from the wastewater and washwater of industrial plants, but also indirectly from water streams containing plastic debris and landfills. In natural waters, BPA is usually present at a concentration range of 0.01 – 1.9 µg L⁻¹; however, landfill leachate has BPA concentrations as high as 17 mg L⁻¹.¹ However, many studies have shown that BPA is an endocrine-disrupting chemical, which can mimic the effects of endogenous hormones and tends to cause harm to human health in terms of disrupting the central nervous system and the reproductive system^{2–4} even at low exposure

levels. BPA also has an acute toxicity in the range of about 1–10 µg mL⁻¹ for a number of freshwater and marine species.⁵ Therefore, it is absolutely necessary to develop methods for the effective removal of BPA from wastewater.

A broad spectrum of scientific studies was reported on BPA removal from aqueous systems through various Advanced Oxidation systems, AOPs,^{6–16} such as sonication, Fenton reaction, photocatalytic reaction, electro-catalytic oxidation, and ozonation. These methods were used either individually or in combination.

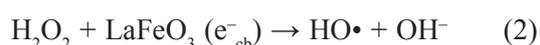
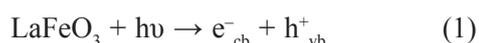
In this study, the combined AOPs of sonication, heterogeneous Fenton oxidation and photodegradation in the presence of visible light was used in degradation of BPA aqueous solution.

The Fenton process is one of the most popular AOPs, and is frequently used to remove non-biodegradable and recalcitrant organic compounds from wastewater. It employs hydroxyl radicals (HO•) with an oxidizing potential of 2.80 V with respect to the normal hydrogen electrode (NHE) at pH = 0,¹⁷ which is substantially higher than other oxidants

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such as permanganate ions. In the Fenton reaction, the generation of HO• involves reactions between the hydrogen peroxide (H₂O₂) as the oxidant and iron species as the catalyst.¹⁸ However, the homogeneous Fenton process has limitations, including: firstly, the need for additional processing to deal with the dissolved iron ions and sludge during the sewage treatment process; secondly, the acidification of effluents before treatment to avoid the formation and subsequent precipitation of iron oxyhydroxides; and thirdly, further treatments for neutralization.¹⁹

These difficulties can be overcome using a heterogeneous catalyst. In this study, Fe containing LaFeO₃ perovskite catalyst was used as a heterogeneous Fenton catalyst. The LaFeO₃ perovskite catalyst also acts as a photocatalyst in the presence of light, so-called photocatalytic reactions. The most known photocatalyst is TiO₂ due to its high catalytic activity, high chemical stability, inexpensiveness, and nontoxicity,²⁰ however, it is only active under UV light irradiation due to the large band gap of 3.2 eV. It is well known that UV energy occupies only less than 5 % of solar energy, and 45 % of solar energy belongs to visible light.²¹ Therefore, development of visible light active photocatalyst is critically important, and LaFeO₃ perovskite-type catalyst is a good candidate for this purpose. In the presence of visible light ($\lambda > 400$ nm) illumination, photogenerated conduction band electron-valance band hole pairs are formed in the LaFeO₃ perovskite catalyst (Eq. 1). As the electrons are easily trapped by the H₂O₂, HO• radicals (Eq. 2) are formed.²²



Energy utilization is reduced due to the dark usage of cheap reagent hydrogen peroxide H₂O₂ in Fenton reaction. Solar radiation or visible light irradiation can be utilized to carry out the photochemical stages of the photo-Fenton reaction so that complete mineralization of organic compounds is possible in a short time.²³

In sonication, the chemical reactions occur through the phenomenon of acoustic cavitation. Cavitation refers to the rapid growth and implosive collapse of bubbles in a liquid, resulting in an unusual reaction environment. The implosive collapse of the cavitation bubbles results in a high temperature up to 5000 °C and a high pressure of 500 atm. Under such extreme conditions, HO•, and H• are created from the H₂O dissociation reactions in the bubble.^{24–28} The reaction between the HO• radicals and the pollutant molecules can take place inside the bubble (pyrolysis) or in the bubble-liquid interface or in the bulk, depending on the nature of the

pollutant.²⁹ Hydrophobic compounds mainly degrade in the cavitation bubble and/or at the interface, whereas, the hydrophilic compounds mostly degrade in the bulk solution with the oxidation of the HO• radicals which escape from the interface.¹¹

Ultrasonic irradiation not only produces HO• radicals that oxidize the organic pollutants, it also generates benefits in heterogeneous catalytic systems by decreasing the mass transfer limitations via generating turbulence, which provides a good mixing. Ultrasonic irradiation continuously cleans the surface of the catalyst, and helps to maintain its reactivity over longer irradiation times.^{29,30}

In this study, the aim was to obtain the operating conditions for the degradation of BPA with a high degradation degree, COD, and TOC removals by the heterogeneous sonication-assisted photo-Fenton process over an iron containing LaFeO₃ perovskite catalyst in the presence of visible light.

Conducting the toxicity test to determine whether the formed end products are less toxic than the initial BPA solution, is also a good contribution to related literature. To the best of our knowledge, no study so far has investigated the reaction parameters and relationship between toxicity and formed intermediates in such detail.

Experimental

Materials

The Bisphenol-A (BPA, C₁₅H₁₆O₂) was obtained from Sigma-Aldrich, and was used without further purification. The H₂O₂ solution (35 wt%) of analytical grade was purchased from Merck. The deionized water obtained from a Millipore Direct Q purification unit was used in the experiments.

Experimental procedure

The sonication-assisted photo-Fenton oxidation of BPA was investigated in the presence of two visible lamps (high pressure Na lamps, each 150 W, Philips), which were placed at both sides of cooling jacketed reactor. The distance between the lamp and reactor was constant at about 5 cm. The reaction temperature was kept constant at desired value by circulating cooling water (PolyScience, MX07R-20-A12E) around the reactor to avoid significant increase in reaction temperature. The reaction vessel (containing 500 mL of BPA aqueous solution (height of solution column = 11 cm)) was maintained in a box to avoid photochemical reactions induced by natural light and noise from ultrasonic probe. Ultrasonic probe system (frequency of 20 kHz and input power of 40 W, Bandelin HD3200), was used as a source of sonication. Samples were

periodically taken from the reactor, centrifuged, and filtrated with 0.45 μm PTFE (Agilent) syringe filters, then analyzed by HPLC (Agilent 1200) with a ZORBAX Eclipse Plus C18 (4.6 x 150 mm, 5 μm) column. Detection of BPA was achieved with an UV detector at 278 nm, with a 20 μL sampling loop. The mobile phase, ultrapure water/acetonitrile (50/50, v/v) was run in an isocratic mode with a flow rate of 0.5 mL min^{-1} . The column oven was maintained at 25 $^{\circ}\text{C}$. BPA degradation degree (x) was calculated according to the following equation:

$$\text{BPA degradation, } x, \% = \frac{c_{\text{BPA},0} - c_{\text{BPA}}}{c_{\text{BPA},0}} \cdot 100 \quad (3)$$

where $c_{\text{BPA},0}$ and c_{BPA} are the initial concentration and the concentration of bisphenol-A, mol dm^{-3} , at taken time, respectively.

The Chemical Oxygen Demand (COD) removal of the BPA solution was determined by measuring the initial COD and final COD (at the end of the run) of the BPA solution with a COD device (Lovibond Checkit Direct COD Vario). The Total Organic Carbon (TOC) reduction was measured with a Teledyne Tekmar Lotix analyzer at the end of each experiment.

The LaFeO_3 perovskite catalyst was prepared using the sol-gel method and calcined at 500 $^{\circ}\text{C}$. Details of experimental set-up, experimental procedure, catalyst preparation procedure, and the characterization of the catalyst are given in the previous study.²²

The stability of the catalysts was tested by measuring the iron leaching into the solution after each run using an Atomic Absorption Spectrometer (Varian 10 plus).

Results and discussion

Parameters affecting the sonication-assisted photo-Fenton oxidation of BPA

In the author's previous study,³¹ individual and different combinations of each advanced oxidation process of Fenton reaction, photodegradation, and sonication (US) in the presence of LaFeO_3 perovskite catalyst were investigated, and it could be said that US plays a crucial role in the oxidation, and LaFeO_3 is a good sonocatalyst rather than a photocatalyst under the experimental conditions in that study. The catalytic activity of LaFeO_3 perovskite catalyst in sono-Fenton process (19.9 %) was higher than that in photo-Fenton process (12.7 %) after a reaction time of 3 h. However, the highest degradation degree (21.8 %) was achieved in the overall process of sonication-assisted photo-Fenton oxidation, as well as the highest COD reduction

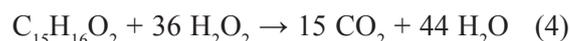
(11.2 %). As the highest BPA degradation and COD removal were obtained in sonication-assisted photo-Fenton process, in the present study, a detailed parametric investigation was conducted for degradation of BPA, effects of the initial BPA concentration, H_2O_2 concentration, catalyst loading, initial pH of the BPA solution, and reaction temperature were studied in the sonication-assisted photo-Fenton oxidation of an aqueous BPA solution.

Effect of H_2O_2 concentration

H_2O_2 is a strong oxidant which takes an active role in producing OH^{\bullet} and/or HO_2^{\bullet} in photo-Fenton and sonication reactions. Although it is an environmentally friendly reagent, efficiency should be maximized with as little oxidant as possible in order not to increase the cost of treatment. The effect of the H_2O_2 concentration on the heterogeneous sonication-assisted photo-Fenton oxidation of BPA was investigated at the temperature of 298 K, with 0.50 L of 15 ppm (0.066 mM) BPA solution, 0.5 g L^{-1} of LaFeO_3 perovskite catalyst, at an initial pH of 6.7, along with keeping the ultrasonic power, visible light power, and stirring speed constant at 40 W, 150 W + 150 W, 500 rpm, respectively.

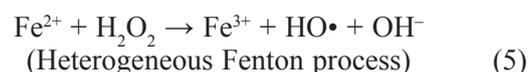
The standard deviation of the average of the two independent runs changed in the range of ± 0.45 and ± 2.7 . The average values were used in the Figures.

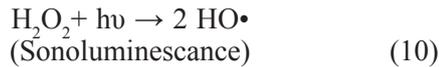
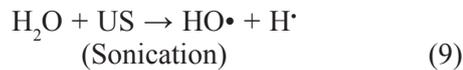
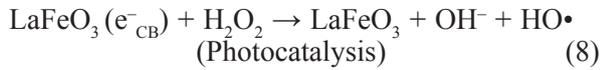
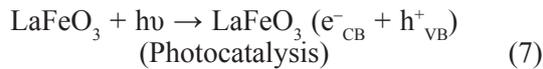
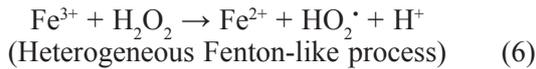
The tested concentrations of H_2O_2 were 1, 2, 3, and 4 times (2.4 mM, 4.8 mM, 7.1 mM, and 9.5 mM) that of the stoichiometric ratio (S.R.) per the following equation:



The results are given in Fig. 1 as degradation degree, COD, and TOC reductions at the end of 3 h of oxidation.

As seen in Fig. 1, at the stoichiometric ratio of BPA and H_2O_2 (2.4 mM H_2O_2), 21.8 % of degradation, and 11.2 % of COD reduction were achieved at the end of 3 h. There was no TOC reduction. When the BPA concentration was constant and the H_2O_2 concentration was doubled (2 times S.R., 4.8 mM H_2O_2), a degradation degree of 36.6 %, along with COD and TOC reductions of 13.5 % and 8.0 %, respectively, were achieved at the end of 3 h of oxidation. The increase in the degradation degree along with the COD and TOC reductions with the H_2O_2 concentration may be due to the increase in the OH^{\bullet} radicals with the heterogeneous sonication-assisted photo-Fenton process, as indicated in Eqs. 5–10^{32–34} as follows:





Eqs. 5–6 present the simple mechanism for HO• radical formation during the heterogeneous Fenton process. Eqs. 7–8 indicate the OH• generation under visible light irradiation in the presence of the LaFeO₃ perovskite catalyst. The source of this light can be visible light or the light produced by the sonoluminescence effect of sonication. During the visible light illumination of the LaFeO₃ perovskite catalyst, the conduction band electrons (e_{CB}⁻) and valance band holes (h_{VB}⁺) are initially formed. The conduction band electrons interact with the hydrogen peroxide to produce OH• radicals, Eq. 8. The transition metal of iron favors electron-hole separation and enhances the photoactivity. During the sonication of water, the HO• radicals occur with Eq. 9. The UV radiation caused by the sonoluminescence (wavelength below 375 nm) effect of sonication can be used to cleave the O–O bond in the H₂O₂ and generates hydroxyl radicals (Eq. 10).

At a higher H₂O₂ dosage (3 times of S.R., 7.1 mM H₂O₂), a decrease in the degradation degree to 28.9 % and COD reduction to 11.5 % were ob-

tained. Similar results were observed at the H₂O₂ concentration of 9.5 mM (4 times of S.R.). This decrease may be due to the hydroxyl radical scavenging effect of H₂O₂ at high concentrations or the reaction between the HO• radicals to form H₂O₂.

The H₂O₂ concentration of 4.8 mM (2 times of S.R.) was selected as the optimum H₂O₂ concentration due to the highest degradation degree, and the COD and TOC removals achieved under the tested conditions.

In the study on the sono-Fenton oxidation of BPA over a Fe₃O₄ catalyst, and in the heterogeneous Fenton oxidation of phenol over a LaFeO₃ perovskite catalyst, similar results were obtained.^{7,35}

Negligible iron leaching from the catalyst into the solution was observed, and it was in the range of 0.12–0.16 ppm (0.13 %–0.17 %).

Effect of the BPA initial concentration

This group of experiments were conducted at the temperature of 298 K, with 0.5 g L⁻¹ of LaFeO₃ perovskite catalyst, in the presence of 2.4 mM H₂O₂, and at initial pH of 6.7. Four different BPA initial concentrations of 5 (0.022 mM), 10 (0.044 mM), 15 (0.066 mM), and 20 (0.088 mM) ppm were tested to investigate the efficiency of catalyst in wastewaters having different concentrations of BPA in effluents. However, it is known that landfill leachate has about 17 mg L⁻¹ BPA concentration, so the BPA concentrations closer to this value were selected in this study. Fig. 2 presents the results.

The standard deviation of the average of two independent runs changed in the range of ±0.01 and ±2.1. The average values were used in the Figures.

As seen in Fig. 2, the degradation degree decreased with the increase in initial concentration of BPA. The degradation degree was measured as 36.5 %, 27.3 %, 21.8 %, and 15 % for the initial concentrations of 5, 10, 15, and 20 ppm, respectively, after a reaction time of 3 h. Similar to the degradation degree values, the COD reductions decreased with increasing initial concentration of BPA.

This result was expected, because the number of active radicals formed by the heterogeneous sonication-assisted photo-Fenton process will be the same under the same operating conditions, resulting in the decrease in degradation degree with the increase in the number of BPA molecules to be oxidized. On the other hand, the number of photons

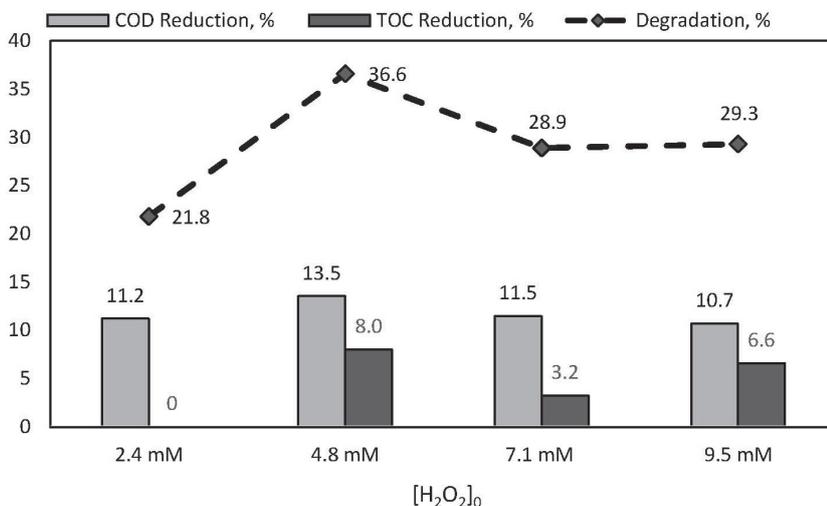


Fig. 1 – Effect of concentration of H₂O₂, [H₂O₂]₀, on the sonication-assisted photo-Fenton oxidation of BPA: Degradation %, and COD and TOC reductions, % after 3 h of oxidation (T = 298 K, [BPA]₀ = 15 ppm, catalyst loading = 0.5 g L⁻¹, ultrasound = 40 W, visible light = 150 + 150 W, pH = 6.7, and stirring speed = 500 rpm)

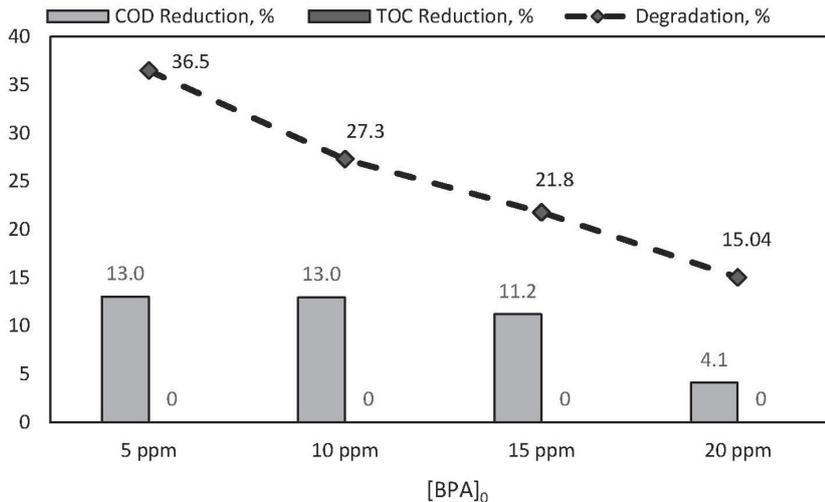


Fig. 2 – Effect of BPA initial concentration on the sonication-assisted photo-Fenton oxidation of BPA: Degradation %, and COD and TOC reductions, % after 3 h of oxidation ($T = 298\text{ K}$, $[H_2O_2]_0 = 2.4\text{ mM}$, catalyst loading = 0.5 g L^{-1} , ultrasound = 40 W , visible light = $150 + 150\text{ W}$, and stirring speed = 500 rpm)

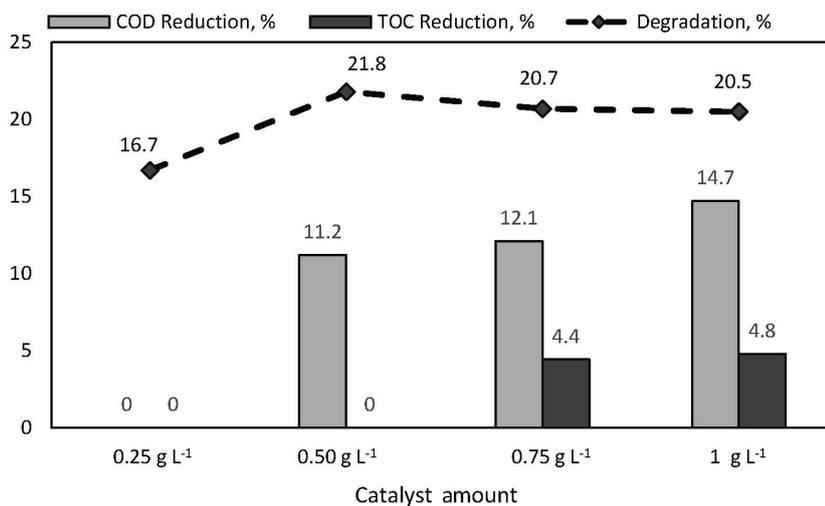


Fig. 3 – Effect of catalyst loading on the sonication-assisted photo-Fenton oxidation of BPA: Degradation %, and COD and TOC reductions, % after 3 h of oxidation ($T = 298\text{ K}$, $[BPA]_0 = 15\text{ ppm}$, $[H_2O_2]_0 = 2.4\text{ mM}$, ultrasound = 40 W , visible light = $150 + 150\text{ W}$, $\text{pH} = 6.7$, and stirring speed = 500 rpm)

penetrating the solution may be decreased due to the association between the BPA molecules. The BPA molecule itself behaves as an internal filter for the incident light, and does not permit the desired light intensity to reach the perovskite particles, so a decrease in degradation efficiency is observed.^{36–38} However, in a low concentration of BPA, the number of photon absorption by the catalyst increases.

There was no TOC reduction at any initial concentration of BPA tested.

Although the highest degradation degree was obtained at 5 ppm initial concentration, the same COD reduction (13 %) was observed at 5 ppm and 10 ppm, hence, 10 ppm initial concentration of BPA can be selected as the optimum concentration. This

BPA concentration is close to the BPA concentration in a landfill leachate.

The leached amount of iron from the catalyst into the solution was in the range of 0.12–0.18 ppm (0.13 %–0.19 %) at the end of oxidation run (3 h).

Effect of catalyst loading

A photocatalyst/sonocatalyst is the foremost element in the oxidation process. Although environmentally friendly catalysts are used, excessive use of catalysts should be avoided to reduce operating and chemical costs. The effect of the catalyst loading on the degradation of BPA was investigated by varying the catalyst loading in the range of 0.25 g L^{-1} to 1.0 g L^{-1} keeping all other parameters constant. The results are given in Fig. 3.

The standard deviation of the average of two independent runs changed in the range of ± 0.11 and ± 1.9 . The average values were used in the Figures.

The degradation degree of BPA increased from 16.7 % to 21.8 % with increasing the catalyst loading from 0.25 g L^{-1} to 0.5 g L^{-1} . There was no COD reduction with the catalyst amount of 0.25 g L^{-1} , whereas, 11.2 % of the COD reduction was achieved in the presence of 0.5 g L^{-1} catalyst. This positive effect may be due to the increase in active centers on the catalyst surface, which is proportional to the catalyst amount.^{39–41} In addition, the presence of solid catalyst particles in the combined system of visible light + H_2O_2 + US increases the intensity of cavitation by providing additional nuclei for generation of cavities. As known, the violent collapse of these cavities releases large magnitudes of energy in millions of places in the reactor (microreactors) resulting in the generation of local hotspots, and subsequently the formation of more reactive hydroxyl and hydroperoxyl radicals.⁴²

However, with further increase in catalyst loading (from 0.75 to 1 g L^{-1}), the degradation degree of BPA decreased slightly. This may be due to the increase in turbidity of the solution. The solid catalyst particles also act as a barrier (opposite effect) for the propagation of sound waves, thereby decreasing the energy transmitted into the system.³⁷

There was no TOC reduction in the presence of 0.25 and 0.5 g L⁻¹ catalyst, whereas, 4.4 % and 4.8 % of TOC reductions were observed for 0.75 and 1.0 g L⁻¹ catalyst, respectively. According to this result, the 0.75 g L⁻¹ catalyst was selected as the optimum concentration.

The leached amount of iron from the catalyst into the solution was in the range of 0.12–0.22 ppm (0.13 %–0.14 %) at the end of the oxidation run (3 h).

Effect of reaction temperature

Reaction temperature is very important since it affects the reaction rate. The effect of reaction temperature on the degradation of BPA by the heterogeneous sonication-assisted photo-Fenton process was investigated at temperatures of 298 K, 303 K, 308 K, and 313 K, while maintaining all the other parameters constant, 0.50 L of 15 ppm BPA solution, 0.50 g L⁻¹ of catalyst, [H₂O₂]₀ = 2.4 mM, ultrasonic power of 40 W, visible light of 150 W + 150 W, and initial pH of 6.7. Fig. 4 presents this effect.

The standard deviation of the average of two independent runs changed in the range of ±0.001 and ±2.2. Average values were used in the Figures.

As may be seen, the degradation degree of BPA increased from 21.8 % to 25.9 % with the increase in temperature from 298 K to 313 K. Similarly, the COD reduction was measured as 11.2 %, 14.2 %, 14.3 %, and 19.7 % at the temperatures of 298, 303, 308, and 313 K, respectively. No TOC reduction was observed at the lowest studied temperature of 298 K, whereas, 1.5 %, 3.0 %, and 4.7 % of the TOC reductions were achieved at temperatures of 303, 308, and 313 K, respectively. This was mainly due to the increase in the rate constant of the heterogeneous Fenton reaction. Photocatalytic systems are operated at room temperature, and generally, weak dependency of the degradation rates with temperature is observed.⁴³ In the case of sonication, an increase in bulk temperature can increase the quantity of cavitation bubbles, enhancing the production of OH[•]. However, at the same time, as the bulk temperature increases, the temperature of the ‘hot spot’ formed by the cavity collapse decreases. As a result, the degradation rate decreases as bulk temperature increases.^{44,45} At higher temperatures a large number of cavitation bubbles are generated concurrently. This could act as a barrier to sound transmission, and thus

dampen the effective ultrasonic energy from the source that enters the liquid medium. In addition, the decomposition of H₂O₂ to H₂O and O₂ increases at high temperatures. Therefore, in the present study, the sonication-assisted photo-Fenton oxidation of BPA was not studied at temperatures higher than 313 K; above this temperature, the increase in temperature is thought to have a negative effect on degradation. In the study by Sunasee *et al.*, sonocatalytic oxidation of BPA was studied in the presence of TiO₂ at 35 kHz frequency and at a power of 50 W in the temperature range of 283–303 K.⁴⁵ The highest BPA removal (~60 %) was achieved at a temperature of 293 K. Similarly, Wang *et al.* investigated sono-Fenton oxidation of Alachlor at an ultrasonic frequency of 20 kHz and ultrasonic power of 100 W in the temperature range of 288–323 K, and the optimum temperature was selected as 293 K.⁴⁶

In literature, the heterogeneous Fenton oxidation of BPA was studied over a CuFeO₂ catalyst at temperatures of 283, 293, 303, and 313, and the highest degradation was achieved at 313 K.¹³ However, the photocatalytic degradation of BPA was studied in the presence of a TiO₂ catalyst and sun light in the temperature range of 383–343 K. It was observed that the degradation of BPA slightly changed with temperature.⁴³

In this study, the optimum temperature was selected as 313 K under the studied conditions.

The small amount of iron that leached from the catalyst into the solution suggested stability of the catalyst, and was in the range of 0.12–0.24 ppm (0.13 %–0.26 %) at the end of the oxidation run (3 h).

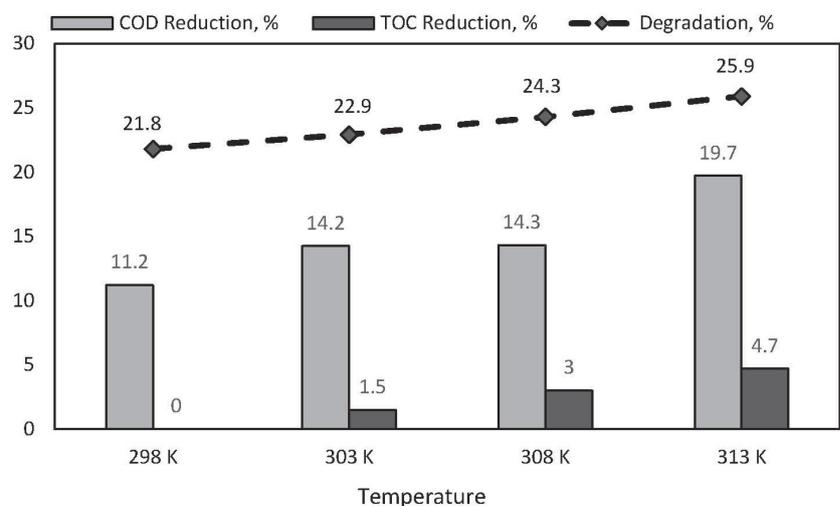


Fig. 4 – Effect of reaction temperature on the sonication-assisted photo-Fenton oxidation of BPA: Degradation %, and COD and TOC reductions, % after 3 h of oxidation ([BPA]₀ = 15 ppm, [H₂O₂]₀ = 2.4 mM, catalyst loading = 0.5 g L⁻¹, ultrasound = 40 W, visible light = 150 + 150 W, pH = 6.7, and stirring speed = 500 rpm)

Effect of initial pH of the BPA solution

The pH is an important parameter in the oxidation process because it may change the physical and chemical behavior of organic pollutants. The effect of initial pH of the BPA solution on its degradation was studied at six different initial pH values of 2.6, 3.5, 6.7, 8.5, 10.3, and 11.0, with the following conditions: 0.50 L of 15 ppm BPA solution, H_2O_2 concentration of 2.4 mM, catalyst loading of 0.5 g L^{-1} , reaction temperature of 298 K, with visible light of $150 \text{ W} + 150 \text{ W}$, and ultrasound power of 40 W. The results are shown in Fig. 5.

The standard deviation of the average of two independent runs changed in the range of ± 0.39 and ± 2.8 . The average values were used in the Figures.

The pH of the aqueous solution is an important controlling parameter in the photocatalytic process. As seen in Fig. 5, in the heterogeneous sonication-assisted photo-Fenton oxidation of BPA, the obtained degradation degrees were 27.4 %, 23.8 %, 21.8 %, 17.5 %, 14.0 %, and 10.6 % at initial pH values of 2.6, 3.5, 6.7, 8.5, 10.3, and 11, respectively. The increase in initial pH value of the BPA solution decreased the degradation degree. Similarly, the COD reduction decreased as the initial pH value increased. The TOC reductions of 8.1 % and 4.5 % were obtained at pH values of 2.6 and 3.5 respectively, whereas, no TOC reduction was observed at pH values equal to or higher than 6.7.

The acidic conditions support the initial adsorption of BPA, which has two negative oxygen atoms in the hydroxyl groups and four negative carbon atoms in the phenolic group on the positively charged $LaFeO_3$ perovskite surface.^{47,48} In addition,

at low pH values, more $HO\cdot$ radicals form, and the oxidation potential of the highly oxidative radicals decreases with the increasing pH (2.65–2.80 V at pH = 3 and 1.90 V at pH = 7).^{49,50} At high pH values, H_2O_2 decomposes into H_2O and O_2 , and that reduces the amount of hydroxyl radicals.⁶

On the other hand, the pH influences the sonication directly. As known, the hydrophilic compounds degrade in the bulk solution, whereas, the hydrophobic compounds decompose in the cavitation bubble and/or cavitation bubble-liquid interface by $HO\cdot$ radicals where they are abundant.¹¹ The hydrophobic and hydrophilic character of the compounds change depending on the pH of the solution. There are two distinct dissociation constants of the BPA at pKa values of 9.6, and 10.2. This means that BPA is in an ionic form at pH values above 10.2, and exists in molecular form below this pH. In other words, the hydrophobic character of BPA is high at pH values lower than pKa values, and thus the possibility of diffusion of BPA into the cavitation-bubble interface, where the concentration of the hydroxyl radicals that react with the BPA is high.⁵¹

Similar results were obtained in the study on sonolytic degradation of BPA, in photocatalytic degradation of azo dyes over a $LaFe_{0.5}Mn_{0.5-x}O_{3-\delta}$ catalyst, in the photocatalytic degradation of BPA over TiO_2 , and in the degradation of BPA using a $US+FeSO_4+H_2O_2$ combined process.^{7, 41,47,51}

The optimum pH value (in terms of BPA degradation, COD and TOC reductions) in this study was selected as 2.6 due to the high values of degradation, along with the COD and TOC reductions.

The leached amount of iron from the catalyst into the solution was in the range of 0.12–1.22 ppm (0.13 %–1.31 %) at the end of the oxidation run (3 h).

Kinetic modelling of BPA oxidation

The kinetic modelling of BPA degradation was accomplished using BPA concentrations measured by HPLC at different time intervals per run. During a run, the reaction mixture was stirred vigorously at around 500 rpm. This vigorous stirring and turbulence created by the ultrasound waves eliminates the external diffusion resistance between the bulk solution and the catalyst surface. Internal diffusion resistance was also negligible due to small size of the catalyst particles.

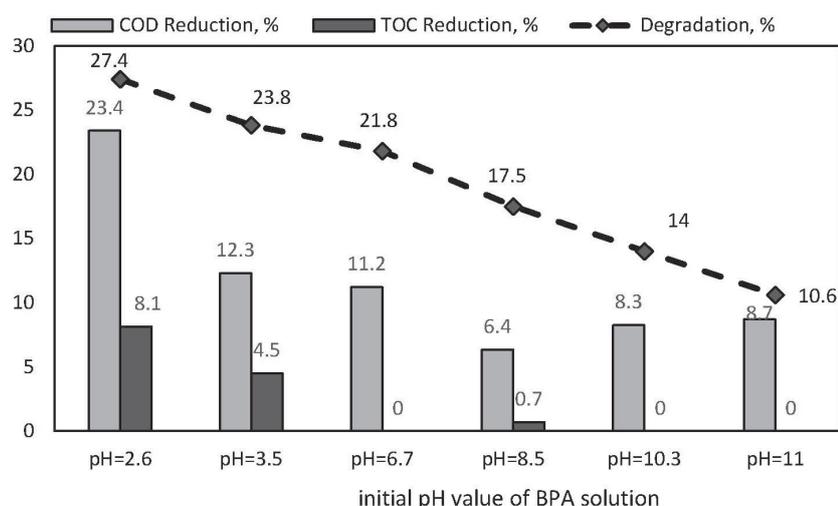


Fig. 5 – Effect of initial pH value of the BPA solution on the sonication-assisted photo-Fenton oxidation of BPA: Degradation %, and COD and TOC reductions, % after 3 h of oxidation ($[BPA]_0 = 15 \text{ ppm}$, $[H_2O_2]_0 = 2.4 \text{ mM}$, catalyst loading = 0.5 g L^{-1} , ultrasound = 40 W, visible light = $150 + 150 \text{ W}$, $T = 298 \text{ K}$, and stirring speed = 500 rpm)

In literature, there are some studies in which oxidation of BPA follows first^{14,49,52–55} and second^{56,57} order kinetics.

Therefore, first and second order reaction kinetics using Eqs. 11 and 12 were tested for sonication-assisted photo-Fenton oxidation of BPA in this study, and the results are given in Fig. 6 with the regression coefficients.

For first order kinetics:

$$-\ln \frac{c_{\text{BPA}}}{c_{\text{BPA},0}} = k_1 t \quad \text{and} \quad -\ln(1-x) = k_1 t \quad (11)$$

And for second order kinetics:

$$\frac{1}{c_{\text{BPA}}} - \frac{1}{c_{\text{BPA},0}} = k_2 t \quad \text{and} \quad \frac{x}{1-x} = k_2 c_{\text{BPA},0} t \quad (12)$$

where c_{BPA} is concentration of BPA for corresponding time, mol dm^{-3} ; $c_{\text{BPA},0}$ is BPA initial concentration, mol dm^{-3} , t is sampling time, min., x is BPA degradation degree, and k_1 and k_2 are first and second order reaction rate constants, respectively.⁵⁸

The validity of the kinetic model was proved by plotting the experimental data obtained in first and second order kinetic expressions under studied temperatures, as shown in Fig. 6.

In addition, it was also tried to minimize the sum of the squared differences of the measured degradation degrees, x_{exp} , and the calculated degradation degrees, x_{cal} . That is, the sum of $\Sigma(x_{\text{exp}} - x_{\text{cal}})^2$ was requested to be minimum. The results are presented in Table 1.

As seen in Table 1, a second order dependency was obtained in the sonication-assisted photo-Fenton oxidation of BPA with higher regression coefficient and smaller $\Sigma(x_{\text{exp}} - x_{\text{cal}})^2$ values in the runs.

The slope ($-E/R$; where $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$, $E =$ activation energy) of the Arrhenius plot of the rate constant versus the reciprocal of temperature ($\ln k$ vs $1/T$) gives the activation energy (E) of the sonication-assisted photo-Fenton oxidation of BPA.

Table 1 – First and second order reaction rate constants in the sonication-assisted photo-Fenton oxidation of BPA, regression coefficients, and $\Sigma(x_{\text{exp}} - x_{\text{cal}})^2$ values at different temperatures

| Parameter | First order reaction | | | Second order reaction | | |
|----------------|-------------------------------------------------|-------------------------------|---------------------------------------------|--------------------------------------------------------------------|-------------------------------|---------------------------------------------|
| | Reaction rate constant, k , min^{-1} | Regression coefficient, R^2 | $\Sigma(x_{\text{exp}} - x_{\text{cal}})^2$ | Reaction rate constant, k , $\text{L mol}^{-1} \text{ min}^{-1}$ | Regression coefficient, R^2 | $\Sigma(x_{\text{exp}} - x_{\text{cal}})^2$ |
| Temperature, K | | | | | | |
| 298 | 0.0014 | 0.94 | 0.0022 | 24.24 | 0.96 | 0.0017 |
| 303 | 0.0015 | 0.91 | 0.0572 | 24.83 | 0.93 | 0.0555 |
| 308 | 0.0017 | 0.87 | 0.0650 | 28.79 | 0.91 | 0.0604 |
| 313 | 0.0018 | 0.92 | 0.0735 | 31.82 | 0.95 | 0.0644 |

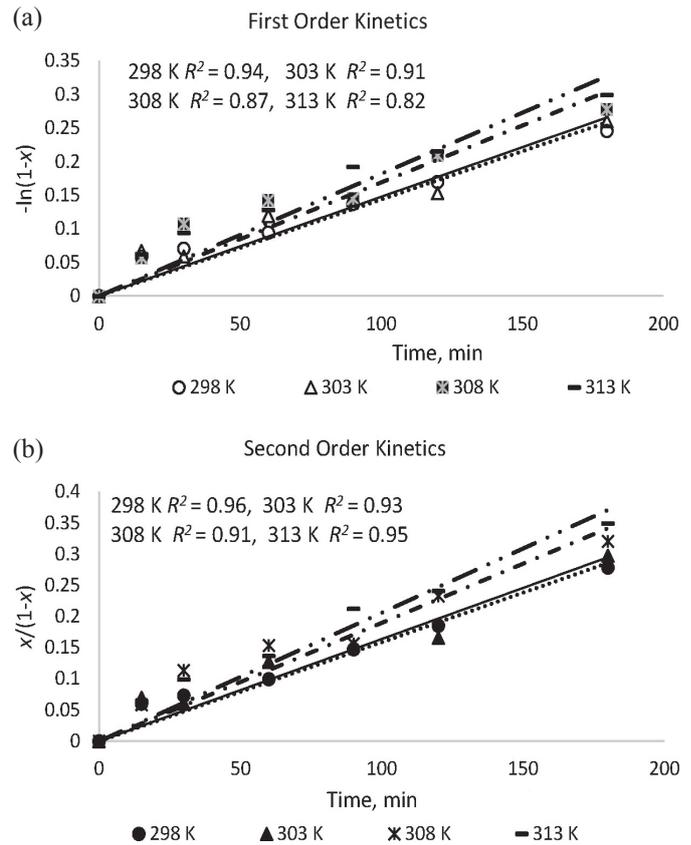


Fig. 6 – a) First and b) second order kinetic model of sonication assisted photo-Fenton oxidation of BPA

This dependency is presented in Fig. 7 with the activation energy of $15.34 \text{ kJ mol}^{-1}$. This value is lower than the calculated activation energies in literature.

Stability of the catalyst at the optimum conditions

The best experimental conditions for the efficient degradation of BPA by heterogeneous sonication-assisted photo-Fenton oxidation were determined as follows:

Initial concentration of BPA = 10 ppm, H_2O_2 concentration = 4.8 mM, catalyst loading = 0.75 g L^{-1} ,

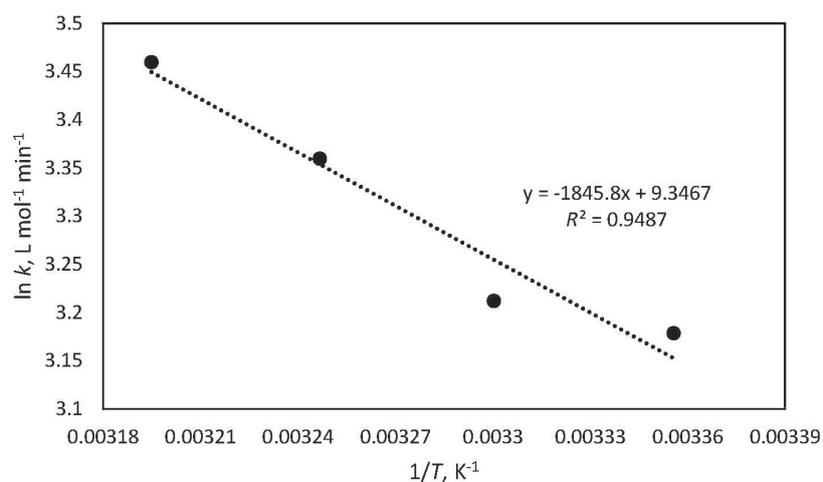
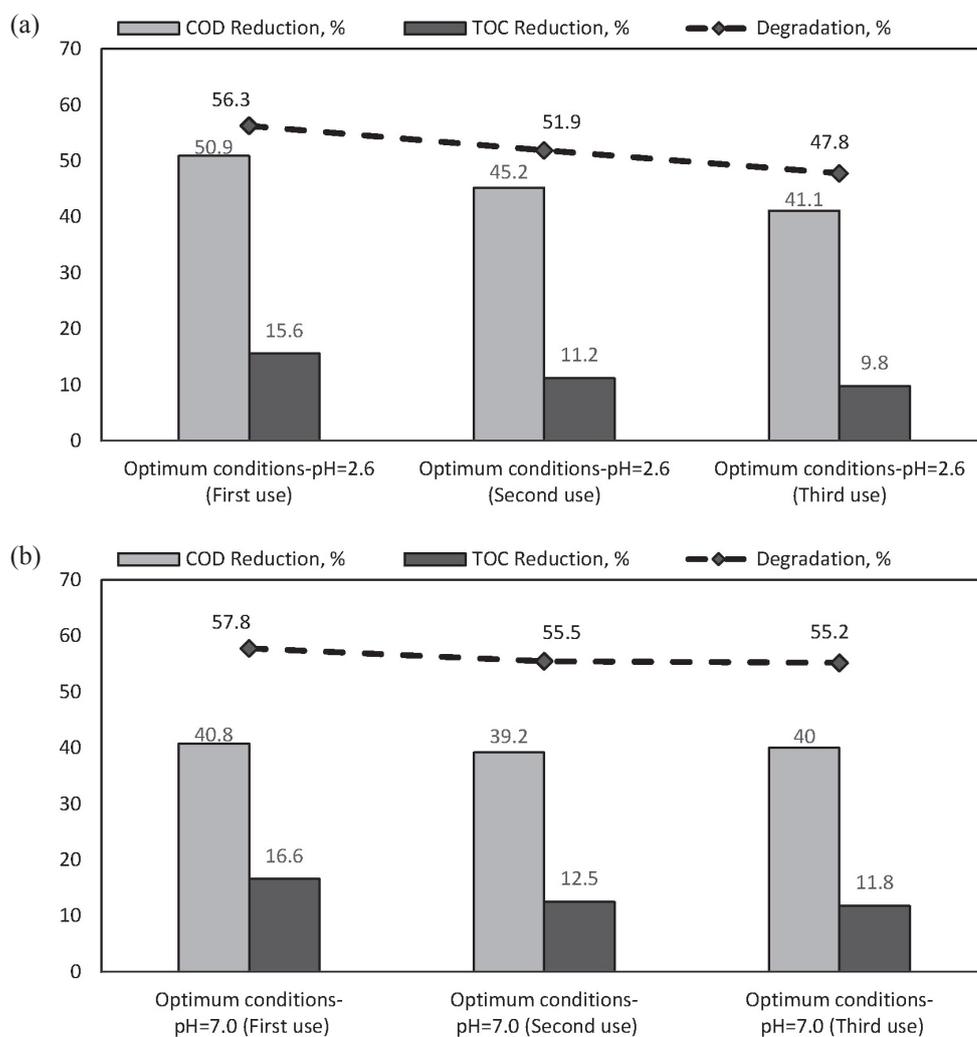
Fig. 7 – $\ln k$ versus $1/T$ relationship

Fig. 8 – Stability of catalyst at optimum conditions: Degradation %, and COD and TOC reduction, % after 6 h of oxidation, a) pH = 2.6; b) pH = 7 ([BPA]₀ = 10 ppm, [H₂O₂]₀ = 4.8 mM, catalyst loading = 0.75 g L⁻¹, ultrasound = 40 W, visible light = 150 + 150 W, T = 313 K, and stirring speed = 500 rpm)

pH = 2.6, and $T = 313$ K. In all studied runs, the volume of the solution, power of the ultrasound and visible lamps, and stirring speed were kept constant at 0.5 L, 40 W, 150 W + 150 W, and 500 rpm, respectively. However, in order to increase the TOC reductions, the reaction duration was extended to 6 h. Under these conditions, 56.3 % of degradation, COD removal of 50.9 %, and TOC removal of 15.6 % were achieved after 6 h of reaction.

The experiments on the catalyst stability were carried out under the optimum conditions. Firstly, the experiment was performed with a fresh LaFeO_3 perovskite catalyst (first use). To recover the catalyst, after 6 h of oxidation, the final effluent was filtered. The used catalyst was washed with water and then ethanol, and dried at 393 K for 3 h, and calcined at 773 K for 6 h. The calcined catalyst was then tested in the sonication-assisted photo-Fenton oxidation of BPA (second use). After 6 h of reaction, the catalyst was recovered as mentioned previously, and its activity was again tested in BPA oxidation (third use). The results are given in Fig. 8a.

As seen in Fig. 8a, the degradation degree of BPA decreased from 56.3 % to 51.9 %, and then 47.8 % for the second and third uses of the catalyst. The COD reduction also decreased from 50.9 % to 45.2 %, and then to 41.1 % for the second and third cycle, respectively. A similar decline was also obtained in the TOC reductions. Whereas, when the sonication-assisted photo-Fenton oxidation of BPA was conducted at optimum conditions but at pH value of 10 ppm BPA (pH = 7.0), the degradation of BPA changed slightly to 57.8 %, 55.5 %, and 55.2 % for the first, second, and third use, respectively. Almost no change in COD reductions was observed using the used catalyst in the oxidation. The TOC reduction decreased slightly from 16.6 % to 12.5, and then to 11.8 % for the first, second, and third cycles, respectively, see Fig. 8b.

Although pH = 2.6 was selected as optimum pH in terms of degradation degree, it was clearly seen that the stability of the catalyst was higher at neutral pH than at acidic pH of 2.6.

Toxicity tests

Garden cress seeds, *Lepidium sativum* L., were used to assess the toxicity of the BPA solution. For this purpose, the toxicity of 10 ppm BPA prior to oxidation and the toxicity of the solution after 6 h of the sonication-assisted photo-Fenton treatment were compared with distilled water. To do this, 5 mL of untreated BPA, treated BPA, and distilled water were pipetted onto a filter paper fitted into a 9-cm glass petri dish. Twenty-five seeds of cress were distributed evenly on filter paper inside the petri dish. These three petri dishes were placed in

the dark for 72 hours, after which the root lengths of the seeds were measured for the distilled water, treated, and untreated wastewaters. The inhibition percentage was calculated for the treated and untreated wastewater using the following equation:⁴²

$$\text{Inhibition, \%} = \frac{\text{Root length}_{\text{distilledwater}} - \text{Root length}_{\text{sample}}}{\text{Root length}_{\text{distilledwater}}} \cdot 100 \quad (13)$$

Toxicity tests were conducted at the optimum conditions but at two pH values of 2.6 (adjusted with 0.1 M H_2SO_4) and 7.0 (without pH adjustment). The inhibition values were 44 % and 27 % for the untreated and treated BPA solutions, respectively, at a neutral pH value of 7.0. Whereas, at the acidic pH value of 2.6, these values were 44 % and 58 % for the untreated and treated BPA solutions, respectively. The decrease in inhibition value indicated reduction in toxicity.

At the two pH values, almost 60 % degradation was obtained, whereas, the TOC reduction was about 16 %. This means the total mineralization of BPA to CO_2 and water could not be achieved in both cases. In addition, some intermediates had formed during the oxidation. The toxicity results revealed that the intermediates formed in the sonication-assisted photo-Fenton oxidation of BPA were less toxic compared to the parent BPA molecule at neutral pH value. However, the same interpretation is not valid at the acidic pH of 2.6. In that case, the inhibition value increased, meaning that the formed intermediates were more toxic than the parent BPA.

A similar result was obtained in literature.⁵⁹ In that study, although the oxidation intermediates obtained from the BPA degradation at a pH 10 were more difficult to degrade, the toxicity analyses showed that these intermediates were less toxic compared to the parent BPA molecule. In contrast, more toxic intermediates were generated in the photocatalytic oxidation of BPA when the experiment was performed at an acidic pH of 3.

Determination of intermediates during sonication-assisted photo-Fenton oxidation of BPA

As mentioned, the TOC was not completely removed even at the optimum conditions. Although the degradation of BPA was 56.3 %, the TOC reduction was only 15.6 % at the optimum conditions at a BPA initial pH value of 2.6 after 6 h of oxidation. Similar results (57.8 % of degradation, and 16.6 % of TOC reduction) were obtained at a pH 7 after the same reaction duration. This result showed that BPA is degraded into oxidation-resistant intermediates rather than CO_2 and water. HPLC analysis was carried out to determine which intermediates were formed in the sonication-assisted photo-Fen-

Table 2 – Formed intermediates with their retention times at an initial BPA pH value of 2.6 and degradation degree of BPA

| Reaction time, min | Degradation, % of BPA (retention time: 9.3 min) | p-hydroxyacetophenone, ppm (retention time: 1.98 min) | hydroquinone, ppm (retention time: 1.6 min) |
|--------------------|----------------------------------------------------|----------------------------------------------------------|------------------------------------------------|
| 0 | 0 | – | – |
| 15 | 3.9 | – | – |
| 30 | 14.0 | – | – |
| 60 | 19.4 | – | – |
| 120 | 28.2 | – | – |
| 180 | 37.9 | – | – |
| 240 | 46.1 | 0.075 | 0.98 |
| 300 | 51.1 | 0.12 | 1.38 |
| 360 | 56.3 | Immeasurable limit | 1.41 |

ton oxidation of BPA. The intermediate products were determined by HPLC analysis with the same analytical method for determining BPA concentration (mentioned in Experimental Part). Therefore, firstly, the retention times of the possible intermediates (hydroquinone, catechol, and p-hydroxyacetophenone) were determined using standard chemicals, and the retention times of hydroquinone, catechol, and p-hydroxyacetophenone were found to be 1.6 min, 1.89 min, and 1.98 min, respectively. Under the studied conditions, the retention time of BPA was 9.3 min. As known, H_2O_2 was used as the oxidant, and the retention time of the peak belonging to H_2O_2 was 1.38 min. The peak that had the retention time of 1.8 min (between hydroquinone and p-hydroxyacetophenone) was detected, but which compound had formed during the experiment at optimum conditions at pH value of 7.0 after 2 h of oxidation could not be confirmed. It could possibly be attributed to p-hydroxybenzaldehyde based on the molecular weight and retention time.⁴¹ Similarly, the intermediates were determined at an initial BPA pH value of 2.6 at optimum conditions. The intermediates of hydroquinone and p-hydroxyacetophenone were confirmed with the retention times of 1.6 min and 1.98 min, respectively. The quantities of these intermediates with their retention times and degradation degree of BPA are given in Table 2.

As seen in Table 2, hydroquinone had formed at the end of 240 min of oxidation and its concentration continued to increase. Whereas, p-hydroxyacetophenone was detected at the end of 240 min of oxidation, its concentration first increased but then decreased to immeasurable limits of the HPLC.

In the “Toxicity tests” section, it was stated that the toxicity of the intermediates formed in the sonication-assisted photo-Fenton oxidation of BPA were less toxic compared to the parent BPA molecule at a neutral pH value. However, the formed intermedi-

ates were more toxic than the parent BPA at an acidic pH value of 2.6. This result was confirmed in this section with the formation of different intermediates at the pH values of 2.6 with respect to those at pH = 7.0.

Considering the role of OH radicals in the sonication-assisted photo-Fenton oxidation and a literature study, the proposed pathway for the sono-photo-Fenton oxidation of BPA at an initial pH value of 2.6 was proposed in Fig. 9.

The formation of monohydroxylated BPA and dihydroxylated BPA from the reaction of BPA with hydroxyl radicals occurred at the cavitation bubble-liquid interface, whereas the formation of aliphatic acid and then CO_2 and water occurred in the bulk solution.¹¹ This is because the hydrophobic character of monohydroxylated BPA and dihydroxylated BPA are much higher than that of aliphatic acids. The retention times of all formed intermediates were shorter than that of BPA, hence, it could be said that the hydrophilic character of the intermediates were stronger than that of BPA, and it was hard to transfer them at the cavitation bubble-liquid interface where the hydroxyl radicals were abundant. Alternatively, it may have arisen from limitation of diffusion of $HO\cdot$ radicals into the bulk solution to react with intermediates.

As mentioned at the beginning of this section, lower TOC reduction was obtained than that degradation degree of BPA (57.8 % of degradation, and 16.6 % of TOC reduction at pH = 7; 56.3 % of degradation, and 15.6 % of TOC reduction at pH = 2.6) and it was stated that this result was due to the formation of oxidation-resistance intermediates (such as aliphatic acids) which have high hydrophilic character. To confirm this result, the carbon balance was done for a pH = 2.6 at the beginning of oxidation and at the end of the 6 h of oxidation using TOC measurements, and the concentration of reac-

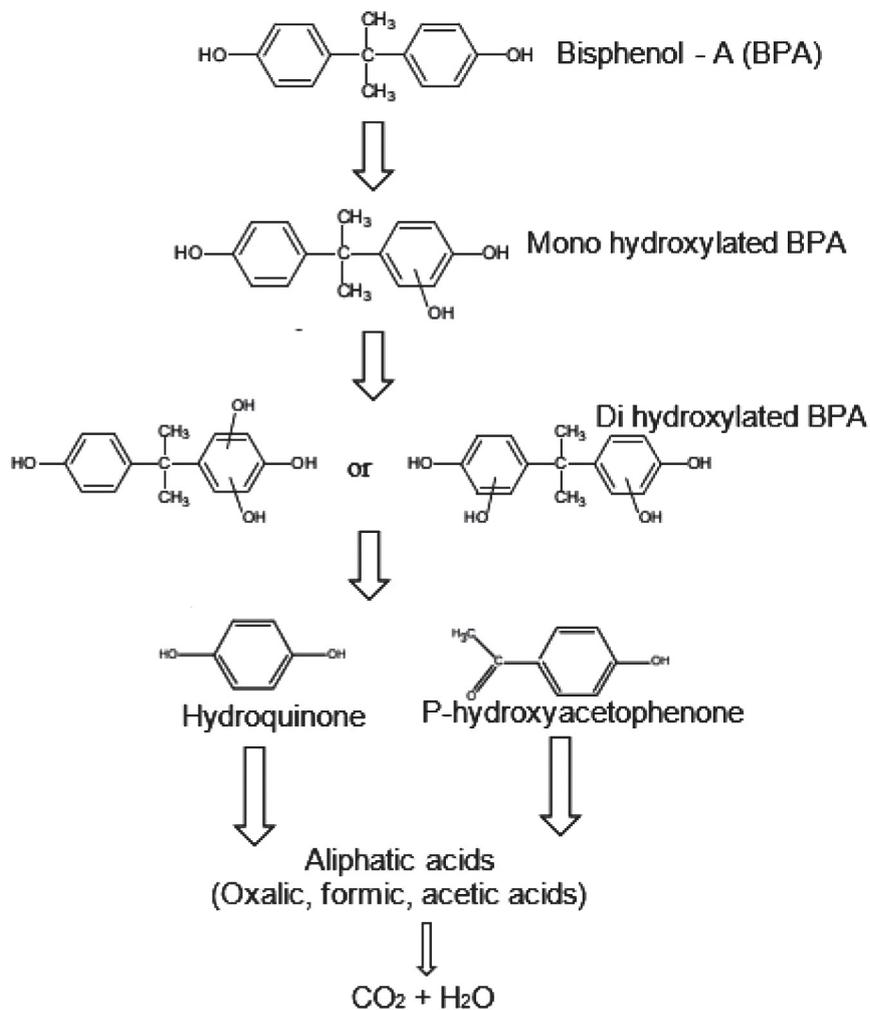


Fig. 9 – Proposed degradation pathway of the BPA during sonication-assisted photo-Fenton oxidation at optimum conditions and pH of 2.6

tant/intermediates measured by HPLC. According to these measurements, the total number of moles of carbon was $0.4 \cdot 10^{-3}$, which was the sum of concentration of carbon coming from the BPA and hydroquinone measured by HPLC at the end of 6 h of oxidation. However, the number of moles of carbon was $0.6 \cdot 10^{-3}$ measured by TOC at the same duration of oxidation. The differences between the numbers of carbon moles showed the formation of recalcitrant aliphatic acids to oxidation with higher hydrophilic character than the BPA.

Conclusion

The present study showed that the combination of ultrasound and visible light with heterogeneous Fenton process is efficient for the degradation of BPA. The iron-containing LaFeO₃ perovskite catalyst acts as an efficient and stable catalyst for this process. The process was found as being sensitive

to H₂O₂ concentration, initial pH of the solution, temperature, catalyst loading, initial concentration of the BPA, and initial pH of the BPA solution. The best experimental conditions for the efficient degradation of BPA were determined as follows:

Initial concentration of BPA = 10 ppm, H₂O₂ concentration = 4.8 mM, catalyst loading = 0.75 g L⁻¹, initial pH of solution = 2.6, and reaction temperature = 313 K. At optimum conditions, the volume of solution, the power of the ultrasound and visible light, and stirring speed were kept constant at 0.5 L, 40 W, 150 + 150 W, and 500 rpm, respectively. Under these conditions, 56.3 % of degradation, a COD removal of 50.9 %, and a TOC removal of 15.6 % were achieved after 6 h of reaction. The low leaching level of iron indicated that the reaction occurred in the heterogeneous phase. A second order dependency was obtained in the sonication-assisted photo-Fenton oxidation of BPA with an activation energy of 15.34 kJ mol⁻¹ with the experimental conditions studied.

It was achieved to decrease toxicity of BPA under the neutral pH of 7.0. Consequently, the heterogeneous sonication-assisted photo-Fenton system appears as a promising process for the treatment of BPA-containing wastewater.

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