

Heterogeneous sonocatalytic degradation of Bisphenol-A and the influence of the reaction parameters and ultrasonic frequency

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ABSTRACT

In the present study, the sonocatalytic oxidation of Bisphenol-A (BPA) was investigated in the presence of a LaFeO_3 perovskite catalyst. The effects of the reaction temperature, initial pH, catalyst loading, presence of inorganic anions and sonication source (power and frequency) on the removal of BPA using heterogeneous sonocatalytic process were investigated. Under the studied temperature range of 288–318 K, 308 K was selected as the optimum temperature and the highest BPA removal and total oxygen demand (TOC) reduction of, 95.8% and 30.4% were achieved at that temperature. The thermodynamic parameters were calculated in the studied temperature range of 288–308 K. It was seen that an acidic pH of 3.0 was favorable for the BPA oxidation with the highest BPA removal and TOC reduction of 95.4% and 31.5%, respectively. Doubling the catalyst amount from 0.25 g/L to 0.5 g/L increased the BPA removal degree from 81.6% to 90.8%. However, further increase in catalyst amount has no remarkable positive effect on the removal of BPA. The removal of BPA was described by the first order kinetics with an activation energy of 14.9 kJ/mol. The results obtained from this study showed that the LaFeO_3 perovskite catalyst was a good sonocatalyst giving high oxidation rates of BPA.

Key words | advanced oxidation processes, Bisphenol-A, pollutants, sonocatalytic oxidation

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INTRODUCTION

Pharmaceuticals and endocrine disrupting compounds (EDCs) are a large group of emerging contaminants (ECs) which are consumed at high quantities worldwide. The presence of these contaminants in the water poses a serious environmental threat due to their adverse effects on the environment and human health (Mirzaei *et al.* 2016). Among various EDCs, Bisphenol-A (BPA) has attracted considerable attention from researchers due to its wide applications (especially for polycarbonate and epoxy resins fabrication) and harmful characteristics. The wastewater/washwater discharged from plants manufacturing BPA often contains high concentrations of BPA ($>100 \text{ mg L}^{-1}$) (Inoue *et al.* 2008) which will highly contaminate the immediate environment. The BPA contaminated sites may cause serious health problems such as increasing breast cancer cells in the human body and/or decreasing estrogenic activity in living subjects (Yamamoto *et al.*

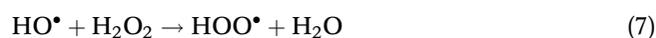
2001). In general, the physicochemical remediation processes are advantageous because rapid BPA removal can be achieved. However, those treatment processes generate large volumes of solid sludge and produce undesirable intermediates which are more harmful than the parent organic compounds and requires removal using additional processes (Lee *et al.* 2018). Although there are some studies which use different adsorbents (such as mesoporous carbon CMK-3, bottom ash, and de-oiled soya) efficiently for removal of organic pollutants (dyes) from water, the regeneration of adsorbents should definitely be considered (Mittal *et al.* 2010; Ahmaruzzaman & Gupta 2011; Mohammedi *et al.* 2011). Ultrasonic assisted adsorption is another option to treat organic pollutants from water (Asfaram *et al.* 2015; Ghaedi *et al.* 2015). Biological treatment is economical; nevertheless, it is not completely effective treating wastewater containing BPA. BPA has a moderate affinity for the solid

with an octanol–water coefficient (log K_{ow}) of 3.32 (Zielin'ska *et al.* 2016). Thus, BPA can adsorb onto suspended solids that were not completely removed in a secondary clarifier. This makes use of a post-treatment to lower the concentration of BPA in the effluent and limit its adverse effects on the water ecosystems. One of the options for such non-biodegradable organic pollutants is the Advanced Oxidation Processes (AOPs). AOPs, which are characterized by the production of highly reactive and non-selective hydroxyl radicals, and by mineralization of refractory pollutants to CO_2 and water, are a powerful technology for the treatment of water and wastewater contaminants. The generally used AOPs include UV/ H_2O_2 , Fenton treatment, photoFenton, photocatalysis, and sonolysis. Among these AOPs, photocatalysis is a promising technology. As photocatalytic processes using different photocatalysts (such as CeO_2 based catalyst, ZnO nanocomposites, and TiO_2) are low cost and environmentally friendly technologies, they are frequently preferred for the treatment of wastewater containing organic pollutants (Gupta *et al.* 2011; Saravanan *et al.* 2013a, 2013b, 2015). However, formation of byproducts tried to be minimized by changing reaction parameters. Besides all these, sonication (US) is one of the versatile techniques due to its safety, cleanliness, and energy efficiency properties. The effect of sonication is the direct result of the production of cavitation microbubbles which are also called microreactors. The generated microbubbles grow with applied ultrasonic frequency and when the resonance frequency size reaches a critical value, the bubbles collapse violently. The violent implosion of bubbles and adiabatic warming of the vapor occurs simultaneously and results in the formation of localized areas with temperature and pressure (hot-spots) of 5,000 K and 1,800 atm, respectively. These extraordinary conditions can dissociate water molecules to form hydrogen and hydroxyl radicals (H^\bullet and OH^\bullet) (Khataee *et al.* 2017a; Khataee *et al.* 2018; Yao *et al.* 2018). The collapse of microbubbles also induces the phenomenon of sonoluminescence that produce a light energy with a relatively wide range of wavelengths (below 375 nm).

However, oxidation of organic pollutants by sonication requires a high amount of energy and it may take a long time to achieve complete oxidation. One of the ways to increase sonodegradation efficiency is using a hybrid process, such as sonocatalytic oxidation in the presence of an appropriate semiconductor.

In the present study, a $LaFeO_3$ perovskite catalyst was used as sonocatalyst and the radicals formation

reactions in the sonocatalytic process are given below (Babu *et al.* 2017):



The HO^\bullet and HOO^\bullet radicals are involved in the mineralization of BPA (Equation (8)).

At the same time, as mentioned, the collapse of the cavitation bubble produces light energy, sonoluminescence, with a relatively wide range of wavelengths (below 375 nm) can excite $LaFeO_3$ particles to act as a photocatalyst and then photo-generated hole-electron pairs are formed (Zhou *et al.* 2015a; Chen *et al.* 2016; Eskandarloo *et al.* 2016; He *et al.* 2016). OH^\bullet radicals are produced by the reaction of electrons with O_2 and H^+ . The generated holes react with OH^- and/or H_2O to produce hydroxyl radicals which react with BPA molecules (Dükkancı 2018):

Moreover, the presence of a solid sonocatalyst could provide additional active sites for nucleation of bubbles which increases the number of cavitation bubbles formed.

Although there are some studies on photocatalytic/photoFenton oxidation or wet air oxidation of organic pollutants (such as *p*-chlorophenol, Rhodamine B dye and salicylic acid) (Yang *et al.* 2007; Hu *et al.* 2012; Ye *et al.* 2018a, 2018b) over $LaFeO_3$ catalyst, there is no detailed study on the sonocatalytic oxidation of BPA using a perovskite type catalyst. However, in the study done by Afifah & Saleh 2016, the activity of $LaFeO_3$ perovskite catalyst was tested under visible light and ultrasonic irradiation separately and simultaneously to degrade methylene blue dye as a model of organic contaminant. They observed better sonocatalytic activity (~90%) than that photocatalytic activity (~80%) after 2 h. The maximum color removal of 100% was obtained for the simultaneous irradiation of visible light and ultrasonic irradiation within 2 h. This result indicates that $LaFeO_3$ perovskite catalyst may also be used as an efficient sonocatalyst for the removal of more refractory organic pollutant of BPA in water under proper conditions. So, in the present

study, the sonocatalytic oxidation of BPA in the presence of the LaFeO₃ perovskite was studied. The effects of the reaction parameters, such as temperature, pH of BPA, and catalyst loading were studied. The thermodynamic activation parameters were calculated, and the efficiency of the low and high frequency was compared with each other.

EXPERIMENTAL STUDY

Experimental setup

BPA was dissolved in water by stirring for 8 h. The sonication using the ultrasonic probe system (20 kHz, Bandelin HD3200) was conducted in a glass reactor which was equipped with a cooling jacket. The reaction temperature was kept constant at the desired temperatures by circulating cooling water (PolyScience, MX07R-20-A12E) around the reactor to avoid a significant overheating of the reaction media. The system was placed in a box to block the noise from the ultrasonic probe system, Supplementary Data (Figure S1(a), available with the online version of this paper). A high frequency ultrasonic reactor (850 kHz, Meinhardt E/805/T, Supplementary Data (Figure S1(b))) was also used for the oxidation of BPA, and the obtained results were compared with that obtained from the ultrasonic probe system. Each run took 6 h and samples were taken from the vessel at specified times and put in an iced-bed to stop the reaction. Then the samples were centrifuged and filtered with 0.45 μm polytetrafluoroethylene (PTFE) syringe filters. The catalyst free samples were analyzed using a high performance liquid chromatography (HPLC) (Agilent 1,200 series) with a ZORBAX Eclipse Plus C18 (4.6 × 150 mm, 5 μm) column. Detection 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. BPA removal, % was calculated using Equation (9).

$$\text{BPA removal, \%} = \frac{C_{\text{BPA},0} - C_{\text{BPA}}}{C_{\text{BPA},0}} \times 100 \quad (9)$$

where $C_{\text{BPA},0}$ and C_{BPA} are the initial concentration and the concentration of BPA at a taken time, respectively.

At the beginning of each run to establish the adsorption/desorption equilibrium of BPA over the catalyst, a known concentration of BPA was stirred with catalyst in the absence of sonication, and H₂O₂ at studied temperatures. The adsorption

of BPA at the end of 30 min was in the range of 1.75–2.1% (except in the run where initial pH of BPA = 3.0, 5.89%). The initial concentration was taken as the concentration at the end of 30 min of adsorption just after the addition of H₂O₂.

In addition to this measurement, the total organic carbon (TOC) removal of the BPA solution was determined by measuring the initial TOC and final TOC (at the end of the run) of the BPA solution (Teledyne, Tekmar, Lotix). TOC was calculated as the difference between the total carbon (TC) and inorganic carbon (IC) in the liquid sample and TOC reduction was calculated using Equation (10). This reduction shows the mineralization degree of BPA to CO₂ and water.

$$\text{TOC reduction, \%} = \frac{\text{TOC}_0 - \text{TOC}}{\text{TOC}_0} \times 100 \quad (10)$$

where TOC₀ and TOC are the initial and final TOC values of BPA, respectively.

Preparation of LaFeO₃ perovskite catalyst

The LaFeO₃ perovskite catalysts were prepared using the sol-gel preparation method and then the resulting material was calcined at 500 °C for 6 h. The catalyst preparation procedure and detailed characterization studies were given in the previous study (Dükkancı 2016).

Calculation of actual sonication power

The actual power of sonication is different from the output power of an ultrasonic generator. The actual power of an ultrasonic generator is measured using the calorimetric method. In calorimetry, the temperature (T) of liquid (here water) is recorded against time (t), with the help of the thermocouple placed in the reactor. The ultrasonic power actually entering the system is obtained according to Equation (11):

$$\text{Power (W)} = \left(\frac{dT}{dt}\right) * C_p * M \quad (11)$$

where (dT/dt) is the temperature rise per second, C_p = heat capacity of water (4.187 kJ kg⁻¹ K⁻¹ at 20 °C) and M = mass of water used in kg (Torres *et al.* 2007; Rayaroth *et al.* 2015).

The actual ultrasonic power for each ultrasonic system determined by calorimetry and power density values are given in the Supplementary Data (Table S1, available online). The calculation of power density (W/mL) is important so as to compare the different ultrasonic equipment as

they contain different solution volumes. Each experiment was performed in triplicate to determine the average values.

RESULTS AND DISCUSSION

Sonocatalytic oxidation of BPA using the ultrasonic probe system

Oxidation of BPA by individual systems

In order to evaluate the efficiency of sonication on BPA oxidation, the following experiments were performed, (i) Cat + H₂O₂ (Fenton), (ii) only US, (iii) US + H₂O₂, and (iv) Cat + US + H₂O₂ (sonocatalytic). As seen in Figure 1, only 3.95% BPA removal was observed using Fenton oxidation. This low BPA removal degree showed that the presence of only H₂O₂ was not effective to activate the catalyst. A BPA removal of 69.9% was achieved in the oxidation of BPA using only sonication (US). The addition of H₂O₂ increased the BPA removal degree to 84.2% after a reaction time of 6 h. The increased BPA removal compared to US alone can be attributed to the formation of some extra hydroxyl radicals from the decomposition of H₂O₂ by sonication (Dükkancı 2018).

The percent of BPA removal strongly increased to 90.8% using sonocatalytic process after 6 h. The high efficiency of the sonocatalytic process is due to the formation of more HO[•] radicals than that of other processes, for example: only US, US + H₂O₂, Cat + H₂O₂.

The highest TOC reduction of 23.5% was obtained in the hybrid system of sonocatalytic (US + H₂O₂ + Cat) oxidation. The synergism was calculated based on Equation (12) and in the mineralization synergism of 2.12 was experienced using this hybrid system. It is worth mentioning that this synergistic effect makes this hybrid system more favorable from the environmental points of view.

$$\text{Synergistic effect} = \frac{[\text{TOC, \%}]_{\text{Cat+H}_2\text{O}_2+\text{US}}}{[\text{TOC, \%}]_{\text{US+H}_2\text{O}_2} + [\text{TOC, \%}]_{\text{Cat+H}_2\text{O}_2}} \quad (12)$$

Effect of temperature on the sonocatalytic oxidation of BPA

The effect of reaction temperature on the oxidation of BPA using the sonocatalytic process was investigated at temperatures of 288, 298, 308, and 318 K with the following conditions: 0.50 L of 66 μM BPA solution, 0.50 g/L of catalyst, concentration of H₂O₂ of 2.4 mM, an ultrasonic power density of 0.064 W/mL, and an initial pH of 8.5 at a stirring speed of 350 rpm. This effect is presented in Figure 2(a).

It is known that the liquid temperature affects the intensity of collapse, rate of the reaction, threshold/nucleation, and almost all physical properties. An increase in the ambient temperature decreases the viscosity and surface tension, as well as increasing the vapor pressure of the solvent. Thus, the cavitation threshold becomes lower and

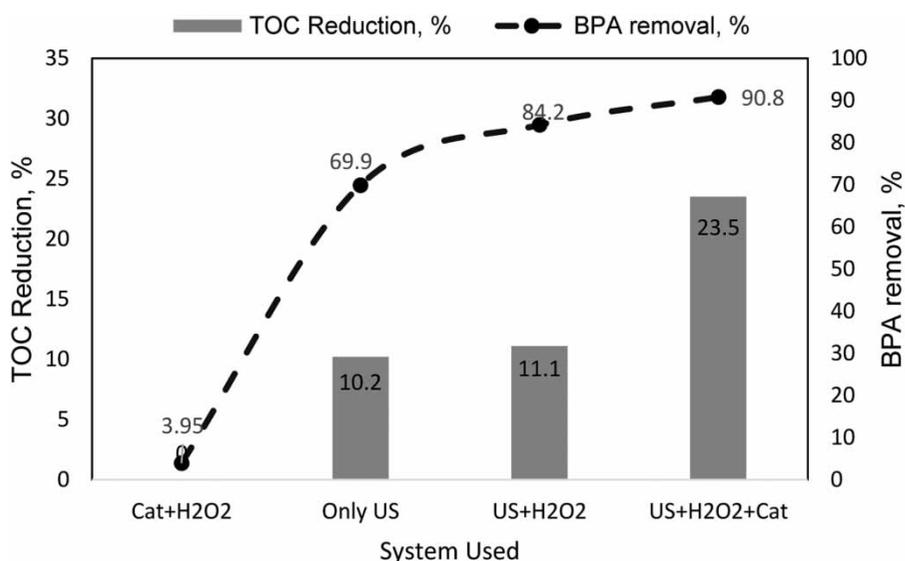


Figure 1 | Oxidation of BPA by individual systems, BPA removal, %, and TOC reduction, % after 6 h of oxidation (initial concentration of BPA = 66 μM, T = 298 K, catalyst = 0.5 g/L, pH = 8.5, H₂O₂ = 2.4 mM, and stirring speed = 350 rpm).

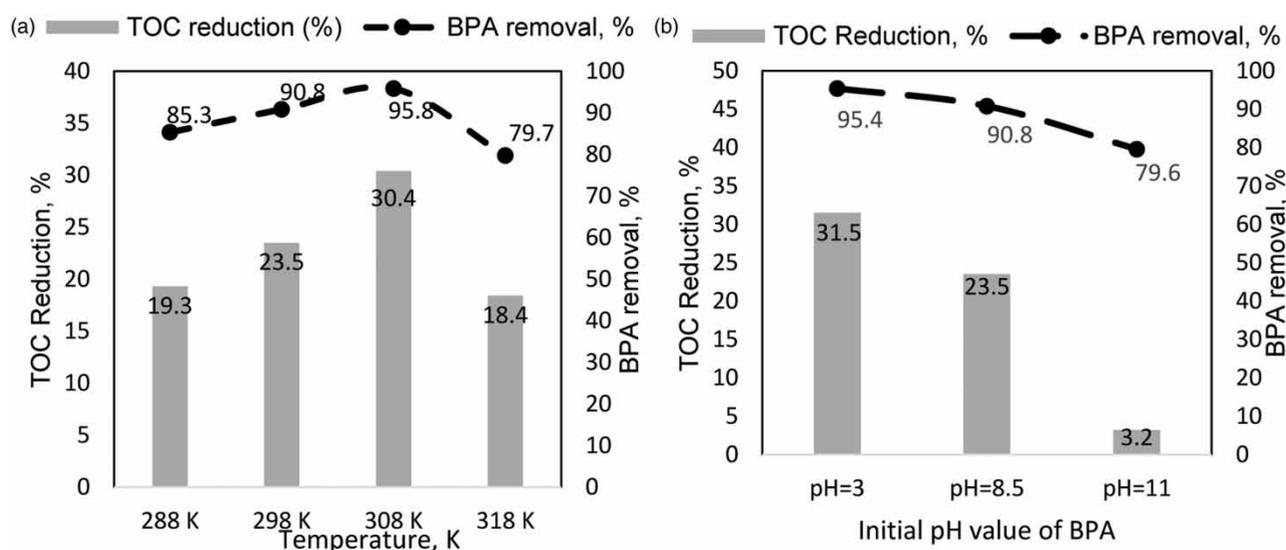


Figure 2 | (a) Effect of temperature on the sonocatalytic oxidation of BPA, BPA removal, %, and TOC reduction, % after 6 h of oxidation (pH = 8.5), (b) effect of pH on the sonocatalytic oxidation of BPA, BPA removal, %, and TOC reduction, % after 6 h of oxidation (T = 298 K) (initial concentration of BPA = 66 μ M, catalyst = 0.5 g/L, H_2O_2 amount = 2.4 mM, and stirring speed = 350 rpm).

a lower intensity is necessary to induce cavitation (Mason & Lorimer 2002; Mason & Peters 2002). In the present study, temperature has a positive effect on the BPA removal in temperatures ranges of 288–308 K. BPA removals of 85.3%, 90.8%, and 95.8% were achieved at 288, 298, and 308 K. A higher temperature increases the rate of the Fenton reaction which occurred between $LaFeO_3$ perovskite catalyst and H_2O_2 . However, at the highest temperature tested in the study, 318 K, BPA removal decreases to 79.7% after 6 h of oxidation. This is because, at higher temperature, the bubble collapse is less violent as more vapor may enter the bubble. In addition, at high temperatures, large numbers of cavitation bubbles are generated and these will act as a barrier to sound transmission and dampen the effective ultrasonic energy from the source that enters the liquid medium (Mason & Peters 2002). In addition to this, additional high temperatures would cause a very quick bubble collapse to take place. In other words, the bubble collapse time is too short for the water molecule cleavage to HO^\bullet radicals, and this is not suitable for increasing the formation of HO^\bullet radicals (Wang *et al.* 2016). Therefore, a suitable reaction temperature for the solution phase is necessary to obtain the optimal oxidation efficiency for organic pollutants in sonication. In this study, 308 K of temperature was selected as the optimal temperature for the oxidation of BPA in the system and conditions used in this study.

The highest TOC reduction was observed at 308 K as 30.4%.

First and second order reaction kinetics were tested for the sonocatalytic oxidation of BPA, see Supplementary Data (Table S2, available with the online version of this paper). It was seen that sonocatalytic oxidation of BPA over an $LaFeO_3$ perovskite catalyst follows the first order kinetics.

The Arrhenius expression, which shows the relationship between the reaction temperature and reaction rate constant, k , is described as follows in Equation (13)

$$k = A \exp\left(-\frac{E_a}{RT}\right) \quad (13)$$

where A is the pre-exponential (or frequency) factor; E_a is the activation energy ($J mol^{-1}$); R is the ideal gas constant ($8.314 J mol^{-1} K^{-1}$), and T is the reaction temperature (K).

The integration of Equation (13) is expressed by the following equation:

$$\ln k = \ln A - \frac{E_a}{RT} \quad (14)$$

From the plot of $\ln k$ and $1/T$, based on the slope $\left(-\frac{E_a}{R}\right)$, E_a in Arrhenius form was calculated as 14.9 kJ/mol, see Supplementary Data (Figure S2, available online).

From E_a the activation enthalpy ΔH can be calculated by means of Equation (15):

$$\Delta H = E_a - RT \quad (15)$$

The activation entropy is described by:

$$\Delta S = R \left(\ln A - \ln \frac{k_B T}{h} - 1 \right) \quad (16)$$

where k_B is the Boltzmann constant ($1.381 \times 10^{-23} \text{ J.K}^{-1}$) and h the Planck constant ($6.626 \times 10^{-34} \text{ J.s}$) (Ammar 2016; Chakma & Moholkar 2016).

By using calculated activation entropy and activation enthalpy, Gibbs free energy can be calculated using the following equation:

$$\Delta G = \Delta H - T\Delta S \quad (17)$$

The calculated values of different thermodynamic activation parameters are listed in Table 1.

Effect of the initial pH value of BPA on the sonocatalytic oxidation of BPA

pH is an important parameter in sonochemical oxidation because it may change the physical and chemical behavior, depending upon the nature of the compound, such as electrostatic and hydrophobic interactions. The effect of the initial pH of the BPA solution on its oxidation was studied at three different initial pH values of 3, 8.5, and 11.0 with the following conditions: 0.50 L of 66 μM BPA solution, an H_2O_2 concentration of 2.4 mM, a catalyst loading of 0.5 g/L, a reaction temperature of 298 K, and an ultrasonic power density of 0.064 W/mL. The results are shown in Figure 2(b).

As shown in Figure 2(b), the BPA removal was adversely affected with the increase in pH. It was clear that an acidic pH of 3.0 was favorable in the sonocatalytic oxidation of BPA. In other words, a higher BPA removal degree of BPA was achieved at a pH lower than pK_{a1} value of BPA ($\text{pK}_{a1} = 9.6$ and $\text{pK}_{a2} = 10.2$). Hence, at an acidic pH of 3.0, BPA exists mainly in molecular form, whereas at a pH of 11.0 it is completely ionic. It is well known that the

hydrophilic character of the ionic form of molecules is much higher than that molecular form. Thus, BPA molecules are less likely to approach the negatively charged cavity bubbles where the hydroxyl radicals are maximized, and the temperatures are high enough to cause thermal decomposition (pyrolysis) (Kidak & İnce 2006; Gültekin & İnce 2008).

In addition to this, the BPA molecule has two negative oxygen atoms in the hydroxyl groups and four negative carbon atoms in the phenolic group and at acidic conditions, more protons could accumulate on the catalyst surface. The heterocharge between the BPA and catalyst surface was in favor of an adsorbing reaction. Hence, the acidic conditions favor the initial adsorption of BPA on the positively charged LaFeO_3 perovskite surface (Wang *et al.* 2009; Wei *et al.* 2012). This result was confirmed with the adsorption/desorption experiment done in the first 30 min of the run. As mentioned in 'Experimental Setup', at the beginning of each run to establish the adsorption/desorption equilibrium of BPA over the catalyst, a known concentration of BPA (here 66 μM) was stirred with catalyst in the absence of H_2O_2 and US. The highest adsorption of 5.89% was observed at the end of 30 min at an initial pH of 3.0. Moreover, the oxidation potential of the highly oxidative $\text{HO}\cdot$ radicals decrease with the increasing pH. The $\text{HO}\cdot$ radicals have an oxidation potential of 2.65–2.80 V at a pH 3, while only 1.90 V at pH 7.0 (Dükkancı 2017). In addition, at high pH values, H_2O_2 decomposes into H_2O and O_2 , and that reduces the amount of hydroxyl radicals (Huang *et al.* 2012).

The highest TOC reduction of 31.5% was achieved at an acidic pH of 3.0.

Dynamic analysis of BPA sonocatalytic oxidation was performed by giving HPLC chromatogram in the following conditions: initial concentration of BPA = 66 μM , catalyst = 0.5 g/L, $T = 298 \text{ K}$, H_2O_2 amount = 2.4 mM, pH = 3.0, and stirring speed = 350 rpm. The related figure is given in the Supplementary Data (Figure S3, available online). The decrease in the concentration of BPA with time can be seen clearly. Under the studied conditions, the retention time of BPA was 7.1 min. As known, H_2O_2 was used as the oxidant and the retention time of the peak belonging to the H_2O_2 was 2.8 min. The other peaks at the retention times of 2.4 min, 3.2 min, 3.5 min, 3.9 min and 5.2 min belong to intermediates formed in the oxidation. The retention time of all formed intermediates are smaller than the BPA, hence, it can be said that the hydrophilic character of the intermediates are stronger than the BPA.

Table 1 | Calculated thermodynamic activation parameters

T (K)	E_a ($\text{kJmol}^{-1}\text{K}^{-1}$)	ΔH ($\text{kJmol}^{-1}\text{K}^{-1}$)	ΔS ($\text{kJmol}^{-1}\text{K}^{-1}$)	ΔG ($\text{kJmol}^{-1}\text{K}^{-1}$)
288	14.89	12.491	-0.2443	82.845
298		12.408	-0.2446	85.289
308		12.325	-0.2448	87.737

Effect of catalyst loading on the sonocatalytic oxidation of BPA

The effect of the catalyst loading on the oxidation of BPA was investigated by varying the catalyst loading in the range of 0.25 g/L to 1.0 g/L for the initial concentration of BPA of 66 μ M at a temperature of 298 K in the presence of 2.4 mM of H₂O₂ and at the stirring speed of 350 rpm. The ultrasonic power density was constant as 0.064 W/mL. The results are seen in Figure 3(a).

As seen in Figure 3(a), doubling the catalyst amount from 0.25 g/L to 0.5 g/L increased the BPA removal degree from 81.6% to 90.8%. However, further increase in catalyst amount has no remarkable positive effect on the removal of BPA. Similarly, as the catalyst loading increased from 0.25 to 0.5 g/L the initial rate increased from 1.67×10^{-4} to 4.190×10^{-4} mol/L min. However, the initial rate did not change significantly as the catalyst loading increased from 0.5 to 1 g/L (4.197×10^{-4} mol/L min). It shows that the external mass transfer resistance is negligible in the catalyst loading range of 0.5–1 g/L. It can be concluded that the reaction rate was not limited by the external mass transfer under the standard reaction conditions involving 0.5 g/L of catalyst. On the other hand, the reaction mixture was stirred vigorously at 350 rpm and due to the turbulence created by sonication, external diffusion resistance between the bulk solution and the catalyst surface can be eliminated. Internal diffusion resistance was also negligible due to the catalyst being used in powder form (Smith 1981).

The presence of solid catalyst particles in the sonocatalytic oxidation increases the intensity of cavitation by providing additional nuclei for generation of cavities and the subsequent violent collapse of these cavities releases large magnitudes of energy and then the formation of more reactive hydroxyl and hydroperoxyl radicals. However, the solid catalyst particles also act as a barrier (opposite effect) for the distribution of sound waves which decreases the energy transmitted into the system (Gogate & Pandit 2004).

The highest TOC reduction of 23.8% was achieved in the presence of 1 g/L catalyst.

Effect of addition of inorganic anions on the sonocatalytic oxidation of BPA

Because inorganic anions such as Cl⁻, NO₃⁻ and SO₄²⁻ commonly exist in wastewaters, the effects of these anions on the sonocatalysis efficiency were investigated by separately adding NaCl, NaNO₃ and Na₂SO₄ as Cl⁻, NO₃⁻ and SO₄²⁻ sources, respectively, in 5 mmol/L to the reaction solution under the following conditions: 0.50 L of 66 μ M BPA solution, 0.50 g/L of catalyst, concentration of H₂O₂ of 2.4 mM, an ultrasonic power density of 0.064 W/mL, and an initial pH of 8.5 at a stirring speed of 350 rpm. This effect is presented in Figure 3(b).

As seen in Figure 3(b), the addition of Cl⁻ anion has a negligible effect on sonocatalytic oxidation of BPA. However, the presence of SO₄²⁻ and NO₃⁻ inhibited the

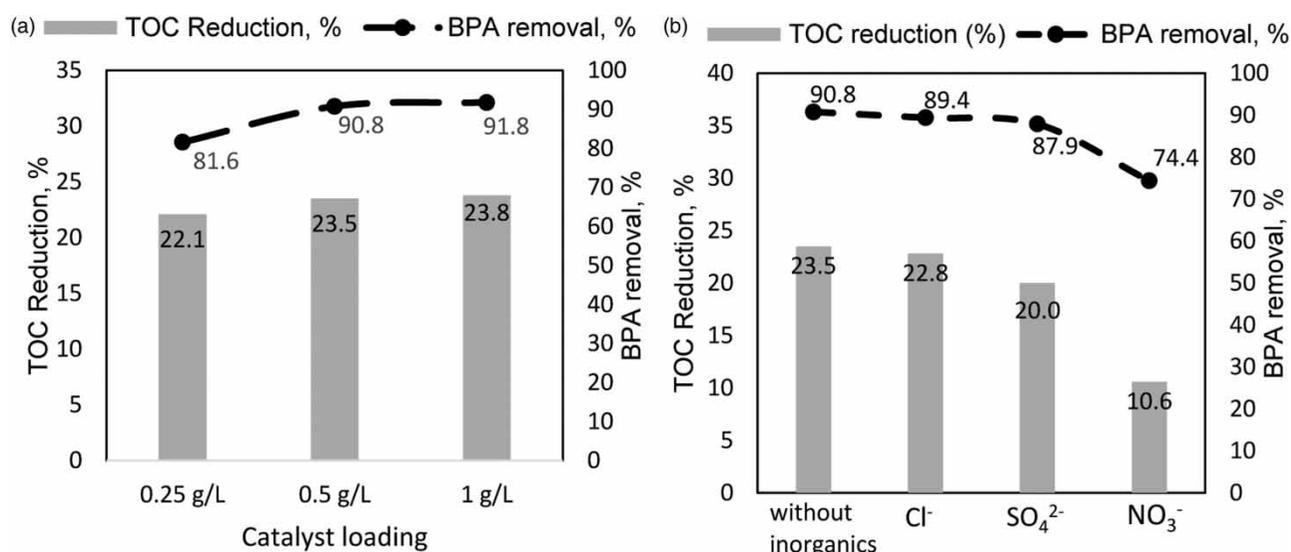


Figure 3 | (a) Effect of catalyst loading on sonocatalytic oxidation of BPA, BPA removal, %, and TOC reduction, % after 6 h of oxidation, (b) effect of addition of inorganic anions on the sonocatalytic oxidation of BPA, BPA removal, %, and TOC reduction, % after 6 h of oxidation (catalyst = 0.5 g/L, NaCl, NaNO₃ or Na₂SO₄ = 5 mM) (initial concentration of BPA = 66 μ M, pH = 8.5, T = 298 K, H₂O₂ amount = 2.4 mM, and stirring speed = 350 rpm).

BPA removal and TOC reduction due to the inorganic anion OH^\cdot radical scavenging effect. These inorganic anions can react with the sonogenerated OH^\cdot radicals to produce NO_3^- , SO_4^{2-} , and Cl^- which have lower oxidation potential than that of OH^\cdot radicals (Zhou *et al.* 2015b; Khataee *et al.* 2017b).

Although presence of inorganic anions in reaction solution reduces BPA removal degree, the sonocatalytic efficiency of LaFeO_3 perovskite catalyst is still high. The BPA removal values were 89.4%, 87.9% and 74.4% in the presence of Cl^- , SO_4^{2-} and NO_3^- , respectively, after a reaction time of 6 h. After the same reaction time, TOC reductions of 22.8%, 20.0% and 10.6% were obtained, respectively. This result indicates that the LaFeO_3 catalyst can also be used as an effective sonocatalyst in the treatment of real industrial wastewater.

Sonocatalytic oxidation of BPA using a high frequency ultrasonic reactor

The sonocatalytic oxidation of BPA was also investigated using a high frequency (850 kHz) ultrasonic reactor at three different powers and power densities of 4, 8, and 32 W and 0.011, 0.023, and 0.091 W/mL, respectively. Experiments were conducted at a temperature of 298 K, with 0.5 g/L of catalyst, in the presence of 2.4 mM H_2O_2 , at an initial BPA concentration of 66 μM at a volume of 350 mL and at an initial pH value of 8.5. For comparison with the results obtained in the high frequency ultrasonic reactor, the experiments were conducted in an ultrasonic

probe system with 350 mL (0.091 W/mL) of BPA solution. The results are seen in Figure 4.

As seen in Figure 4, the results demonstrated that increasing the power has a positive effect on the sonocatalytic oxidation of BPA. BPA removal increased from 11.3% to 29.0% and then to 96.8% as the power increased from 4 W (0.011 W/mL) to 8 W (0.023 W/mL) then to 32 W (0.091 W/mL). The measured TOC reductions were 3.4%, 10.6%, and 37.8% at the ultrasonic powers of 4, 8, and 32 W, respectively.

At a proper power, the cavitation bubble forms, grows and reaches the resonant size. This is followed by the violent collapse and subsequent production of hydroxyl radicals. The rise in power can enhance the negative pressure exerted by ultrasound. So, the cavitation bubble expands more in the rarefaction stage and the cavity reaches the resonance size immediately; this results in the pyrolysis of water and reaction with OH^\cdot . By increasing the power, the energy of cavitation can be increased and also lowers the threshold limit of cavitation, thus the number of the cavitation bubbles increases. The increase in the size of the cavitating bubble by increasing the power was reported as well. This situation will result in an enhancement in cavitation efficiency and radical formation (Rayaroth *et al.* 2015; Khataee *et al.* 2017a). Boutamine *et al.* (2017) also reported a positive effect of increasing the power in the production of the active bubbles for the production of the oxidants. Higher ultrasound power brings more violent turbulence that enhances the mass transfer in the BPA solution (Gao

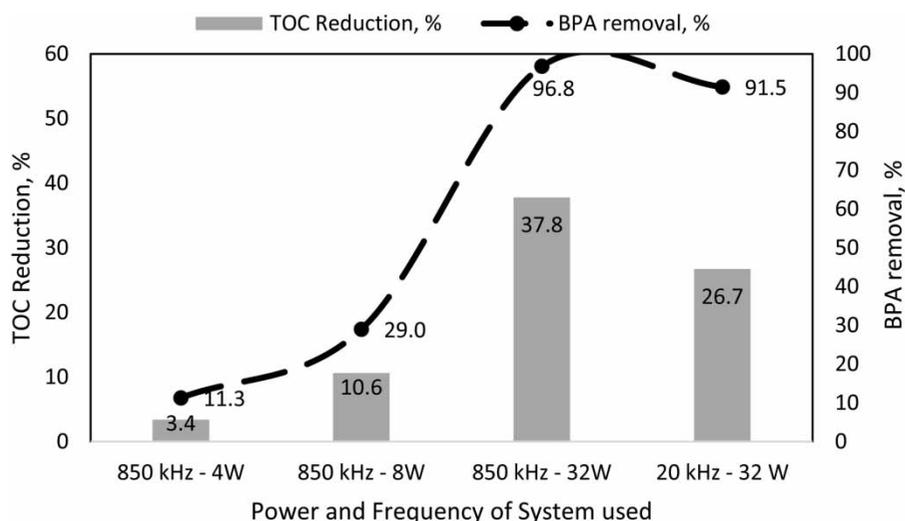


Figure 4 | Effect of high frequency on sonocatalytic oxidation of BPA, BPA removal, %, and TOC reduction, % after 6 h of oxidation (initial concentration of BPA = 66 μM , $T = 298\text{ K}$, H_2O_2 amount = 2.4 mM, catalyst = 0.5 g/L, and stirring speed = 350 rpm).

et al. 2018). In addition, it caused a continuous cleaning of the catalyst surface for the sonocatalytic process.

When the effect of frequency, 20 kHz and 850 kHz, was studied at the same power density of 0.091 W/mL, the results emphasized that a more or less equal amount of BPA removal was observed with 20 kHz (91.5%) and 850 kHz (96.8%) sonoreactor in the presence of a LaFeO₃ perovskite catalyst. However, higher mineralization of BPA was achieved in 850 kHz ultrasonic reactor (37.8%) than that 20 kHz probe system (26.7%), Figure 4. The diameter of the cavitation bubbles decreases as the frequency increases. At higher frequencies, smaller bubbles require fewer acoustic cycles before reaching the essential resonant size. This leads to transient cavitation events developing at a faster rate per unit time as the frequency is increased because bubble the lifetimes are shorter. A greater number of oscillations increases the mass transfer of HO[•] radicals into the surrounding medium and concurrently increase the diffusion of gases and volatile compounds into the bubble. At high frequencies, however, the resonance bubble size may not be large enough to produce enough energy upon collapse to form sufficient numbers of HO[•] radicals from water, and a point of diminishing returns is reached (Beckett & Hua 2001).

On the other hand, larger bubbles created in the low frequency of 20 kHz can be split into smaller bubbles, thus the number of bubbles and OH[•] production increases (Kang *et al.* 2015). Ayanda *et al.* (2018) studied the sonocatalytic oxidation of aqueous phenolsulfonphthalein in the presence of nano-Fe/H₂O₂, and under the studied frequency range of 20–100 kHz, 60 kHz was selected as the optimum frequency. Kang *et al.* (2015) found the optimum frequency of 35 kHz in the sonocatalytic

oxidation of ibuprofen under the studied frequency range of 35–1,000 kHz.

In each run, the obtained TOC reduction was lower than that BPA removal degree. This result indicates that the BPA mineralization cannot be achieved totally. In other words, it shows that BPA transformed into oxidation-resistant intermediates rather than CO₂.

Comparison of the results obtained from this study and the literature data

The sonocatalytic oxidation of BPA is rarely reported in literature and it is not found in any study on sonocatalytic oxidation of BPA over LaFeO₃ perovskite type catalyst. Table 2 presents the comparison of studies on sonocatalytic oxidation of BPA over several catalysts in literature and the present study with the studied experimental conditions. In the study done by Huang *et al.* (2012), sonocatalytic oxidation of BPA was investigated over Fe₃O₄ sonocatalyst and BPA removal of 100% and TOC reduction of 45.8% were achieved after 8 h with 200 mL of BPA solution. However, in the present study, 500 mL of BPA aqueous solution was used in the runs. In another study done by Lee *et al.* (2018), β-Bi₂O₃/Bi₂O₂CO₃ was used as sonocatalyst and under the studied conditions, 60–100% BPA removal was achieved after 6 h of oxidation. However, there was no information on TOC reduction. In the study done by Ioan *et al.* (2007), sonocatalytic oxidation of BPA was studied over homogeneous Fenton catalyst of FeSO₄·7H₂O. As expected, high BPA removal of 95% was achieved in very short time. However, the usage of homogeneous Fenton catalyst has a number of disadvantages such as sludge generation due to post treatment process, limited pH range, high

Table 2 | Comparison of the results obtained from this study and the literature data

Reference	Huang <i>et al.</i> (2012)	Lee <i>et al.</i> (2018)	Lee <i>et al.</i> (2018)	Lee <i>et al.</i> (2018)	Ioan <i>et al.</i> (2007)	This study
Catalyst	Fe ₃ O ₄ , 585 mg/L	β-Bi ₂ O ₃ / Bi ₂ O ₂ CO ₃ 50 mg/L	β-Bi ₂ O ₃ / Bi ₂ O ₂ CO ₃ 50 mg/L	β-Bi ₂ O ₃ / Bi ₂ O ₂ CO ₃ 10 mg/L	FeSO ₄ ·7H ₂ O 2.5 mg/L	LaFeO ₃
H ₂ O ₂	160 mM	–	–	–	0.2 mM	2.4 mM
pH	7	No inf.	No inf.	No inf.	4	3
BPA initial conc., ppm	20 ppm	10 ppm	10 ppm	10 ppm	25 ppm	15 ppm
Volume of BPA	200 mL	1 L	1 L	1 L	250 mL	500 mL
BPA removal,%	~100% after 8 h	100% after 6 h	~70% after 6 h	~60% after 6 h	~95% after 10 min	95.4% after 6 h
TOC reduction,%	48.5% after 8 h	No inf.	No inf.	No inf.	No inf.	31.5% After 6 h
Frequency of ultrasound	40 kHz	35 kHz	100 kHz	100 kHz	43–47 kHz	20 kHz

iron discharge to environment and difficulty in iron ion recovery (Sreeja & Sosamony 2016). Besides this, there was no information on TOC reduction. Considering literature survey on the sonocatalytic oxidation of BPA, it can be concluded that LaFeO₃ showed a high sonocatalytic activity under the studied experimental conditions and it is a promising sonocatalyst for the treatment of wastewater containing BPA.

CONCLUSION

In this study, the sonocatalytic oxidation of BPA was investigated in the presence of an iron containing perovskite catalyst, LaFeO₃. The ultrasonic probe system at 20 kHz and high frequency ultrasonic reactor (850 kHz) were used as the sonication source. The effects of temperature, initial pH value of BPA, catalyst loading, and ultrasonic power were investigated on the sonocatalytic oxidation of BPA. The sonocatalytic process in the presence of LaFeO₃ perovskite catalyst offers a valuable alternative for the removal and mineralization of BPA. The highest BPA removal of 95.8% was achieved at 308 K, in the presence of 2.4 mM H₂O₂ and 0.5 g/L catalyst at 0.064 W/mL power density using the ultrasonic probe system. An acidic pH of 3.0 was favorable in the sonocatalytic oxidation of BPA. The initial BPA removal rate increased as the catalyst amount increased from 0.25 to 0.5 g/L; however, with a further increase in the catalyst amount to 1 g/L, the initial rates were almost the same. The sonocatalytic oxidation of BPA on a LaFeO₃ perovskite catalyst was described by the first order kinetics with an activation energy of 14.9 kJ/mol. The obtained BPA removal (96.8%) using high frequency (850 kHz) ultrasonic reactor was slightly higher than that obtained using low frequency (20 kHz) ultrasonic probe system (91.5%) at the same power density of 0.091 W/mL. Higher mineralization (TOC reduction) of BPA was achieved in 850 kHz ultrasonic reactor (37.8%) than that of the 20 kHz probe system (26.7%). In presence of inorganic anions, the sonocatalytic efficiency of LaFeO₃ perovskite catalyst is still high and this result indicates that the LaFeO₃ catalyst can also be used as an effective sonocatalyst in the treatment of real industrial wastewater.

Consequently, it may be said that the heterogeneous sonocatalytic oxidation system appears as a promising process for the treatment of BPA containing wastewater.

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